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Abstract approved:
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Several new solid-state inorganic borates have been prepared and characterized. Single crystals of the simple orthoborate $\mathrm{ScBO}_{3}$ were grown and its structure was determined by single-crystal $X$-ray methods. The new borates $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}, \operatorname{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}, \mathrm{NdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$, $\mathrm{SrNaBO}_{3}$, and $\mathrm{Li}_{4} \mathrm{Ln}_{4} \mathrm{MB}_{9} \mathrm{O}_{23}(\mathrm{Ln}=\mathrm{Y}, \mathrm{Er}$, and $\mathrm{Gd} ; M=\mathrm{Al}$ and Ga$)$ were identified from phase analyses in the systems $\mathrm{Li}_{2} \mathrm{O}-\mathrm{Sc}_{2} \mathrm{O}_{3}-\mathrm{B}_{2} \mathrm{O}_{3}$, $\mathrm{La}_{2} \mathrm{O}_{3}-\mathrm{Sc}_{2} \mathrm{O}_{3}-\mathrm{B}_{2} \mathrm{O}_{3}, \mathrm{Nd}_{2} \mathrm{O}_{3}-\mathrm{Sc}_{2} \mathrm{O}_{3}-\mathrm{B}_{2} \mathrm{O}_{3}, \mathrm{SrO}-\mathrm{Na}_{2} \mathrm{O}-\mathrm{B}_{2} \mathrm{O}_{3}$, and $\mathrm{Li} 2 \mathrm{O}-\mathrm{Ln}_{2} \mathrm{O}_{3}-$ $\mathrm{M}_{2} \mathrm{O}_{3}-\mathrm{B}_{2} \mathrm{O}_{3}$. Structural characteristics of these compounds have been established by single-crystal X-ray methods. The orthoborate $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}$ exhibits strings of alternating Sc-centered octahedra and Li -centered rectangular planes. The compounds $\mathrm{LaSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ and $\mathrm{NaSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ are isostructural to other examples of the mineral Huntite. The La derivative crystallizes in a monoclinic space group with no evidence obtained for a phase transition to a higher symmetry variant. The Nd derivative crystallizes in a high symmetry, rhombohedral structure. The structure of $\mathrm{SrNaBO}_{3}$ is similar to that of the compound $\mathrm{K}_{2} \mathrm{CO}_{3}$, exhibiting a small distortion of the
packing of the $\mathrm{Sr}^{2+}$ and $\mathrm{O}^{2-}$ ions from that observed for the $\mathrm{Ba}^{2+}$ and $0^{2-}$ ions in the oxide $\mathrm{BaNiO}_{3}$. The structure of the compound $\mathrm{Li}_{4} \mathrm{Ln}_{4} \mathrm{MB}_{9} \mathrm{O}_{23}$ contains the unique, isolated borate ring $\left[\mathrm{B}_{8} \mathrm{O}_{20}\right]^{16-}$. These rings stack over fused rings of Ln-centered square antiprisms to afford one-dimensional channels filled with Li atoms and an orthoborate $\mathrm{BO}_{3}$ group.

Optical properties including fluorescence, infrared absorption, and second harmonic generation have been measured for the compounds $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}, \mathrm{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$, and $\mathrm{NaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$. When doped with the ion $\mathrm{Cr}^{3+}$, the compounds $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}$ and $\mathrm{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ exhibit broad emission bands in the near infrared, indicating the presence of weak crystal fields at the $\mathrm{Sc}^{3+}\left(\mathrm{Cr}^{3+}\right)$ sites. Energy transfer is observed in the doped compound $\mathrm{Cr}^{3+}: \mathrm{NdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$; excitation into the $\mathrm{Cr}^{3+}$ absorption band affords strong luminescence only from the $\mathrm{Nd}^{3+}$ ion. The low conversion efficiency of the compound $\operatorname{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ for second harmonic generation of the 1064 nm line of a $\mathrm{Nd}^{3+}$ :YAG laser is rationalized from the symmetry characteristics of the calculated components of the hyperpolarizability tensor.

# Syntheses and Structures of New Inorganic Borates 

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DEDICATION
to my parents

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## Contribution of Authors

Mr. Jinfan Huang performed the computations on the optical conversion efficiencies for the compounds $\operatorname{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ and $\mathrm{YAl}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ described in Chapter 4.

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# SYNTHESES AND STRUCTURES OF NEW INORGANIC BORATES 

## CHAPTER 1 INTRODUCTION

Inorganic borates comprise those boron-oxygen species of synthetic or natural origin in the crystalline or vitreous states that exhibit boron atoms linked either to three oxygen atoms at the corners of a triangular plane or to four oxygen atoms at the vertices of a tetrahedron. They are useful materials that are exploited each year in vast quantities. Alkali borates are present in a variety of cleaning agents. Barium and zinc borates are added to various paints, serving as anticorrosive and antifungal agents. Borosilicate glass (Pyrex) is used extensively while synthetic borates of the tourmaline family comprise the largest selling class of gemstones in the U.S. Interest in borates as optical materials has recently increased with the commercialization of the laser $\mathrm{Cr}^{3+}: \mathrm{ScBO}_{3}$ (1) and the frequency converters $\mathrm{BaB}_{2} \mathrm{O}_{4}$ (2) and $\mathrm{LiB}_{3} \mathrm{O}_{5}$ (3).

Despite the extensive utility of anhydrous borates, only a rather limited number of studies on their preparation and properties have been reported. Prompted, in part, by this level of development and the general interest in this laboratory in synthesizing new optical materials, I have undertaken the study of new borates of potential interest as solid-state laser materials or optical frequency converters.

In this thesis, I document investigations of the preparation and crystal structures of new borates and measurement of their physical properties. Continuing in this chapter, I present the background necessary to firmly establish my motivation. In Chapter 2, the structure of the simple orthoborate $\mathrm{ScBO}_{3}$ is established for purposes of comparison to other borates containing scandium atoms that are discussed in ensuing chapters. In Chapter 3, the structural and optical characteristics of the new orthoborate $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}$ are described. In Chapter 4, the characteristics of the first examples of the Huntite structure containing scandium atoms, $\operatorname{LaSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ and $\mathrm{NaSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$, are discussed. In Chapter 5, a general contribution of importance to the flux growth of borates of strontium is presented with the synthesis and crystal structure of the compound $\mathrm{SrNaBO}_{3}$. In Chapter 6, a peculiar ring borate is described that was found to exist for a family of compounds of formula $\mathrm{Li}_{4} \operatorname{Ln}_{4} \mathrm{MB}_{9} \mathrm{O}_{23}$ ( $\mathrm{Ln}=\mathrm{Y}, \mathrm{Er}$, and $\mathrm{Gd} ; \mathrm{M}=\mathrm{Al}$ and Ga ). Additional results on the synthesis of other new borates are summarized in the Appendix.

## Structural Chemistry of Anhydrous Solid-State Borates

The structural characteristics of crystalline metal borates have been summarized (4)-(6). The boron atom may occupy either a triangular or tetrahedral site or both in a single compound. The borate may be monomeric or polymeric; polymerization resulting from condensation of boron-oxygen triangles and tetrahedra through shared oxygen vertices affords the formation of chains, layers, or three-
dimensional frameworks. A classification scheme that includes ortho-, pyro-, meta-, and higher polyborates is given below (4):
(1) Orthoborates contain the monomeric, triangular-planar unit $\mathrm{BO}_{3}{ }^{3-}$ (Figure 1.1a). The calcite structural type adopted by the compound $\mathrm{ScBO}_{3}(7)$ exhibits such borate units.
(2) Pyroborates contain the unit $\left[\mathrm{B}_{2} \mathrm{O}_{5}\right]^{4-}$ (Figure 1.1b) which consists of two $\mathrm{BO}_{3}$ triangles joined by a common oxygen atom. The compound $\mathrm{Sr}_{2} \mathrm{~B}_{2} \mathrm{O}_{5}$ (8) exhibits only pyroborate groups.
(3) Metaborates comprise certain compounds having the B:0 ratio 1:2. They contain either the trimeric ring $\left[\mathrm{B}_{3} \mathrm{O}_{6}\right]^{3-}$ (Figure 1.1c) or the chain ${ }_{\omega}^{1}\left[\mathrm{BO}_{2}\right]_{n}^{n-}$ (Figure 1.1d) with each borate triangle sharing two of its oxygen atoms. The compounds $\mathrm{BaB}_{2} \mathrm{O}_{4}$ (9) and $\alpha-\mathrm{LiBO} 2$ (10) exhibit the ring $\left[\mathrm{B}_{3} \mathrm{O}_{6}\right]^{3-}$ and the chain ${ }_{\infty}^{1}\left[\mathrm{BO}_{2}\right]_{n}^{\mathrm{n}^{-}}$, respectively.
(4) Higher polyborates include triborates, tetraborates, pentaborates, octaborates, nonaborates, etc. The structures of these polyborates are complex because of the presence of both triangular $\mathrm{BO}_{3}$ and tetrahedral $\mathrm{BO}_{4}$ units that condense to form a variety of unusual chains, rings, and three-dimensional networks. For example, the compound $\mathrm{CdB}_{4} \mathrm{O}_{7}$ (11) crystallizes with a three-dimensional framework that contains a unit of two tetrahedral $\mathrm{BO}_{4}$ groups sharing a common oxygen atom and additional oxygen vertices with two triangular $\mathrm{BO}_{3}$ groups (Figure 1.1e).

The adoption of a specific structure by a borate will depend primarily on the nature of the associated cations and the overall stoichiometry of the compound. To realize a simple orthoborate, $\mathrm{BO}_{3}{ }^{3-}$, sufficient electron density must be available to support the

a


C

e

Figure 1.1 Borate anions: (a) orthoborate $\left[\mathrm{BO}_{3}\right]^{3-}$, (b) pyroborate $\left[\mathrm{B}_{2} \mathrm{O}_{5}\right]^{4-}$, (c) metaborate $\left[\mathrm{B}_{3} \mathrm{O}_{6}\right]^{3-}$, (d) metaborate ${ }_{\infty}^{1}\left[\mathrm{BO}_{2}\right]_{n}^{n-}$, and (e) tetraborate $\left[\mathrm{B}_{4} \mathrm{O}_{7}\right]^{2-}$.
$\pi$-electron system $-\mathrm{BO}_{3}{ }^{3-}$ is isoelectronic to $\mathrm{CO}_{3}{ }^{2-}$. Hence, it is not surprising that compounds rich in alkali or alkaline earth metals exist as simple orthoborates; examples are $\mathrm{Li}_{3} \mathrm{BO}_{3}$ (12) and $\mathrm{Sr}_{3}\left(\mathrm{BO}_{3}\right)_{2}$ (13). In compounds stoichiometrically richer in boron atoms, the strong covalency of the boron-oxygen $\sigma$ bond effectively competes with neighboring boron-oxygen bonds to remove electron density that would otherwise support the $\pi$ system. The result is the occurrence of 4 -coordinate $B$ atoms as exemplified by the compound $\mathrm{SrB}_{4} \mathrm{O}_{7}$ which contains a network of 4-coordinate E atoms only. To a certain degree one can then control the coordination number of the $B$ atom in synthesis through judicious selection of associated cations and the overall stoichiometry.

## Solid-State Lasers and Effects of the Crystal Field

Development of new solid-state laser materials is primarily concerned with adjustment of the color of the laser beam, its tuning range, the overall efficiency, or extracteible power. These features and finding methods to alter them may be addressed by applying various aspects of crystal-field theory to a transition-metal (3d shell) or rare-earth (4f shell) ion doped onto a crystallographic site of known symmetry. One useful result of this theory is the Tanabe-Sugano energy level diagram (15) depicted in Figure 1.2 for the $\mathrm{d}^{3}, \mathrm{Cr}^{3+}$ ion occupying an octahedral site. Normalized electronic energy states in units $E / B$ (ordinate) are presented as a function of the normalized crystal-field strength $D q / B$ (abscissa) where $D q$ is a measure of the


Figure 1.2 Tanabe-Sugano diagram for a $d^{3}$ transition metal in an octahedral environment. Dashed vertical line 1 corresponds to the crystal field strength Dq/B in Cr:GFG, dashed line 2 corresponds to $\mathrm{Dq} / \mathrm{B}$ in Alexandrite, and dashed line 3 corresponds to $\mathrm{Dq} / \mathrm{B}$ in Ruby.
strength of the crystal field and $B$ is a parameter representing the effects of electron-electron interactions. The utility of this diagram may be realized by considering its application to three known laser materials.

When doped into the oxide $\mathrm{Al}_{2} \mathrm{O}_{3}$ to form ruby, the $\mathrm{Cr}^{3+}$ ion exhibits narrow emission lines emanating from the transition ${ }^{2} E \rightarrow{ }^{4} \mathrm{~A}_{2}$ (16) (cf. Figure 1.2 and Figure 1.3a); the state ${ }^{4} \mathrm{~T}_{2}$ is $2300 \mathrm{~cm}^{-1}$ above the ${ }^{2} E$ levels (17). Because the emission lines correspond to transitions between levels of similar configurations $\left(\mathrm{t}_{2}{ }^{3}\right)$, their breadth remains small. A value of $D q / B=3.2$ may be derived from the measured energy of the ${ }^{4} T_{2}$ state, a value representing a very strong crystal field at the $\mathrm{Cr}^{3+}$ site.

The laser material Alexandrite, $\mathrm{Cr}^{3+}: \mathrm{BeAl}_{2} \mathrm{O}_{4}$, exhibits a much different luminescence spectrum (18). It is characterized by the presence of sharp lines and a broad band peaking at a lower energy (Figure 1.3b). The state ${ }^{4} \mathrm{~T}_{2}$ is only $800 \mathrm{~cm}^{-1}$ (19) above the state ${ }^{2}$ E (Figure 1.2). This state may then be thermally populated to afford the broad-band luminescent transition ${ }^{4} T_{2} \rightarrow{ }^{4} \mathrm{~A}_{2}$ in addition to the sharp lines derived from relaxation of the ${ }^{2} \mathrm{E}$ state. The broad-band nature of the transition results from the change in configuration ${ }^{4} T_{2}\left(t_{2}{ }^{2} e\right) \rightarrow{ }^{4} A_{2}\left(t_{2}{ }^{3}\right)$ that occurs. In the excited state ${ }^{4} T_{2}$ electrons occupy levels of $e_{g}$ character that are metal-ligand antibonding in character, destabilizing the metal-1igand bonds, enlarging interatomic distances, and effectively coupling to the local vibrational modes. Transitions from the excited states to the various levels of the ground-state vibrational manifold then afford


Figure 1.3 Diagrammatic representations of the fluorescence spectra for (a) Ruby, (b) Alexandrite, and (c) Cr:GFG.
the broad luminescence band. Consistent with the spin-allowed character of the transition ${ }^{4} T_{2} \rightarrow{ }^{4} A_{2}$ a very short lifetime of $7 \mu \mathrm{~s}$ is observed which contrasts to the longer lifetime of 1.6 ms observed for the spin-forbidden transition ${ }^{2} E \rightarrow{ }^{4} A_{2}$.

The fluoride garnet $\mathrm{Cr}^{3+}: G F G, \mathrm{Cr}^{3+}: \mathrm{Na}_{3} \mathrm{Ga}_{2} \mathrm{Li}_{3} \mathrm{~F}_{12}$, exhibits only a broad emission band (Figure 1.3c). The crystal-field strength, $D q / B=1.8$ (20), piaces the state ${ }^{4} T_{2}$ well below the state ${ }^{2} E$ in energy. This broad emission band is of great utility as a tunable laser transition.

These three examples demonstrate the important effects that the host lattice and crystal field can have on the optical characteristics of the $\mathrm{Cr}^{3+}$ ion. The synthesis of new borate host lattices could be expected to afford different crystal-field strengths, hence, new emission wavelengths and tuning ranges. Following inception of this work, the material $\mathrm{Cr}^{3+}: \mathrm{ScBO}_{3}$ was reported to function as an efficient infrared tunable laser at room temperature. The efficiency ranks fifth among all $\mathrm{Cr}^{3+}$ lasers and is much higher than would be anticipated from simple models (20)-(21) of the relationship between excited-state absorption and efficiency. Examining these results and synthesizing new complex scandium borates for achieving high efficiencies have been important projects in this laboratory. Incorporating electropositive elements into a scandium borate matrix has been reported by members of this laboratory as an approach to achieving higher efficiencies (22). The work described here on alkali scandium borates was done for similar reasons.

New scandium borates containing a lanthanide were discovered
during various phase studies. These studies were prompted by an interest in examining the possibility for energy transfer from a $\mathrm{Cr}^{3+}$ ion to $\mathrm{Nd}^{3+}$ ion. A severe limitation of $\mathrm{Nd}^{3+}$ lasers is their low pumping efficiency that results from the weak $4 f-4 f$ parity forbidden absorptions of the $\mathrm{Nd}^{3+}$ ion. Attempts to limit this deficiency by codoping hosts with $\mathrm{Cr}^{3+}$ and $\mathrm{Nd}^{3+}$ have afforded the efficient laser material $\mathrm{Nd}^{3+}: \mathrm{Cr}^{3+}: G S G G\left(\mathrm{Nd}^{3+}: \mathrm{Cr}^{3+}: \mathrm{Gd}_{3} \mathrm{Sc}_{2} \mathrm{Ga}_{3} \mathrm{O}_{12}\right)$. In the garnet family, GSGG exhibits the optimum overlap of the $\mathrm{Cr}^{3+}$ emission band and the $\mathrm{Nd}^{3+}$ absorption bands with suitable lifetimes that afford an efficient transfer of energy (23). A similar transfer of energy has been observed for compounds described in this thesis. A schematic representation of this process of energy transfer is illustrated in Figure 1.4.

## Optical Frequency Conversion

Optical frequency converters are useful materials for extending the output of an infrared laser to shorter wavelengths. Borates are important substances for such purposes. The metaborate $\mathrm{BaB}_{2} \mathrm{O}_{4}$ exhibits a wide transparency range and a high birefrigence that allow the production of the fifth harmonic of a $\mathrm{Nd}^{3+}$ :YAG laser (24). The borate $\mathrm{LiB}_{3} \mathrm{O}_{5}$ has recently been developed and shown to exhibit a threshold power for $50 \%$ conversion efficiency that is two orders of magnitude lower than that of the popular frequency converter potassium dihydrogen phosphate; it also exhibits the highest optical damage threshold yet observed for a solid-state converter (25).


Figure 1.4 Schematic illustration of energy transfer from the sensitizer $\mathrm{Cr}^{3+}$ to the activator $\mathrm{Nd}^{3+}$.

Optical frequency conversion or harmonic generation results from the polarization $P$ induced in a substance by a local electric field of strength E as described in Equation (1)

$$
\begin{equation*}
\mathbf{P}=\chi^{(1)} E+\chi^{(2)} E^{2}+\chi^{(3)} E^{3}+\cdots \tag{1}
\end{equation*}
$$

where the susceptibility coefficients $\chi^{(n)}(n>1)$ define the degree of the nonlinearity. As an example of harmonic generation, we may consider inducing a second-order polarization by using an electric field that varies with time, $E=E_{0} \cos \omega t$, a light wave. With substitution of $E$ into Equation (1), we arrive at Equation (2).

$$
\begin{align*}
\chi^{(2)} E^{2} & =\chi^{(2)} E_{0}^{2} \cos ^{2} \omega t \\
& =1 / 2 \chi^{(2)} E_{0}^{2}(1+\cos 2 \omega t) \tag{2}
\end{align*}
$$

From this equation we see that a two-photon process can afford a polarization and outgoing light wave at twice the frequency of the incident waves.

As chemists, we prefer to view such phenomena on a microscopic rather than macroscopic scale so that we can understand and attempt to control their characteristics. In solids there are typically ionic groups, i.e. $\mathrm{BO}_{3}{ }^{3-}$, or molecules that are readily polarized in an electric field. A description of the induced polarization of a single molecule or group can be written (Equation (3)) in a form similar to that provided in Equation (1).

$$
\begin{equation*}
P_{i}=\alpha_{i j} E_{j}+\beta_{i j k} E_{j} E_{k}+\gamma_{i j k 1} E_{j} E_{k} E_{1}+\ldots \tag{3}
\end{equation*}
$$

The subscripts refer to the molecular soordinate system and the terms $E_{j}, E_{k}$, etc. denote the components of the applied field in this system. Considering now second harmonic generation, it is the components, $\beta$, of the hyperpolarizability tensor that provide the
microscopic information that we are interested in. In this laboratory, a collection of computer programs has been written for the calculation of these components using a procedure derived from second-order perturbation theory with use of CNDO and MNDO methods for calculation of molecular orbital coefficients. The expression for the second-order hyperpolarizability responsible for the second-harmonic generation is given by Equation (4)

$$
\begin{equation*}
\beta_{i j k}(\omega, \omega)=1 / 4 h^{2} \sum_{p} \sum_{e, e^{\prime}} \frac{\langle g| \tilde{u}_{i}|e\rangle\langle e| \tilde{u}_{j}\left|e^{\prime}\right\rangle\left\langle e^{\prime}\right| \tilde{u}_{k}|g\rangle}{\left(\omega_{e}-\omega_{g}-2 \omega\right)\left(\omega_{e}-\omega_{g}-\omega\right)} \tag{4}
\end{equation*}
$$

where $|g\rangle$ represents the ground electronic states and $|e\rangle$ and $\left|e^{\prime}\right\rangle$ represent excited electronic states. The integrals in the numerator represent the transition dipole moments which are related to the intensity of optical transitions between the indicated states and the ground state. These microscopic coefficients may then be summed by use of Equation (5) to afford the macroscopic susceptibility coefficients

$$
\begin{equation*}
\chi_{I J K}^{(2)}(\omega, \omega)=\sum_{i j k} R_{I_{i}} R_{J_{j}} R_{K_{k}} \beta_{i j k}(\omega, \omega) \tag{5}
\end{equation*}
$$

where $R$ is a rotation matrix relating molecular coordinates (ijk) to the crystallographic coordinates (IJK). The expression given above has been simplified by neglecting local field corrections. As such it represents a free ionic group or "oriented gas" model.

Equations (4) and (5) provide the information necessary for a qualitative understanding of the characteristics of second harmonic generation (SHG). First, to achieve high efficiency in SHG a large $\chi^{(2)}$ is required which necessarily means the magnitude of certain
components of $\beta_{i j k}$ should be large. To achieve very large values for the $\beta_{i j k}$, it is necessary, as indicated by the denominator of equation (4), to have electronic absorption bands near in energy to the incident and outgoing waves. Of course, if there is a very good match for SHG it is unlikely the material will be useful for generation of higher harmonics as higher harmonics would most likely be absorbed by the material. The numerator of Equation (4) tells us that we seek large dipole transition moments between ground states and excited states. In practical terms, this means a large redistribution of charge should occur in a ligand-to-metal charge transfer transition. In borates, strong bond dipoles are present in the ground state that are directed toward the 0 atoms. In the excited states these dipoles are reversed and directed at the $B$ atoms, affording large transition dipoles. In triangular $\mathrm{BO}_{3}$ groups, the presence of the $\pi$ system is very important for lowering the HOMO-LUMO gap as well as functioning as the carrier for the resulting difference dipoles.

Having large hyperpolarizibility coefficients does not necessarily afford large values of $\chi^{(2)}$. The microscopic coefficients must add constructively via Equation (5) to afford large macroscopic nonlinearities. This may be readily appreciated by consideration of a centrosymmetric structure. For every $+\chi$ c. center of symmetry will generate $a-\chi$. These two values will sum to zero, affording the nonexistence of second harmonic generation in a centrosymmetric crystal. The crystal structure adopted by a group of ions or molecules becomes the most important aspect in the realization of
large nonlinear effects. This importance of structure is examined here for materials similar to the mineral Huntite by application of the procedure described above.

Synthesis Methodology

A successful study of the relationships between the optical properties and structures in new materials requires that the product of each synthesis be a pure phase whose chemical and structural identity is known and whose morphology is suitable for optical characterization. In general, to determine accurately luminescence properties, SHG powder efficiencies, and crystal structures, single crystal about $100 \mu \mathrm{~m}$ in size are needed. For absorption measurements and determination of phase-matching characteristics, crystals about 1-2 mm must be available.

Powder reactions are a necessary initial step in any solid-state synthesis procedure, but alone they are usually insufficient to produce materials with adequate morphology. Therefore, it is necessary to append to the initial step additional thermal analyses to determine the melting behavior of a compound and, if necessary, a systematic search for solvents to perform the flux growth of incongruent phases. A simple flowchart exhibiting the steps undertaken to prepare suitable samples is given in Figure 1.5.


Figure 1.5 Flowchart for complete crystal synthesis of new materials.

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## CHAPTER 2

## STRUCTURE OF $\mathrm{ScBO}_{3}$

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## Abstract

Scandium borate, $\mathrm{ScBO}_{3}: M_{r}=103.76$, trigonal, $\mathrm{R}-3 \mathrm{c}, \mathrm{a}=4.748(1)$, $c=15.262(2) \AA, V=298.0 \AA^{3}, Z=6, D_{X}=3.47 \mathrm{~g} \mathrm{~cm}^{-3}, M o K \alpha, \lambda=$ $0.71069 \AA, \mu=33.95 \mathrm{~cm}^{-1}, F(000)=300, T=298 \mathrm{~K}, \mathrm{R}=0.017$ for 444 averaged reflections. The octahedral environment of oxygen anions about the scandium(III) ion exhibits a small trigonal elongation, as demonstrated by the value, $92.28(1)^{\circ}$, for the bond angle $0-\mathrm{Sc}-0$.

## Introduction

As a part of our program in new optical materials, we have recently synthesized and structurally characterized a number of new ternary and quaternary borates containing the ion Sc(III) [Sun, Thompson \& Keszler, results to be submitted]. To aid in our understanding and comparisons of the metrical details of these compounds and their spectroscopic features when doped with luminescent ions, we have determined the structure of the symmetric parent $\mathrm{ScBO}_{3}$. When doped with the ion $\operatorname{Cr}(I I I)$, this material functions as a room temperature near-infrared tunable laser (1). The reported fluoresence lifetime of $115 \mu s$ for the ion $\mathrm{Cr}(I I I)$ in the laser material indicates that the environment of the $\operatorname{Sc}(I I I)$ ion is only slightly distorted from $O_{h}$ symmetry. The results of the structure determination are consistent with this result.

## Experimental

Crystals of the title compound were grown from a melt composed of $14 \mathrm{~mol} \% \mathrm{ScBO}_{3}$ and $86 \mathrm{~mol} \% \mathrm{LiBO}_{2}$. The solution was cooled at $8 \mathrm{~K} \mathrm{hr}^{-1}$ from 1273 K to 1023 K with subsequent removal of the solvent by dissolution in water. A crystalline block of dimensions $0.09 \times 0.08$ $\times 0.08 \mathrm{~mm}$ was used for data collection. Unit-cell parameters were derived from a least-squares analysis of the angle settings of 15 reflections in the range $41^{\circ}<2 \theta<48^{\circ}$ that were automatically centered on a Rigaku AFC6R diffractometer. Intensity data were collected with the $\omega-2 \theta$ scan technique; irtensities of 3 standard reflections monitored throughout data collection exhibited an average fluctuation of $1.8 \%$. From the 2228 reflections measured to $\left(\sin \theta_{\max }\right) / \lambda=1.22 \AA^{-1}$ in the index range $0 \leq h \leq 11,-11 \leq k \leq 11$, $-37 \leq 1 \leq 37,444$ unique data with $\mathrm{F}_{0}{ }^{2} \geq 3 \sigma\left(\mathrm{~F}_{0}{ }^{2}\right)$ were obtained.

All calculations were performed on a microVax II computer with programs from the TEXRAY crystallographic software package. The position of the Sc atom was derived by analogy with the calcite structure, with the remaining atomic positions determined from a difference electron density map. Following refinement with isotropic thermal parameters the data were corrected for absorption with the computer program DIFABS (2) and subsequently averaged $\left[R_{\text {int }}=\right.$ 3.8]. Final refinement on $F_{0}$ for those data having $F_{0}{ }^{2}>3 \sigma\left(F_{0}{ }^{2}\right)$ with 11 variables and 444 observations resulted in $\mathrm{R}=0.017, \Delta / \sigma=$ 0.48 , and $R_{W}=0.027$ where the weights are derived from counting statistics and a value of $p=0.05$. The isotropic extinction
parameter $=7.4 \times 10^{-6}(3)$ and $S=0.91$. A maximum peak of 0.46 e $\AA^{-3}$ is observed in the final difference electron density map, corresponding to $0.47 \%$ of a Sc atom. Fractional atomic coordinates and atomic displacement coefficients are given in Tables 2.1 and 2.2, respectively.

Table 2.1. Positional Parameters for $\mathrm{ScBO}_{3}$.

$$
\begin{array}{lll}
x & y & z
\end{array}
$$

| Sc | 0 | 0 | 0 |
| :--- | :--- | :--- | :---: |
| B | 0 | 0 | $1 / 4$ |
| 0 | $0.71038(9)$ | 0 | $1 / 4$ |

Table 2.2. Anisotropic Temperature Coefficients for $\mathrm{ScBO}_{3}$.

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $\mathrm{U}_{23}$ | $B\left(\dot{A}^{2}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Sc | 0.00396(8) | 0.00396 | 0.00374(6) | 0.00198 | 0 | 0 | $0.307(4)$ |
| B | 0.0044(3) | 0.0044 | 0.0052(3) | 0.0022 | 0 | 0 | $0.37(2)$ |
| 0 | 0.00425(9) | 0.0059(1) | 0.0067(1) | 0.0029 | -0.0008 | -0.00165(9) | 0.43(1) |

From symmetry constraints $U_{22}=U_{11}, U_{12}=\frac{W_{2}}{U_{11}}$, and $U_{13}=U_{23}=0$
for the atoms $S c$ and $B$, and for the atom $0, U_{12}=\mathcal{W}_{2} U_{22}$ and
$U_{13}=\frac{1}{2} U_{23} ; \quad B=\left(8 \pi^{2} / 3\right) \sum_{i} \Sigma_{j} U_{i j} a^{*}{ }_{i} a^{*}{ }_{j} a_{i} \cdot a_{j}$.

Discussion

The compound $\mathrm{ScBO}_{3}$ is reported to be the only thermodynamically stable compound in the system $\mathrm{Sc}_{2} \mathrm{O}_{3}-\mathrm{B}_{2} \mathrm{O}_{3}$, having a congruent melting point of $1883 \mathrm{~K}(4)$. From analys is of powder diffraction photographs, it was predicted to be isostructural to the mineral calcite (5). Analysis of precession photographs from single crystals grown from a flux of barium borate established the presence of trigonal symmetry and the space group $R-3 c$, consistent with the calcite structure (6). The structure determination verifies these results, providing refined atomic parameters of high precision.

A drawing of the structure is given in Figure 2.1. The general features of the structure are the same as those described for calcite (7). Bond distances and bond angles are provided in Table 2.3. The bond distance, $1.3752(5) \&$, for the $B-0$ interaction in the planar $\mathrm{BO}_{3}$ group is comparable to similiar bonding distances in the calcite-type materials $\mathrm{AlBO}_{3}, 1.380 \AA(8), \mathrm{FeBO}_{3}, 1.379(2) \AA(9)$, and $\mathrm{LuBO}_{3}, 1.370(3) \AA(10)$. The angle $0-\mathrm{Sc}-0,92.28(1)^{\circ}$, demonstrates the small trigonal elongation of the octahedron of oxide ions about the Sc center. The distance $\mathrm{Sc}-0,2.1200(4) \AA$, compares to the distances 2.120(1) - 2.164(1) \& for the two types of octahedrally coordinated $\mathrm{Sc}\left(\right.$ III) ions in the compound $\mathrm{Sc}_{2} \mathrm{O}_{3}$ (11) and to similar distances, 2.07-2.17 A, observed in the compound $\mathrm{CaSc}_{2} \mathrm{O}_{4}$ (12). Only in $\mathrm{ScPO}_{4}$ with the zircon structure where the Sc(III) ion occupies a distorted cube are dissimilar distances proposed, 2.09 and $2.37 \AA$ (13).


Figure 2.1. Schematic ORTEP drawing of a unit cell of the compound $\mathrm{ScBO}_{3}$. The largest circles represent 0 atoms and the smallest circles represent $B$ atoms. The layers of planar $\mathrm{BO}_{3}$ groups extend orthogonal to the long, c axis.

Table 2.3. Bond Distances ( $A$ ) and Bond Angles $\left({ }^{\circ}\right)$ for $\mathrm{ScBO}_{3}$.

| $\mathrm{SC}-0$ | $2.1200(4)$ | $0-S C-0$ | $87.72(1)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{B}-0$ | $1.3752(5)$ | $0-S C-0$ | $92.28(1)$ |
|  |  | $0-\mathrm{B}-0$ | 120 |
|  |  | SC-0-SC | $123.78(2)$ |
|  |  | B-0-SC | $118.11(1)$ |

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## CHAPTER 3

PREPARATION, STRUCTURE, AND OPTICAL PROPERTIES OF THE NEW ORTHOBORATE $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}$

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## Abstract

The new orthoborate $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}$ has been prepared and structurally characterized by single-crystal $X$-ray methods. It crystallizes in the monoclinic space group $P 2_{1} / n$ in a cell of dimensions $a=4.778(2)$, $b=5.951(1), c=8.158(1) \AA$, and $\beta=90.73(2)^{\circ}$. The structure of the compound is a unique type exhibiting strings comprised of alternating Sc-centered octahedra and Li-centered rectangular planes that extend in the [010] direction. These strings are bridged by 4 -coordinate Li atoms and triangular $\mathrm{BO}_{3}$ groups. The fluorescence spectrum of the doped compound $\mathrm{Li}_{3} \mathrm{Cr}_{0.02} \mathrm{Sc}_{0.98}\left(\mathrm{BO}_{3}\right)_{2}$ exhibits a broad emission band peaking at 790 nm that arises from the vibronic transition ${ }^{4} \mathrm{~T}_{2} \rightarrow{ }^{4} \mathrm{~A}_{2}$ of the $\mathrm{Cr}^{3+}$ ion.

## Introduction

We are involved in the synthesis and study of new borates, with a particular emphas is on those compounds containing the ion $\mathrm{Sc}^{3+}$ for substitutional doping with the ion $\mathrm{Cr}^{3+}$. When doped with the ion $\mathrm{Cr}^{3+}$, the compound $\mathrm{ScBO}_{3}$ functions as a room-temperature, efficient near-infrared tunable laser (1) despite a wavelength of operation that indicates inefficient operation should be observed. From models of the relationship between excited-state absorption and laser efficiency we have proposed (2) that higher efficiencies could be achieved in new, $\mathrm{Cr}^{3+}$-doped scandium borates where the emission band is blueshifted relative to that observed in the simple material $\mathrm{Cr}^{3+}: \mathrm{ScBO}_{3}$.

As part of our ongoing studies of the structural and optical properties that are conducive to highly efficient $\mathrm{Cr}^{3+}$ lasing, we have examined the phase 1 ine $\mathrm{Li}_{3} \mathrm{BO}_{3}-\mathrm{ScBO}_{3}$ for new compounds. We report here the preparation, crystal structure, and optical properties of the new compound $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}$ that has resulted from this study.

## Experimental

Synthes is
The powder sample of $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}$ was prepared by heating a stoichiometric mixture of the reagents $\mathrm{LiNO}_{3}$ (ALFA, ultrapure), $\mathrm{Sc}_{2} \mathrm{O}_{3}$ (ALFA, $99.9 \%$ ), and $\mathrm{B}_{2} \mathrm{O}_{3}$ (ALFA, $99.99 \%$ ) at $600^{\circ} \mathrm{C}$ for 6 hours followed by grinding and an additional heating at $875^{\circ} \mathrm{C}$ for 20 hours. Phase identification was performed by using a Philips powder X-ray diffractometer.

Single crystals were grown from a stoichiometric melt by a horizontal zone-melting method. A 500 mg pellet of the sample was placed in a vitreous graphite boat and inductively heated via a graphite tube susceptor (POCO graphite, Grade DFP2) that was enclosed in a quartz tube. The system was flushed with Ar and heated to a maximum temperature of $975^{\circ} \mathrm{C}$. The induction coil was translated at $1 \mathrm{~mm} \mathrm{hr}^{-1}$ until it had traveled approximately 25 mm beyond the trailing edge of the sample. A number of crystals of maximum edge length 1 mm were separated from the cooled melt.

Crystals of $\mathrm{Li}_{3} \mathrm{Cr}_{0.02} \mathrm{SC}_{0.98}\left(\mathrm{BO}_{3}\right)_{2}$ used for the fluoresence measurement were prepared in a manner similar to that used for the compound $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}$; the ion $\mathrm{Cr}^{3+}$ was substituted for the ion $\mathrm{Sc}^{3+}$ by addition of the reagent $\mathrm{Cr}\left(\mathrm{NO}_{3}\right)_{3} \cdot 8 \mathrm{H}_{2} \mathrm{O}$ (AESAR, $99.99 \%$ ).

## X-ray Work

A single crystal with dimensions $0.2 \times 0.2 \times 0.1 \mathrm{~mm}$ was selected for the structure determination. X-ray data were collected on a

Rigaku AFC6R diffractometer with graphite-monochromated Mo K $\alpha$ radiation. Accurate unit-cell parameters were derived from a leastsquares analysis of the angle settings of 15 reflections in the range $30^{\circ} \leq 2 \theta \leq 45^{\circ}$ that had been automatically centered on the diffractometer. Intensity data were collected with the $\omega-2 \theta$ scan technique with a scan rate of $16^{\circ} /$ minute in $\omega$; three standard reflections measured after each block of 199 reflections exhibited a random fluctuation of less than $1.7 \%$. From the 2196 reflections measured to $2 \theta=90^{\circ}$ in the range of indices $0 \leq h \leq 9,0 \leq k \leq 11$, $-14 \leq 1 \leq 14$, 1514 unique data with $F_{0}{ }^{2} \geq 3 \sigma\left(F_{0}{ }^{2}\right)$ were obtained. Crystal data and experimental conditions are summarized in Table 3.1.

All calculations were performed on a microVax II computer with programs from the TEXRAY crystallographic software package (3). The systematic absences: h01, $\mathrm{h}+1=2 \mathrm{n}+1$, and $0 \mathrm{KO}, \mathrm{k}=2 \mathrm{n}+1$, are consistent with the space group $P 2_{1} / n$. The positional parameters for the Sc atom were determined from the direci methods program MITHRIL (4). The atoms Li(1), B and 0 were located from analys is of subsequent difference electron density syntheses. The position of atom $\mathrm{Li}(2)$ was determined from an analysis of a drawing of the unit cell; the position was proved by successful refinement that led to a significant decrease in the residual and by the chemically reasonable internuclear separations that result.

Following refinement with isotropic thermal parameters the data were corrected for absorption with the computer program DIFABS (5). The final cycle of refinement was performed on $F$ for those 1514 reflections having $\mathrm{F}_{0}{ }^{2}>3 \sigma\left(\mathrm{~F}_{0}{ }^{2}\right)$ and included anisotropic thermal

Table 3.1. Crystal Data and Experimental Conditions for $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}$.

Formula Wt., amu
183.40

Space Group
$P 2_{1} / n$
Lattice Parameters:

| $\mathrm{a}, \AA$ | $4.778(2)$ |
| :--- | :--- |
| $\mathrm{b}, \AA$ | $5.951(1)$ |
| $\mathrm{c}, \AA$ | $8.158(1)$ |
| $B$, deg. | $90.73(2)$ |
| $V, \AA^{3}$ | $231.97(8)$ |

Z 2

Temperature, ${ }^{\circ} \mathrm{C} 23$
$2 \theta$ Scan Range $\quad 4^{\circ} \leq 2 \theta \leq 90^{\circ}$
No. Unique Data with $\mathrm{F}_{0}{ }^{2}>3 \sigma\left(\mathrm{~F}_{0}{ }^{2}\right)$ 1514
$R$ (on $F$ for $F_{0}{ }^{2}>3 \sigma\left(F_{0}{ }^{2}\right)$
0.030
$R_{W}(F)$
0.042

Error in Observation of Unit Wt., $e^{2}$
1.31

Maximum Shift in Final Cycle 0.01
parameters for each atom. The final values for $R$ and $R_{W}$ are 0.030 and 0.042 , respectively. The largest peak in the final difference electron density map corresponds to $0.53 \%$ of a Sc atom. Positional parameters and equivalent isotropic parameters are listed in Table 3.2.
$X$-ray powder data for $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}$ were obtained with $\mathrm{Cu} \mathrm{K} \alpha$ radiation on an automated Philips diffractometer. Values of $2 \theta$ were corrected with the use of NBS Si powder (640b) as an internal standard (6). The unit cell parameters were determined from least-squares analysis of 13 reflections in the range of $2 \theta, 26^{\circ}-70^{\circ}$, with use of the computer program POLSQ. The refined cell of dimensions $\mathrm{a}=$ $4.774(2) \&, b=5.940(2) ~ \&, c=8.148(4) \&, \beta=90.31(8)^{\circ}$, and $V=$ 231.1(2) $\dot{A}^{3}$, is in agreement with that observed from the singlecrystal data.

Other Measurements
The melting point of $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}$ was measured with use of a Harrop Model DT-726 differential thermal analyzer that is interfaced to a PC via a Metrabyte DAS-8 A/D converter and Series M1000 signal conditioner. The sample and reference $\mathrm{Al}_{2} \mathrm{O}_{3}$ ( 100 mg each) were loaded in Pt cups and heated at $10^{\circ} \mathrm{C} /$ minute. These data indicate that the compound melts at $927(4)^{\circ} \mathrm{C}$.

The fluorescence measurement was performed with use of lock-in techniques and an automated 0.5 m Jarrell-Ash monochromator equipped with an S-1 photomultiplier tube that was cooled with liquid $N_{2}$. The sample was excited with an Ar laser operated at 514.5 nm .

The infrared spectrum was recorded from a KBr pellet on a Mattson

Table 3.2. Positional Parameters and Equivalent Isotropic Thermal Parameters for $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}$.

| atom | X | y | z | $B_{e q}{ }^{\text {a }}, \dot{A}^{2}$ |
| :---: | :---: | :---: | :---: | :---: |
| Sc | 0 | 0 | 0 | 0.410(7) |
| Li(1) | 0.5147(6) | 0.2491(5) | 0.2018(3) | 1.04(8) |
| Li(2) | 0 | 1/2 | 0 | 1.7(1) |
| O(1) | 0.3104(2) | 0.2464(1) | 0.0018(1) | 0.60(2) |
| O(2) | $0.7670(2)$ | $0.2617(2)$ | -0.1104(1) | 0.69(2) |
| O(3) | 0.3718(2) | 0.4129(2) | -0.2604(1) | 0.66(2) |
| B | 0.4849 (2) | 0.3042(2) | -0.1255(1) | 0.45(3) |
| ${ }^{a} B_{e q}=\left(8 \pi^{2} / 3\right) \Sigma_{i} \Sigma_{j} U_{i j} a^{*}{ }_{i} a^{*}{ }_{j} a_{i} \cdot a_{j}$ |  |  |  |  |

Sirius 100 FTIR spectrometer. A spectral resolution of $1.0 \mathrm{~cm}^{-1}$ was employed with 10 scans of the sample and background averaged to obtain the spectrum.

## Results and Discussion

A labeled drawing of the unit cell is given in Figure 3.1. Selected bond distances and angles are listed in Table 3.3.

The structure is a new type exhibiting strings (Figure 3.2) comprised of alternating Sc-centered octahedra and Li-centered rectangular planes that extend in the [010] direction; they are joined by tetrahedral $\mathrm{LiO}_{4}$ groups and triangular $\mathrm{BO}_{3}$ groups.

The Sc atoms occupy distorted octahedra that are isolated by intervening Li - and B -centered polyhedra. The average $\mathrm{Sc}-\mathrm{O}$ distance, $2.105(2) \AA$, compares to that, $2.1200(4) \AA$, reported for the simple compound $\mathrm{ScBO}_{3}(7)$. The most prominent angular distortion, $0(1)-\mathrm{Sc}-0(2), 81.69(4)^{\circ}$, of the octahedron involves the edge $O(1) \cdots O(2)$ that is shared by the rectangular plane centered by atom $\mathrm{Li}(2)$. The remaining $0-\mathrm{Sc}-0$ angles (cf. Table 3.3) are comparable to the small trigonal distortion of the octahedron in $\mathrm{ScBO}_{3}$ which exhibits the 0-Sc-0 angle, $92.28(1)^{\circ}$.

Each of the two crystallographically independent Li atoms exhibit 4-coordination; atom $\mathrm{Li}(1)$ resides in a distorted tetrahedral environment while atom $\mathrm{Li}(2)$ occupies a rectangular planar site. The tetrahedron about atom $\mathrm{Li}(1)$ exhibits large distortions from ideal tetrahedral angles; irregular angles include $0(2)-\operatorname{Li}(1)-0(3), 90.6(1)^{\circ}$, and $O(1)-\mathrm{Li}(1)-O(3), 124.3(1)^{\circ}$. Such distortions from a regular tetrahedron are comparable to those reported in the compound $\mathrm{Li}_{2} \mathrm{CuO}_{2}$ (8) with 0-Li-0 angles, $91^{\circ}$ and $144^{\circ}$. The average bond distance of $\mathrm{Li}(1)-0,2.0(1) \AA$, compares to those, $1.91(2) \AA$ and $1.97 \AA$, observed


Figure 3.1 Drawing of a unit cell of $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}$. The largest open circles represent 0 atoms, the smallest circles represent $B$ atoms, and the open circles with shaded bonds represent Sc atoms.

Table 3.3. Selected Bond Distances ( $\AA$ ) and Bond Angles ( ${ }^{\circ}$ ) for $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}$.

| $\mathrm{Sc}-0(1)$ | $2.0855(9) \times 2$ | $0(1)-\mathrm{Sc}-0(2)$ | $81.69(4)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{Sc}-0(2)$ | $2.1093(9) \times 2$ | $0(1)-\mathrm{Sc}-0(3)$ | $87.97(4)$ |
| $\mathrm{Sc}-0(3)$ | $2.1201(9) \times 2$ | $0(2)-\mathrm{Sc}-0(3)$ | $86.80(4)$ |
|  |  |  |  |
| $\mathrm{Li}(1)-0(1)$ | $1.891(3)$ | $0(1)-\mathrm{Li}(1)-0(2)$ | $111.5(1)$ |
| $\mathrm{Li}(1)-0(2)$ | $1.949(3)$ | $0(1)-\mathrm{Li}(1)-0(3)$ | $124.3(1)$ |
| $\mathrm{Li}(1)-0(3)$ | $1.981(3)$ | $0(1)-\mathrm{Li}(1)-0(3)$ | $109.1(1)$ |
| $\mathrm{Li}(1)-0(3)$ | $2.136(3)$ | $0(2)-\mathrm{Li}(1)-0(3)$ | $113.1(1)$ |
|  |  | $0(2)-\mathrm{Li}(1)-0(3)$ | $90.6(1)$ |
|  |  | $0(3)-\mathrm{Li}(1)-0(3)$ | $102.0(1)$ |


| $\operatorname{Li}(2)-0(1)$ | $2.1162(9) \times 2$ | $0(1)-\operatorname{Li}(2)-0(1)$ | 180 |
| :--- | :--- | :--- | :--- |
| $\mathrm{Li}(2)-0(2)$ | $2.0090(9) \times 2$ | $0(2)-\operatorname{Li}(2)-0(2)$ | 180 |
|  |  | $0(1)-\operatorname{Li}(2)-0(2)$ | $96.67(4)$ |


| $B-0(1)$ | $1.384(1)$ | $0(1)-B-0(2)$ | $119.1(1)$ |
| :--- | :--- | :--- | :--- |
| $B-0(2)$ | $1.376(1)$ | $0(1)-B-0(3)$ | $118.8(1)$ |
| $B-0(3)$ | $1.381(1)$ | $0(2)-B-0(3)$ | $122.1(1)$ |



Figure 3.2 A string comprised of alternating Li-centered rectangular planes and Sc-centered octahedra extending along the $b$ axis.
for the tetrahedral sites in the compounds $\mathrm{Ba}_{2} \mathrm{LiB}_{5} \mathrm{O}_{10}$ (9) and $\mathrm{Li}_{2} \mathrm{CO}_{3}$ (10), respectively. The rectangular planar environment around the Li atom is uncommon in the structural chemistry of oxides. A rectangular planar site for the Li atom has been observed in the compound $\mathrm{NdLiP}_{4} \mathrm{O}_{12}$ (11). The average bond distance, 2.0(1) $\dot{A}$ and the bond angle, $96.67(4)^{\circ}$, observed for the rectangular planar site of atom $\mathrm{Li}(2)$ in the title compound are comparable to those, $2.0(1) \AA$ and $102.8(6)^{\circ}$, reported for the similar site in the compound $\mathrm{NdLiP}_{4} \mathrm{O}_{12}$.

The $B$ atom binds to atoms $O(1), O(2)$, and $O(3)$ in a triangular manner. The average B-O distance, $1.380(4) \AA$, compares to the corresponding distance, $1.3752(5) \&$, reported for the compound $\mathrm{ScBO}_{3}$. Each 0 atom is coordinated by four cations in approximate tetrahedral coordination. Atoms $O(1)$ and $O(2)$ are bound by atoms Sc, $B$, $\mathrm{Li}(1)$, and $\mathrm{Li}(2)$ while atom $\mathrm{O}(3)$ binds to cations $\mathrm{Sc}, \mathrm{B}$, and two Li(1).

The assignment of the IR spectrum recorded for the title compound was accomplished by comparison of the observed IR bands to the compounds $\mathrm{MBO}_{3}$ where $\mathrm{M}=\mathrm{Sc}$, La , and In (12). The anion $\mathrm{BO}_{3}{ }^{3-}$ with symmetry $D_{3 h}$ is expected to exhibit four vibrational modes that are infrared active (Figure 3.3). As observed in the compound $\mathrm{ScBO}_{3}$, the anion $\mathrm{BO}_{3}{ }^{3-}$ with symmetry $\mathrm{D}_{3 \mathrm{~h}}$ affords four frequencies $\nu_{1}=$ $939 \mathrm{~cm}^{-1}, \nu_{2}=759 \mathrm{~cm}^{-1}$ ( $789 \mathrm{~cm}^{-1}$ for the ${ }^{10} \mathrm{~B}$ isotope), $\nu_{3}=1221.5$ $\mathrm{cm}^{-1}$, and $\nu_{4}=639.6 \mathrm{~cm}^{-1}$. Similarly, as seen in the spectrum of the compound $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}$ (Figure 3.4), the strong, broad band in the vicinity of $1260 \mathrm{~cm}^{-1}$ is attributable to the antisymmetric stretching mode $\nu_{3}$ and the band at $739 \mathrm{~cm}^{-1}$ is assigned to the out-of-plane


Figure 3.3 Vibrational modes for the $\mathrm{BO}_{3}{ }^{3-}$ group: (a) $\nu_{1}$, the symmetric stretching mode, (b) $\nu_{2}$, the out-of-plane bending mode, (c) $\nu_{3}$, the doubly-degenerate antisymmetric stretching mode, and (d) $\nu_{4}$, the doublydegenerate planar bending mode. The symbol + indicates motion above the plane of the paper. The symbol indicates motion below the plane of the paper.


Figure 3.4 The infrared absorption spectrum of $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}$.
bending mode $\nu_{2}$. The weakest band at $940 \mathrm{~cm}^{-1}$ arises from the symmetric stretch $\nu_{1}$ that is weakly infrared active due to the $C_{2 v}$ symmetry. The small, narrow peak observed at $789 \mathrm{~cm}^{-1}$ probably results from a high-frequency component of $\nu_{2}$ caused by the simple ${ }^{10} \mathrm{~B}$ isotope shift. The bands at $617 \mathrm{~cm}^{-1}$ and $658 \mathrm{~cm}^{-1}$ derive from the degenerate planar bending mode $\nu_{4}$ that is split by the lower symmetry $\mathrm{C}_{2 \mathrm{~V}}$ of the the $\mathrm{BO}_{3}$ group; the degenerate mode $\nu_{3}$ also splits.

A room temperature fluorescence spectrum of $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}$ doped to $2 \mathrm{~mol} \%$ with the ion $\mathrm{Cr}^{3+}$ is shown in Figure 3.5. The broad emission band peaking at about 790 nm is associated with the vibronic transition ${ }^{4} T_{2} \rightarrow{ }^{4} A_{2}$. No $R$ lines $\left({ }^{2} E \rightarrow{ }^{4} A_{2}\right)$ were observed. This result indicates the presence of a relatively weak crystal field at the $\mathrm{Cr}^{3+}$ site where the broad-band emission only occurs if the energy of ${ }^{4} T_{2}$ state is well below that of the ${ }^{2} E$ state as indicated in the Tanabe-Sugano diagram for a $d^{3}$ trarisition-metal (13). The fluorescence band is similar to that observed in the compound $\mathrm{Cr}^{3+}: \mathrm{ScBO}_{3}$ except the peak maximium is blue-shifted approximately 20 nm , indicating a stronger crystal field in the Li compound. The Li atoms in the compound $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}$ play an important role in affecting the accumulation of charge on the borate groups which affords the increased crystal field. In the compound $\mathrm{ScBO}_{3}$, the doped ion $\mathrm{Cr}^{3+}$ competes with neighboring $\mathrm{Sc}^{3+}$ ions for bonding electron density associated with the $\mathrm{BO}_{3}{ }^{3-}$ group. In the compound $\mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}$, the $\mathrm{Cr}^{3+}$ ion competes effectively with the more electropositive neighboring $\mathrm{Li}^{+}$ions which tend to contribute more electron density to the orthoborate group. The blue shift, however, is much smaller


Figure 3.5 The luminescence spectrum of $\mathrm{Cr}^{3+}: \mathrm{Li}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{2}$.
The fluorescence intensity is given in arbitrary units.
than the 60 nm observed for the compound $\mathrm{Cr}^{3+}: \mathrm{Sr}_{3} \mathrm{Sc}\left(\mathrm{BO}_{3}\right)_{3}$ (2) even though $\mathrm{Li}^{+}$and $\mathrm{Sr}^{2+}$ are considered to have similar values of electronegativity. This result is consistent with our expectations and the higher covalency of the Li-0 bond as compared with the $\mathrm{Sr}-\mathrm{O}$ bond that results from the greater overlap of orbitals with the same principal quantum number. This covalent bonding tempers the electropositive nature of the $\mathrm{Li}^{+}$ion to afford in this case only a small increase in the crystal field.

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## CHAPTER 4

# CRYSTAL STRUCTURES AND OPTICAL PROPERTIES OF HUNTITE-TYPE RARE-EARTH SCANDIUM BORATES $\mathrm{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ AND NdSc ${ }_{3}\left(\mathrm{BO}_{3}\right)_{4}$ 

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Abstract

The rare-earth scandium borates $\operatorname{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ and $\mathrm{NdSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ crystallizing in the Huntite-type structures have been synthesized and structurally characterized by single-crystal X-ray methods. Crystal data for $\mathrm{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}:$ monoclinic, $\mathrm{Cc}, \mathrm{a}=7.728(1), \mathrm{b}=9.843(1), c=$ 12.043(1) $\AA, \beta=105.39(1)^{\circ}, Z=4$, and $V=883.1 \AA^{3}$. Crystal data for $\mathrm{NdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}:$ rhombohedral, $\mathrm{R} 32, a=9.7723(9), c=7.928(2) \AA$, $Z=3$, and $V=655.7(2) \AA^{3}$. Both structures exhibit layers of triangular $\mathrm{BO}_{3}$ groups interleaved by Sc atoms in octahedral sites and La (Nd) atoms in trigonal prismatic sites. Fluorescence data for ions $\mathrm{Cr}^{3+}$ and $\mathrm{Nd}^{3+}$ doped into crystals of $\mathrm{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ and $\mathrm{NdSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ are presented. The higher efficiency for second harmonic generation that results for the rhombohedral structure derives from a favorable orientation of the $\mathrm{BO}_{3}$ groups.

## Introduction

Borates having the formula $\operatorname{LnE} E_{3}\left(\mathrm{BO}_{3}\right)_{4}$ where $\mathrm{Ln}=$ selected lanthanides and $E=A 1$ or $G a$ are isomorphous to the mineral Huntite $\mathrm{CaMg}_{3}\left(\mathrm{CO}_{3}\right)_{4}$, which crystallizes in the acentric space group R32 (1)(3); monoclinic derivatives have also been reported for the compounds $\mathrm{NdAl}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ (4) and $\mathrm{GdAl}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ (5). Because of their acentric structures and wide ranges of transparency, these borates have attracted attention as optical frequency conversion materials (6) and selfdoubling laser hosts. The compound $\mathrm{NdAl}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ has also been demonstrated as a CW laser operating at 1054 nm (7). The initial observation of efficient cross pumping of a $\mathrm{Nd}^{3+}$ ion by energy transfer from a $\mathrm{Cr}^{3+}$ ion was reported for the borate $\mathrm{Nd}(\mathrm{Al}, \mathrm{Cr})_{3}\left(\mathrm{BO}_{3}\right)_{4}$ (8).

Study of many of the optical characteristics of this class of materials requires that single crystals of suitable sizes be available for characterization. As all the Al and Ga anologs melt incongruently, single crystals must be grown from a flux.

Surprisingly, despite the interest in these compounds, no reports have been made on the existence of derivatives containing Sc atoms in place of the Al or Ga atoms. Such derivatives could offer some advantages in crystal growth as well as providing the opportunity to realize stable compounds with larger cations on the Ln site. In this report we describe some initial results on the first examples of Huntite borates containing the atoms Sc and La, namely the monoclinic phase $\mathrm{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ and the rhombohedral phase $\mathrm{NdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$.

## Experimental

A homogeneous powder of $\operatorname{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ was prepared by heating a stoichiometric mixture of the reagents, $\mathrm{La}\left(\mathrm{NO}_{3}\right)_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ (AESAR, $99.9 \%$ ), $\mathrm{Sc}_{2}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ (ALFA, $99.9 \%$ ), and $\mathrm{B}_{2} \mathrm{O}_{3}$ (ALFA, $99.99 \%$ ) at $650^{\circ} \mathrm{C}$ for 6 hours. The resulting powders were ground and heated at $950^{\circ} \mathrm{C}$ for 20 hours. Phase identification was performed on an automated Philips powder diffractometer. Crystals of $\operatorname{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ were grown from a melt composed of $33 \mathrm{wt} \.% \mathrm{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ and $67 \mathrm{wt} \.% \mathrm{LiBO}_{2}$. The melt was cooled at $8^{\circ} \mathrm{Chr}{ }^{-1}$ from $1000^{\circ} \mathrm{C}$ to $750^{\circ} \mathrm{C}$, then air quenched. A number of crystals with an average edge length of 1 mm were isolated by dissolution of the excess $\mathrm{LiBO}_{2}$ in boiling $\mathrm{H}_{2} \mathrm{O}$.

The compound $\mathrm{NdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ has been prepared in powder form. A stoichiometric mixture of reagents, $\mathrm{Nd}_{2}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3} \cdot 10 \mathrm{H}_{2} \mathrm{O}$ (ALFA, 99.9\%), $\mathrm{Sc}_{2}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$, and $\mathrm{B}_{2} \mathrm{O}_{3}$, was heated at $750^{\circ} \mathrm{C}$ for 6 hours, and then $900^{\circ} \mathrm{C}$ for 20 hours with intermittent grindings. Single crystals of $\mathrm{NdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ were grown from a flux of $\mathrm{LiBO}_{2}$ in a manner similar to that used for $\operatorname{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$; purple crystals of hexagonal shape were obtained.

Crystals of $\mathrm{LaCr}_{0.30} \mathrm{Sc}_{2 \cdot 70}\left(\mathrm{BO}_{3}\right)_{4}, \mathrm{La}_{0.99} \mathrm{Nd}_{0.01} \mathrm{SC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$, and $\mathrm{NdCr}_{0.03} \mathrm{SC}_{2.97}\left(\mathrm{BO}_{3}\right)_{4}$ used for the fluorescence measurements were prepared in a manner similar to that used for their parent compounds. The reagents $\mathrm{Cr}\left(\mathrm{NO}_{3}\right)_{3} \cdot 9 \mathrm{H}_{2} \mathrm{O}$ (AESAR, $99.99 \%$ ) and $\mathrm{Nd}_{2}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3} \cdot 10 \mathrm{H}_{2} \mathrm{O}$ were used to prepare the doped compounds.

## X-ray Data Collection

Crystals of $\operatorname{LaSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ and $\mathrm{NdSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ with dimensions $0.1 \times$ $0.2 \times 0.3 \mathrm{~m}$ and $0.2 \times 0.2 \times 0.3 \mathrm{~mm}$, respectively, were mounted on glass fibers with silicone, and X-ray data were collected on a Rigaku AFC6R diffractometer with Mo Ka radiation. Accurate unit cell parameters for $\operatorname{LaSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ and $\mathrm{NdSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ were derived from the least-squares refinement of the angular settings of 25 and 17 reflections, respectively, in the range $30^{\circ} \leq 2 \theta \leq 45^{\circ}$ that had been automatically centered on the diffractometer. Intensity data were collected with the $\omega-2 \theta$ scan technique; intensities of 3 standard reflections were measured after every 199 reflections and exhibited no significant fluctuation. Crystallographic data and experimental conditions for each compound are reported in Table 4.1.

## Structure Solution and Refinement

Crystal structures were solved by using a microvax II computer with the TEXRAY crystallographic software package (9).
$\operatorname{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$. The crystal was determined to belong to Laue group $2 / \mathrm{m}$. The systematic extinctions indicated two possible space groups: acentric space group Cc and centrosymmetric space group $C 2 / c$. The acentric group was confirmed by observation of a signal from an optical second harmonic measurement. The atoms La and Sc were located with the use of the direct methods program MITHRIL (10). The positions of the remaining atoms were revealed by successive difference electron density syntheses. Following refinement with isotropic thermal parameters on each atom the data were corrected for absorption with the program DIFABS (11). The refinement with 1102

Table 4.1. Crystal Data and Experimental Conditions for the Compounds $\mathrm{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ and $\mathrm{NdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$.

$$
\mathrm{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4} \quad \mathrm{NdSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}
$$

formula wt., amu
space group
a, $\AA$
b, $\AA$
c, A
$\beta$, deg.
$V, \AA^{3}$
$Z$
$\rho_{\text {calcd }}, \mathrm{g} \mathrm{cm}^{-3}$
temp., ${ }^{\circ} \mathrm{C}$
$\mu\left(\mathrm{Mo} \mathrm{K} \alpha\right.$ ), $\mathrm{cm}^{-1}$
70.47
81.73
$R\left(\right.$ on $F$ for $\left.F_{0}>3 \sigma\left(F_{0}{ }^{2}\right)\right)$
0.023
0.039
$R_{W}(F)$
0.029
0.049
reflections having $\mathrm{F}_{0}{ }^{2}>3 \sigma\left(\mathrm{~F}_{0}{ }^{2}\right)$ converged to $\mathrm{R}=0.023$ and $R_{W}=0.029$.
$\mathrm{NdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$. The phase was determined to belong to Laue group $-3 m 1$. The systematic absence, $n k l,-n+k+1=3 n$, is consistent with the space group R32 that is observed in other rhombohedral Huntite borates. Atomic parameters reported for the rhombohedral phase $\mathrm{NdAl}_{3}\left(\mathrm{BO}_{3}\right)_{4}(2)$ were used as the starting point for refinement. The data were corrected for absorption with the use of the computer program DIFABS. The final cycle of refinement performed on $F_{0}$ with those 369 unique reflections having $\mathrm{F}_{0}{ }^{2}>3 \sigma\left(\mathrm{~F}_{0}{ }^{2}\right)$ afforded residuals $R=0.039$ and $R_{W}=0.049$.

Fractional atomic coordinates and isotropic temperature coefficients for each compound are listed in Table 4.2.

## Optical Measurements

The fluorescence measurement of $\mathrm{Cr}^{3+}: \mathrm{NdSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ crystals was performed by using a Jarrell-Ash long wavelength monochromator and an Ar-laser operated at 514.5 nm for excitation. The signal was detected with an S-1 photomultiplier tube and lock-in techniques.

The fluorescence spectra of $\mathrm{Cr}^{3+}: \operatorname{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ and $\mathrm{Nd}^{3+}: \mathrm{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ were recorded at Lawrence Livermore National Laboratory (LLNL) with use of a $\mathrm{He} / \mathrm{Ne}$ laser operated at 632.8 nm for excitation, a PbS detector, and lock-in techniques.

The harmonic generation experiment was performed at LLNL following standard procedures (6). The signal observed corresponded to $10 \%$ of that produced by the standard quartz.

Table 4.2a. Atomic Parameters and Equivalent Isotropic Thermal Parameters for the Compound $\operatorname{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$.

| atom | $x$ | y | $z$ | $B(e q)$ |
| :---: | :---: | :---: | :---: | :---: |
| La | 0.2277 | 0.03565(4) | 0.6201 | 0.572(9) |
| Sc(1) | 0.2768(7) | 0.2527 (6) | 0.8954(5) | 0.16(7) |
| Sc(2) | $0.1802(7)$ | 0.2490(7) | 0.3444 (5) | 0.68(8) |
| $\mathrm{Sc}(3)$ | -0.274(1) | 0.0749(1) | 0.6203(6) | 0.38(2) |
| O(1) | 0.290(2) | 0.246(1) | 0.515(1) | 0.9(2) |
| O(2) | -0.118(1) | 0.236(1) | 0.5764(8) | 0.4(2) |
| O(3) | $0.323(2)$ | -0.088(1) | 0.805(1) | 0.4(2) |
| O(4) | $0.329(1)$ | 0.410(1) | 0.3024(8) | 0.3(2) |
| O(5) | 0.523(2) | -0.058(1) | 0.623(1) | 0.6(2) |
| O(6) | -0.072(2) | -0.057(1) | 0.605(1) | 0.6(2) |
| $0(7)$ | 0.475(1) | 0.116(1) | -.858(1) | 0.4(2) |
| O(8) | -0.016(2) | 0.114(1) | 0.370(1) | 0.8(3) |
| O(9) | $0.112(1)$ | 0.401(1) | $0.9403(8)$ | 0.5(2) |
| O(10) | $0.156(1)$ | 0.233(1) | 0.7206(9) | 0.4(2) |
| $0(11)$ | $0.557(1)$ | $0.221(1)$ | 0.6644(8) | 0.5(2) |
| O(12) | $0.124(2)$ | -0.097(1) | 0.438(1) | 0.8(3) |
| $B(1)$ | 0.472(3) | -0.022(2) | $0.866(2)$ | 0.3(4) |
| $B(2)$ | $0.035(2)$ | $0.303(2)$ | $0.641(2)$ | 0.9(4) |
| $B(3)$ | -0.020(3) | -0.030(2) | 0.366(2) | 0.5(4) |
| $B(4)$ | -0.065(2) | -0.193(2) | 0.593(1) | $0.1(3)$ |

Table 4.2b. Atomic Parameters and Equivalent Isotropic Thermal Parameters for the Compound $\mathrm{NdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$.

| atom | $x$ | y | $z$ | $B(e q)$ |
| :---: | :---: | :---: | :---: | :---: |
| Nd | 0 | 0 | 0 | 0.43(2) |
| Sc | 0.4534(2) | 0 | 0 | 0.57(3) |
| O(1) | 0.1413(9) | 0 | 1/2 | $0.7(1)$ |
| $O(2)$ | 0.5428(7) | $0.8580(7)$ | 0.4857(7) | 0.90(7) |
| O(3) | 0.410(2) | 0 | 1/2 | 3.6(3) |
| $B(1)$ | 0 | 0 | 1/2 | 0.5(2) |
| $B(2)$ | 0.548(1) | 0 | 1/2 | 1.0(1) |

## Results and Discussion

## Crystal Structure

The results of the single-crystal studies indicate that the compound $\operatorname{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ is similar to the high-temperature form of $\mathrm{NdAl}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ while the compound $\mathrm{NdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ is isostructural to the low-temperature form of $\mathrm{NdAl}_{3}\left(\mathrm{BO}_{3}\right)_{4}$. One general feature of the two structures is the presence of layers of triangular $\mathrm{BO}_{3}$ groups linked by the metal ions. The layers in $\operatorname{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ are stacked approximately along the diagonal of the ac face, as shown in Figure 4.1, and the layers in $\mathrm{NdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ are stacked along the c axis, as shown in Figure 4.2. Selected bond distances and bond angles are given in Table 4.3.

Three crystallographically independent Sc atoms are present in the structure of $\mathrm{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$. Each Sc atom occupies a distorted 0 octahedron with bond distances ranging from 2.00(1) to 2.17(1) $\AA$ and angular distortions from the orthogonal angles of an ideal octahedron that include $0(2)-\mathrm{Sc}(1)-0(7), 98.5(4)^{\circ}, 0(4)-\mathrm{Sc}(2)-0(11), 77.1(4)^{\circ}$, and $0(4)-\mathrm{Sc}(3)-\mathrm{O}(5), 96.3(5)$. These are comparable to the $\mathrm{Sc}-0$ distances, $2.062(6)-2.13(1) \dot{A}$, observed in the compound $\mathrm{NdSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ with the Sc atom occupying a distorted 0 octahedron that exhibits the angular distortions $0(2)-\mathrm{Sc}-\mathrm{O}(2), 101.7(4)^{\circ}$, and $\mathrm{O}(1)-\mathrm{Sc}-\mathrm{O}(3)$, $76.4(6)^{\circ}$. The Sc-centered octahedra in both structures are condensed by sharing edges to form twisted chains. The repeat units in the chains of the structures of $\operatorname{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ ar.d $\mathrm{NdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ consist of links of six octahedra and three octahedre. (Figures 4.3 and 4.4),


Figure 4.1 Drawing of a unit cell of $\operatorname{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$. The largest circles represent 0 atoms, the small filled circles represent La atoms, and the open circles with shaded bonds represent Sc atoms. The layers of $\mathrm{BO}_{3}$ groups are stacked approximately along the diagonal of the ac face.


Figure 4.2 Drawing of a unit cell of $\mathrm{NaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$. The largest circles represent 0 atoms, the smallest circles represent $B$ atoms, and the open circles with shaded bonds represent Sc atoms. The layers of $\mathrm{BO}_{3}$ groups extend orthogonal to the $c$ axis.

Table 4.3a. Selected Bond Distances ( $A$ ) and Bond Angles ( ${ }^{\circ}$ ) for the Compound $\mathrm{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$.


| Table 4,3b. | Selected Bond Distances ( $\AA$ ) and Bond Angles ( ${ }^{\circ}$ ) for the Compound $\mathrm{NdSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$. |  |  |
| :---: | :---: | :---: | :---: |
| Nd-0(2) | $2.432(6) \times 6$ | $\mathrm{O}(2)-\mathrm{Nd}-\mathrm{O}(2)$ | 72.8(3) |
|  |  | $\mathrm{O}(2)-\mathrm{Nd}-\mathrm{O}(2)$ | 88.8(2) |
|  |  | $\mathrm{O}(2)-\mathrm{Nd}-\mathrm{O}(2)$ | 125.6(3) |
|  |  | $\mathrm{O}(2)-\mathrm{Nd}-\mathrm{O}(2)$ | 139.3(3) |
| $\mathrm{Sc}-\mathrm{O}(1)$ | 2.108(5) $\times 2$ | $0(1)-\mathrm{Sc}-0(2)$ | 92.6(2) |
| $\mathrm{Sc}-\mathrm{O}(2)$ | $2.062(6) \times 2$ | O(1)-Sc-O(3) | 94.2(5) |
| $\mathrm{Sc}-\mathrm{O}$ (3) | $2.13(1) \times 2$ | 0 (1)-Sc-0(3) | 76.4(6) |
|  |  | $0(2)-\mathrm{Sc}-0(2)$ | 101.7(4) |
|  |  | $0(2)-\mathrm{Sc}-0$ (3) | 86.6(2) |
|  |  | 0 (3)-Sc-0(3) | 87.1(1) |
| $B(1)-O(1)$ | $1.381(8) \times 3$ | $O(1)-B(1)-O(1)$ | 120.00 |
| $B(2)-O(2)$ | $1.37(1) \times 2$ | $O(2)-B(2)-O(2)$ | 124(1) |
| $B(2)-0(3)$ | $1.35(3)$ | $O(2)-B(2)-O(3)$ | 118.2(6) |



Figure 4.3 A chain of Sc-centered octahedra extending through the structure of $\mathrm{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ and a projected view of the chain.


Figure 4.4 A chain of Sc -centered octahedra extending through the structure of $\mathrm{NdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ and a projected view of the chain.
respectively. The presence of a noncrystallographic pseudo center of symmetry in $\operatorname{LaSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ is realized as demonstrated in a projected view of the chain where the positions 1 and 6,2 and 5,3 and 4 representing the Sc atoms are related one to the other through the pseudo center. In the compound $\mathrm{NaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$, this center is necessarily absent.

The La atom resides in a distorted trigonal prism. The trigonal prismatic site for the La atom is a unique environment that has not been observed previously in a borate. The average La-0 distance, $2.48(4) \&$, compares to that calculated from crystal radii (12), 2.42 A. The trigonal prisms centered by the La atom are well isolated from one another (Figure 4.5) ; one 0 atom of each $\mathrm{BO}_{3}$ group is attached to one La atom while the other two 0 atoms are attached only to Sc atoms (cf. Table 4.3). Likewise, the Nd atom occupies a distorted trigonal prism with the Nd-0 distance, $2.432(6) \&$, which compares to that, $2.371(7) \AA$, reported for the compound $\mathrm{NdAl}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ (2) where the Nd atom also occupies a trigonal prism. The $\mathrm{NdO}_{6}$ trigonal prism is also isolated by the Sc-centered octahedra in a manner similar to that observed in the compound $\operatorname{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$.

The $B$ atom binds to three 0 atoms in a trigonal manner. The $B-0$ distances, $1.34(2)-1.42(3) \&$, in the compound $\mathrm{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$, and $1.35(3)-1.381(8) A$, in the compound $\mathrm{NdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$, compare to those, 1.3752(5) $\AA$ and $1.352(2)-1.429(4) \AA$, observed in the compounds $\mathrm{SCBO}_{3}$ (13) and $\mathrm{NdAl}_{3}\left(\mathrm{BO}_{3}\right)_{4}(2)$, respectively. The $\mathrm{BO}_{3}$ triangles are packed into two-dimensional layers. Drawings of individual layers in the monoclinic phase and the rhombohedral phase appear in Figures 4.6


Figure 4.5 A La-centered trigonal prism isolated by two layers of Sc-centered octahedra.

















Figure 4.6 A layer of planar $\mathrm{BO}_{3}$ groups in the structure of $\mathrm{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$.














Figure 4.7 A layer of planar $\mathrm{BO}_{3}$ groups in the structure of $\mathrm{NaSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$.
and 4.7, respectively. Each layer may be viewed as consisting of individual vertical columns of triangular $\mathrm{BO}_{3}$ groups. Considering each $\mathrm{BO}_{3}$ group as an arrowhead, we see that each head points up or down with specific relative orientations in each column. In the compound $\operatorname{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$, the first, left column exhibits an antiparallel arrangement of the $\mathrm{BO}_{3}$ groups. In the second column, all $\mathrm{BO}_{3}$ groups are directed up, antiparallel in the third column, and in the fourth column directed down and antiparallel to the second column. In the compound $\mathrm{NdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$, each of columns one and three exhibits an antiparallel arrangement of adjacent groups. In contrast to the compound $\operatorname{LaSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$, columns two and four are parallel, with all the groups directed up. The consequence of these arrangements on the observed SHG efficiency is discussed below.

Each 0 atom is coordinated by three cations in a trigonal manner. One half of the twelve 0 atoms in the compound $\operatorname{LaSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ are bound by one $B$ and two Sc atoms while the others are bound by atoms $\mathrm{La}, \mathrm{Sc}$, and B. Likewise, the atoms $O(1)$ and $O(3)$ in the compound $\mathrm{NdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ bind to one $B$ and two $S c$ atoms and the atom $O(2)$ binds to the $\mathrm{Nd}, \mathrm{Sc}$, and $B$ atoms.

## Optical Data

A room-temperature emission spectrum of $\mathrm{Cr}{ }^{3+}: \operatorname{LaSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ is shown in Figure 4.8. The major feature of the spectrum is the broad band peaking at 890 nm that arises from the transition ${ }^{4} \mathrm{~T}_{2} \rightarrow{ }^{4} \mathrm{~A}_{2}$. The broadening of the peak results from the existence of the three crystallographically independent Sc sites onto which the $\mathrm{Cr}^{3+}$ ions may


Figure 4.8 The luminescence spectrum of $\mathrm{Cr}^{3+}: \mathrm{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$. The fluorescence intensity is given in arbitrary units.
substitute. The luminescence of the compound $\mathrm{Cr}^{3+}: \operatorname{LaSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ is similar to that observed in the laser material $\mathrm{Cr}^{3+}: \mathrm{ScBO}_{3}$ (14) except a red shift of approximately 80 nm is observed. Because the Sc-0 distances are similar in the compounds $\mathrm{ScBO}_{3}$ and $\operatorname{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$, this red shift likely results from the high dopant concentration of the $\mathrm{Cr}^{3+}$ ion and the attendant weakening of the crystal field that results when multiple $\mathrm{Cr}^{3+}$ ions share a common $\mathrm{BO}_{3}$ group. An absorption measurement is required to determine the strength of the crystal field and the relaxation in the excited state (Stokes shift).

The fluorescence spectrum of the compound $\mathrm{Nd}^{3+}: \operatorname{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ is shown in Figure 4.9. It exhibits the expected transitions ${ }^{4} \mathrm{~F}_{3 / 2} \rightarrow$ ${ }^{4} \mathrm{I}_{11 / 2}$ near 1060 nm and ${ }^{4} \mathrm{~F}_{3 / 2} \rightarrow{ }^{4} \mathrm{I}_{9 / 2}$ near 900 nm . The fluorescence spectrum of $\mathrm{Cr}^{3+}: \mathrm{NdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$, excited with an Ar laser tuned to 514.5 nm is given in Figure 4.10. The spectrum exhibits $\mathrm{Nd}^{3+}$ fluorescence only which is similar to that observed for the compound $\mathrm{Nd}^{3+}: \mathrm{LaSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ even though the $\mathrm{Nd}^{3+}$ ion exhibits no absorption feature at 514.5 nm . Like the compound $\mathrm{Nd}(\mathrm{Al}, \mathrm{Cr})_{3}\left(\mathrm{BO}_{3}\right)_{4}$ (8), no $\mathrm{Cr}^{3+}$ fluorescence is observed, indicating a complete transfer of energy from the strongly absorbing $\mathrm{Cr}^{3+}$ ion to the $\mathrm{Nd}^{3+}$ ion.

## SHG data

The second harmonic generation measurement indicates that the frequency conversion efficiency of $\operatorname{LaSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ is only one-tenth of that observed for the reference sample quartz and is smaller than that reported for the sample $\mathrm{YAl}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ (6) by a factor of 100 . The low SHG efficiency of $\operatorname{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ arises from the pseudo centers of


Figure 4.9 The luminescence spectrum of $\mathrm{Nd}^{3+}: \mathrm{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$. The fluorescence intensity is given in arbitrary units.


Figure 4.10 The luminescence spectrum of $\mathrm{Cr}^{3+}: \mathrm{NdSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$.
symmetry associated with the $\mathrm{BO}_{3}$ layers in $\operatorname{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ (Figure 4.6) that are absent in the case of the compound $\mathrm{NdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ (Figure 4.7) which is isostructural to the phase $\mathrm{YAl}_{3}\left(\mathrm{BO}_{3}\right)_{4}$.

We have computed the nonlinearity of the monoclinic phase and rhombohedral phase from the anionic group theory (15) with application of CNDO methods (16). In application of the anionic group theory to the present materials, the $\mathrm{BO}_{3}$ groups are identified as the only chromophore contributing to the harmonic generation process. Because the $\mathrm{BO}_{3}$ groups are common to both $\mathrm{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ and $\mathrm{YAl}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ it is primarily their relative orientations that determine the magnitude of the nonlinearity that is observed.

In the compound $\mathrm{YAl}_{3}\left(\mathrm{BO}_{3}\right)_{4}$, two crystallographically distinct $\mathrm{BO}_{3}$ groups are present. For each unit cell there are three groups of one type and nine of the other; they are oriented approximately antiparallel to one another (Figure 4.11). We choose a cartesian coordinate system with the $x$ axis directed along the crystallographic axis $\underline{a}$ and the $z$ axis directed along the crystallographic axis $\underline{c}$, hence, the $\mathrm{BO}_{3}$ group rests in the $x$, y plane with a B-0 vector directed along the $x$ axis. From these definitions the coefficients of the hyperpolarizability tensor allowed by symmetry and their relative signs for a $B O_{3}$ group in point group $D_{3 h}$ are $\beta_{x x x}=-\beta_{x y y}$ $=-\beta_{y x y}=-\beta_{y y x}$. We find for $\beta_{x x x}$ a value of $0.475 \times 10^{-30}$ esu. We can now qualitatively predict the magnitude of the macroscopic nonlinearity to be proportional to $6 \times \beta_{X X X}$ since the constructive summation of the group of nine $B O_{3}$ units will be reduced by the three $\mathrm{BO}_{3}$ units of opposite orientation. When summed with the correct


Figure 4.11 Two sets of $B O_{3}$ groups in the compound $Y A I_{3}\left(B O_{3}\right)_{4}$.


Figure 4.12 Four sets of $\mathrm{BO}_{3}$ groups in the compound $\mathrm{LaSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$.
orientation matrices, we observe $\chi_{111}=3.2813 \times 10^{-30}$ esu. Applying a correction for the volume of unit cell, we obtain $\chi_{111}=6.1 \times 10^{-9}$ esu, a value in general agreement with the experimental determination, $\chi_{111}=5.7 \times 10^{-9} \mathrm{esu}$ (17).

In the case of the compound $\operatorname{LaSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$, there are four crystallographically independent sets of four $\mathrm{BO}_{3}$ groups (Figure 4.12). In each set, members are related to another by the $C$-centering of the cell or a $\mathbf{c}-\mathrm{glide}$ plane which in the absence of the translation becomes equivalent to a mirror plane. In simple terms, each set of four $\mathrm{BO}_{3}$ units exhibits two units aligned approximately antiparallel to the other two units. By summing the hyperpolarizability coefficients we find the small nonlinearity $\chi_{111}=$ $0.96 \times 10^{-9}$ esu, a result in general agreement with experiment.

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## CHAPTER 5

# SYNTHESIS AND STRUCTURE OF THE SIMPLE ORTHOBORATE $\mathrm{SrNaBO}_{3}$ 

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## Abstract

The new borate $\mathrm{SrNaBO}_{3}$ has been prepared and its structure has been established by single-crystal $X$-ray methods. The compound crystallizes in space group $P 2_{1} / \mathrm{c}$ with four formula units in a cell of dimensions $a=6.042(1), b=5.400(2), c=9.157(3) \mathrm{A}$, and $\beta=102.16(2)^{\circ}$. The structure is similar to those of the compounds $r-\mathrm{Na}_{2} \mathrm{CO}_{3}, \mathrm{~K}_{2} \mathrm{CO}_{3}$, and $\mathrm{BaNiO}_{3}$, exhibiting chains of face-sharing Na -centered O octahedra that are linked by 9 -coordinate Sr atoms and triangular $\mathrm{BO}_{3}$ groups.

## Introduction

Borates of the alkali metals are useful fluxes for the crystal growth of a variety of oxides that melt incongruently. Their usefulness is predicated in part by their chemical inertness with respect to the solute. During attempts to grow single crystals of new alkaline-earth borates from alkali borate fluxes we have observed a variety of chemical reactions between the solute and solvent. To aid our selection of potential solvents for the crystal growth of these new compounds, we have examined the phase equilibria of some simple ternary borate systems. We describe here the preparation and structure of the simple orthoborate $\mathrm{SrNaBC}_{3}$ that has resulted from an examination of the system $\mathrm{SrO}-\mathrm{Na}_{2} \mathrm{O}-\mathrm{B}_{2} \mathrm{O}_{3}$.

## Experimental

Synthesis. Preparation of the title compound has been studied by decomposition of oxalates and nitrates. Stoichiometric quantities of the reagents $\mathrm{Sr}\left(\mathrm{NO}_{3}\right)_{2}$ (AESAR, reagent grade), $\mathrm{NaNO}_{3}$ (AESAR, 99.99\%), and $\mathrm{B}_{2} \mathrm{O}_{3}$ (ALFA, 99.99\%) were dissolved in warm water followed by precipitation of the cations by addition of 1.5 moles of oxalic acid dihydrate for each mole of the reagent $\operatorname{Sr}\left(\mathrm{NO}_{3}\right)_{2}$. The mixture was dried at $135^{\circ} \mathrm{C}$ in a drying oven and then heated at $570^{\circ}, 675^{\circ}$, and $725^{\circ} \mathrm{C}$ for 10 hours at each temperature. A stoichiometric mixture of the reagents that had been ground under hexane was also heated in a similar manner. Products were identified from data obtained with an automated Philips powder X-ray diffractometer equipped with $\mathrm{Cu} \mathrm{K}_{\alpha}$ radiation.

A powder sample was prepared by grinding a mixture of $36.2 \mathrm{~mol} \%$ $\mathrm{Sr}\left(\mathrm{NO}_{3}\right)_{2}, 44.3 \mathrm{~mol} \% \mathrm{NaNO}_{3}$, and $19.5 \mathrm{~mol} \% \mathrm{E}_{2} \mathrm{O}_{3}$ with several drops of $\mathrm{NH}_{4} \mathrm{OH}$ (aq) and heating the resulting solia for 216 hours in a gold crucible at $600^{\circ} \mathrm{C}$. The product of the reaction afforded a powder X-ray pattern that agrees well with a pattern calculated with use of the computer program LAZY-PULVERIX and the results of the singlecrystal X-ray study.

Single crystals of $\mathrm{SrNaBO}_{3}$ were grown from a flux composed of $22 \mathrm{~mol} \% \mathrm{PbO}, 30 \mathrm{~mol} \% \mathrm{SrO}, 33 \mathrm{~mol} \% \mathrm{Na}_{2} \mathrm{O}$, and $15 \mathrm{~mol} \% \mathrm{~B}_{2} \mathrm{O}_{3}$. The melt was cooled in a Pt crucible from $975^{\circ} \mathrm{C}$ to $800^{\circ} \mathrm{C}$ at a rate of $6^{\circ} \mathrm{Chr}^{-1}$, then air quenched. Extensive attack of thie melt on the Pt crucible was observed. A number of crystals of maximum dimension 0.1 mm
were physically isolated from the flux and found to be suitable for X-ray diffraction studies. We have found some of the crystals in the flux to be an additional new strontium sodium borate (1).

X-ray Work. A crystal of dimensions $0.1 \times 0.05 \times 0.05 \mathrm{~mm}$ was selected and mounted on a glass fiber with silicone. X-ray data were collected with a Rigaku AFC6R diffrac*ometer and graphitemonochromated Mo Ka radiation. Accurate cinit cell parameters were obtained by automatic centering and least-squares analysis of 14 reflections with $2 \theta$ values between $30^{\circ}$ and $45^{\circ}$. The crystal was determined to belong to Laue group $2 / \mathrm{m}$, and one-fourth of the sphere of reflection was collected with the $\omega-2 \theta$ scan technique. Three standard reflections collected after every 199 data exhibited no significant fluctuations. Pertinent crystallographic parameters are listed in Table 5.1.

The structure was solved and refined with computer programs from the TEXSAN crystallographic software package (2). The systematic extinctions, h01, $1=2 n+1$ and $001,1=2 n+1$, are consistent with space group $\mathrm{P} 2_{1} / \mathrm{c}$. The atoms Sr and Na were located with the use of the direct methods program MITHRIL (3). The remaining atoms were determined from analysis of subsequent difference electron density maps. Following refinement of the model with isotropic thermal parameters on each atom the data were corrected for absorption with the program DIFABS (4). The final cycle of refinement was performed on $F$ with those 345 reflections having $F_{0}{ }^{2}>3 \sigma\left(F_{0}{ }^{2}\right)$ and included isotropic thermal parameters for each atom. The final values for $R$ and $R_{W}$ are 0.040 and 0.043 ,

Table 5.1. Crystal Data and Intensity Collection for $\mathrm{SrNaBO}_{3}$.

| formula weight, amu | 169.42 |
| :---: | :---: |
| space group | $\mathrm{P} 1_{1} / \mathrm{c}$ (No. 14) |
| a, $\AA$ | 6.042(1) |
| b, $\dot{A}$ | 5.400(2) |
| c, $\AA$ | 9.157(3) |
| $\beta$, deg. | 102.16(2) |
| $V, A^{3}$ | 292.1(3) |
| Z | 4 |
| $\rho_{\text {calcd }}, \mathrm{g} \mathrm{cm}^{-3}$ | 3.85 |
| temperature, ${ }^{\circ} \mathrm{C}$ | 23 |
| $\mu\left(\mathrm{Mo} \mathrm{K} \alpha\right.$ ) , $\mathrm{cm}^{-1}$ | 192.48 |
| $R\left(\right.$ on $F$ for $F_{0}{ }^{2}>3 \sigma\left(F_{0}{ }^{2}\right)$ ) | 0.040 |
| $R_{W}(F)$ | 0.043 |

respectively. The final difference electron density map contains no features greater than $0.85 \%$ of the height of a Sr atom. An analysis of $F_{0}$ vS $F_{C}$ as a function of $\left|F_{0}\right|, \lambda^{-1} \sin \theta$, and Miller indices reveals no unusual trends. Final atomic parameters and equivalent isotropic thermal parameters for the compound are provided in Table 5.2.

Table 5.2. Positional Parameters and Equivalent Isotropic Thermal Parameters for $\mathrm{SrNaBO}_{3}$.

| atom | $x$ | $y$ | $z$ | $B, \AA^{2}$ |
| :--- | :--- | :--- | :--- | :--- |
| Sr | $0.7637(2)$ | $0.0098(8)$ | $0.3284(1)$ | $0.64(3)$ |
| $\mathrm{Na}(1)$ | 0 | 0 | 0 | $1.2(1)$ |
| $\mathrm{Na}(2)$ | $1 / 2$ | 0 | 0 | $1.2(1)$ |
| B | $0.250(2)$ | $0.018(5)$ | $0.338(1)$ | $0.6(2)$ |
| $\mathrm{O}(1)$ | $0.344(1)$ | $0.014(5)$ | $0.2111(8)$ | $0.9(2)$ |
| $O(2)$ | $0.180(3)$ | $0.213(4)$ | $0.388(2)$ | $1.3(4)$ |
| $O(3)$ | $-0.212(3)$ | $0.222(4)$ | $-0.404(2)$ | $1.0(3)$ |
|  |  |  |  |  |

## Results and Discussion

Synthesis. The compound $\mathrm{SrNaBO}_{3}$ exists at the crossing point of the tie lines $\mathrm{Sr}_{3} \mathrm{~B}_{2} \mathrm{O}_{6}-\mathrm{Na}_{3} \mathrm{BO}_{3}$ and $\mathrm{Sr}_{2} \mathrm{~B}_{2} \mathrm{O}_{5}-\mathrm{Na}_{2} \mathrm{O}$ in the phase diagram of the system $\mathrm{SrO}-\mathrm{Na}_{2} \mathrm{O}-\mathrm{B}_{2} \mathrm{O}_{3}$ (Figure 5.1). Reactions between $\mathrm{Sr}_{3} \mathrm{~B}_{2} \mathrm{O}_{6}$ and $\mathrm{Na}_{3} \mathrm{BO}_{3}$ or $\mathrm{Sr}_{2} \mathrm{~B}_{2} \mathrm{O}_{5}$ and $\mathrm{Na}_{2} \mathrm{O}$ in the ratio 1:1 can then be envisioned to afford the compound $\mathrm{SrNaBO}_{3}$. Inspection of X -ray powder diffractograms indicates the preserce of $\mathrm{Sr}_{3} \mathrm{~B}_{2} \mathrm{O}_{6}$ after heating a precipitated mixture of the oxalates and $\mathrm{B}_{2} \mathrm{O}_{3}$ at $570^{\circ} \mathrm{C}$ while heating a ground mixture of the nitrates in a similar manner initially affords $\mathrm{Sr}_{2} \mathrm{~B}_{2} \mathrm{O}_{5}$. The state of the sodium oxide or sodium borate is not evident from the $X$-ray patterns as all lines observed are attributable to a strontium borate. Continued heating of the powder resulting from the nitrates affords only a sluggish reaction with a low yield of the desired product after a few days of heating. Continued heating of the powder derived from the oxalates at $675^{\circ} \mathrm{C}$ for 10 hours affords primarily $\mathrm{SrNaBO}_{3}$ with $\approx 10 \% \mathrm{Sr}_{3} \mathrm{~B}_{2} \mathrm{O}_{6}$. Heating this sample at $725^{\circ} \mathrm{C}$ affords decomposition of $\mathrm{SrNaBO}_{3}$ with diffraction peaks attributable to a new strontium sodium borate appearing in the X-ray pattern.

These results indicate that the reaction between $\mathrm{Sr}_{3} \mathrm{~B}_{2} \mathrm{O}_{6}$ and $\mathrm{Na}_{3} \mathrm{BO}_{3}$ represents a more favorable pathway to $\mathrm{SrNaBO}_{3}$ as compared with the reaction between $\mathrm{Sr}_{2} \mathrm{~B}_{2} \mathrm{O}_{5}$ and $\mathrm{Na}_{2} \mathrm{O}$. This result is consistent with the low melting point, $675^{\circ} \mathrm{C}$, of $\mathrm{Na}_{3} \mathrm{BO}_{3}$ which contrasts with the melting points, $>1000^{\circ} \mathrm{C}$, for the strontium borates and $\mathrm{Na}_{2} \mathrm{O}$. We have prepared a sample of $\mathrm{SrNaBO}_{3}$ with a high degree of crystallinity


Figure 5.1 Phase diagram of the system $\mathrm{SrO}-\mathrm{Na}_{2} \mathrm{O}-\mathrm{B}_{2} \mathrm{O}_{3}$.
and a clean X-ray pattern only by extended heating of a sample containing excess $\mathrm{Na}_{3} \mathrm{BO}_{3}\left(0.45 \mathrm{Sr}_{3} \mathrm{~B}_{2} \mathrm{O}_{6}: 0.55 \mathrm{Na}_{3} \mathrm{BO}_{3}\right)$. This prolonged firing and successful synthesis confirm the thermodynamic stability of the phase at lower temperatures. Because the material is stable only at lower temperatures, achieving an intimate mixture of the reactants is important for the development of an efficient method for preparation of the compound. This mixing should prevent the formation of the compound $\mathrm{Sr}_{2} \mathrm{~B}_{2} \mathrm{O}_{5}$, even in those reactant mixtures corresponding to the presence of excess $\mathrm{Na}_{3} \mathrm{BO}_{3}$.

Crystal Structure. A drawing of the unit cell is given in Figure 5.2; selected bond distances and angles are listed in Table 5.3. The structure is composed of a 9 -coordinate Sr atom, two crystallographically independent Na atoms occupying distorted octahedral sites, and a trigonal planar $\mathrm{BO}_{3}$ group. The discerning feature of the structure is the presence of isolated one-dimensional chains of Na-centered octahedra that extend along the a axis. The octahedra share triangular faces with successive alternation of the independent atoms $\mathrm{Na}(1)$ and $\mathrm{Na}(2)$ along the chain. As shown in Figure 5.3, these chains pack in an approximate close-packed manner with the Sr and B atoms bridging the chairis. Similar structures have been reported for the compounds $\gamma-\mathrm{Na}_{2} \mathrm{CO}_{3}$ (5) and $\mathrm{K}_{2} \mathrm{CO}_{3}$ (6); each exhibits infinite chains of face-sharing $\mathrm{NaO}_{6}\left(\mathrm{KO}_{6}\right)$ octahedra 1 inked by 9 -coordinate $\mathrm{Na}(\mathrm{K})$ atoms and triangular $\mathrm{CO}_{3}$ groups.

Each of these structures is related to the high symmetry, hexagonal parent $\mathrm{BaNiO}_{3}$ (7). In this structure one-dimensional chains of face-sharing $\mathrm{NiO}_{6}$ octahedra are bridged by 12 -coordinate $\mathrm{Ba}^{2+}$ ions.


Figure 5.2 Drawing of a unit cell of $\mathrm{SrNaBO}_{3}$. The largest open circles represent 0 atoms, the small filled circles represent $B$ atoms, and the open circles with shaded bonds represent Sr atoms.

Table 5.3. Selected Bond Distances ( A ) and Bond Angles ( ${ }^{\circ}$ ) for $\mathrm{SrNaBO}_{3}$.

| $\mathrm{Sr}-\mathrm{O}(1)$ | 2.539(7) | O (1) $\mathrm{Sr}-\mathrm{O}(1)$ | 76.5(5) |
| :---: | :---: | :---: | :---: |
| $\mathrm{Sr}-\mathrm{O}(2)$ | 2.63(2) | 0 (1) $-\mathrm{Sr}-\mathrm{O}(1)$ | 75.7(5) |
| $\mathrm{Sr}-\mathrm{O}(3)$ | 2.61(2) | $0(1)-\mathrm{Sr}-\mathrm{O}(2)$ | 152.9(8) |
| Sr -0(3) | 2.68(2) | $0(1)-\mathrm{Sr}-\mathrm{O}(2)$ | 79.1(5) |
| $\mathrm{Sr}-\mathrm{O}(2)$ | 2.69(2) | $0(1)-\mathrm{Sr}-\mathrm{O}(2)$ | 120.9(5) |
| $\mathrm{Sr}-\mathrm{O}(1)$ | 2.76(3) | 0 (1) $-\mathrm{Sr}-\mathrm{O}(3)$ | 82.7(5) |
| $\mathrm{Sr}-\mathrm{O}(1)$ | 2.81(3) | $0(2)-\mathrm{Sr}-\mathrm{O}(3)$ | 49.4(2) |
| Sr -0(2) | 2.81(2) | O (2) $\mathrm{Sr} \mathrm{S}-\mathrm{O}(2)$ | 98.0(4) |
| $\mathrm{Sr}-\mathrm{O}(3)$ | 2.93(2) | $0(2)-\mathrm{Sr}-0(2)$ | 115.2(2) |
|  |  | 0 (2) $-\mathrm{Sr}-\mathrm{O}(3)$ | 71.5(3) |
|  |  | $0(3)-\mathrm{Sr}-0$ (3) | 102.9(4) |
|  |  | 0 (3) $-\mathrm{Sr}-\mathrm{O}(3)$ | 95.5(5) |
| $\mathrm{Na}(1)-\mathrm{O}(2)$ | 2.26(2) $\times 2$ | $\mathrm{O}(1)-\mathrm{Na}(1)-\mathrm{O}(2)$ | 94.1(6) |
| $\mathrm{Na}(1)-0(3)$ | $2.27(2) \times 2$ | $\mathrm{O}(1)-\mathrm{Na}(1)-\mathrm{O}(3)$ | 97.2(6) |
| $\mathrm{Na}(1)-\mathrm{O}(1)$ | $2.522(7) \times 2$ | $\mathrm{O}(2)-\mathrm{Na}(1)-\mathrm{O}(3)$ | 94.9(3) |
| $\mathrm{Na}(2)-\mathrm{O}(3)$ | 2.33(2) $\times 2$ | $\mathrm{O}(1)-\mathrm{Na}(2)-\mathrm{O}(2)$ | 95.4(6) |
| $\mathrm{Na}(2)-\mathrm{O}(1)$ | $2.325(7) \times 2$ | $0(1)-\mathrm{Na}(2)-\mathrm{O}(3)$ | 94.0(7) |
| $\mathrm{Na}(2)-\mathrm{O}(2)$ | $2.52(2) \times 2$ | $0(2)-\mathrm{Na}(2)-\mathrm{O}(3)$ | 101.8(3) |
| B-O(1) | 1.40(1) | $O(1)-B-O(2)$ | 123(2) |
| B-O(2) | 1.26(3) | $0(1)-E-O(3)$ | 117(2) |
| B-0(3) | 1.47(3) | $O(2)-B-O(3)$ | 120(1) |



Figure 5.3 The packing of the chains of Na -centered octahedra as viewed along the a axis. The small open
circles represent Sr atoms and the small filled circles represent B atoms.

As the $\mathrm{Ba}^{2+}$ and $\mathrm{O}^{2-}$ ions are of equivalent sizes and larger than the small, formally $\mathrm{Ni}^{4+}$ ion, the structure may be considered to be an hexagonal close-packed arrangement of the $\mathrm{Ba}^{2+}$ and $\mathrm{O}^{2-}$ ions with $\mathrm{Ni}^{4+}$ ions ordered on octahedral interstices. In the borate and the carbonates the larger sizes of the $\mathrm{Na}^{+}$and $\mathrm{K}^{+}$ions in the octahedral sites relative to that of the $\mathrm{Ni}^{4+}$ ion afford the lower symmetry observed by contributing to the distortions of the close packing. In the borate, the chains $\left[\mathrm{NaO}_{3}\right]_{\infty}{ }^{1}$ are displaced relative to one another to afford the nonorthogonal cell angle $\beta=102.16^{\circ}$ and the 9 -coordination of the $\mathrm{Sr}^{2+}$ atom as compared with the 12 -coordination of the $\mathrm{Ba}^{2+}$ ion in the nickelate. A similar, yet different displacement occurs in the structure of $\mathrm{K}_{2} \mathrm{CO}_{3}$. The orientation of the chains is controlled by the size and charge of the cation in the large site. The $\mathrm{Sr}^{2+}$ ion is not large enough to support the 12 -fold site, but the coulombic interactions are sufficient to afford an even distribution of the nine $\mathrm{Sr}-\mathrm{O}$ bond lengths. This contrasts with the environment of the 9 -fold site in $\mathrm{K}_{2} \mathrm{CO}_{3}$ where the reduced coulombic interactions of the $K^{+}$ion support a $[6+3]$ coordination geometry having six shorter $K-0$ interactions, < $3.0 \AA$, and three longer $K-0$ interactions, > $3.0 \AA$.

Bond distances range from $2.26(2)$ to $2.522(7) \AA$ for the interactions $\mathrm{Na}(1)-0$ and from $2.325(7)$ to $2.52(2) \AA$ for the interactions $\mathrm{Na}(2)-0$. These distances compare to those reported in the compounds $\mathrm{Na}_{2} \mathrm{~B}_{4} \mathrm{O}_{7}$ (8) and $\alpha-\mathrm{Na}_{2} \mathrm{~B}_{6} \mathrm{O}_{10}$ (9), 2.260-2.809 $\AA$ and $2.280-2.742 \AA$, respectively. The angular distortions from an orthogonal octahedron include $O(1)-\mathrm{Na}(1)-\mathrm{O}(3), 97.2(6)^{\circ}, \mathrm{O}(2)-\mathrm{Na}(1)-0(3), 94.9(3)^{\circ}$,
$\mathrm{O}(1)-\mathrm{Na}(2)-\mathrm{O}(2), 95.4(6)^{\circ}$, and $\mathrm{O}(2)-\mathrm{Na}(2)-\mathrm{O}(3), 101.8(3)^{\circ}$.
The Sr atom occupies an irregular nonacoordinate site (Figure 5.4). The Sr-0 distances vary from $2.539(7)$ to $2.93(2) \AA$ with an average value of $2.7(1) \AA$. The polyhedron may be described as a bicapped tetragonal base, trigonal base with atoms $O(2)$ and $O(3)$ forming a tetragonal face, atoms $O(2), O(\Xi)$, and $O(1)$ forming a trigonal face, and two atoms $O(1)$ occupying the capping positions. Large and irregular coordination environments for the Sr atom are a common occurrence in the structure of borates. The Sr atoms in the compound $\mathrm{Sr}_{2} \mathrm{ScLi}\left(\mathrm{B}_{2} \mathrm{O}_{5}\right)_{2}$ (10) exhibit a coordination number of seven with an average $\mathrm{Sr}-0$ distance of $2.589(4) \AA$; eight- and ten-fold coordination environments are observed in the compound $\beta-\mathrm{Sr}_{2} \mathrm{Cu}\left(\mathrm{BO}_{3}\right)_{2}$ (11) with distances ranging from $2.600(4)$ to $2.974(4) \AA$. In the compound $\mathrm{La}_{2} \mathrm{Sr}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ (12) eight-, nine-, and ten-fold coordination geometries have been reported with average bond distances of 2.62 , 2.67 , and $2.76 \AA$, respectively.

The $B$ atom binds to three 0 atoms to form $\mathrm{BO}_{3}$ triangles. The average value, $1.4(1) \AA$, of the $B-0$ interactions compares to similar distances, $1.3752(2)$ and $1.379(2) \AA$, reported for the compounds $\mathrm{ScBO}_{3}$ (13) and $\mathrm{FeBO}_{3}$ (14), respectively.

Each 0 atom binds to six cations in approximate octahedral coordination. It is common for 0 atoms to occupy sites of high coordination numbers when the cation-oxygen polyhedra are large and irregular.


Figure 5.4 Irregular nonacoordinate site of the Sr atom.

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## CHAPTER 6

$$
\begin{gathered}
\text { THE NEW RING BORATES } \\
\mathrm{Li}_{4} \mathrm{Ln}_{4} \mathrm{MB}_{9} \mathrm{O}_{23}(\mathrm{Ln}=\mathrm{Y}, \mathrm{Er} \text {, and } \mathrm{Gd} ; \mathrm{M}=\mathrm{Al} \text { and } \mathrm{Ga})
\end{gathered}
$$

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## Abstract

Compounds of the new type $\mathrm{Li}_{4} \mathrm{Ln}_{4} \mathrm{MB}_{9} \mathrm{O}_{23}$ ( $\mathrm{Ln}=\mathrm{Y}$, Er and Gd ; $M=\mathrm{A}$ 1 and Ga) have been synthesized. These compounds all crystallize in the tetragonal space group $P 42_{1} 2$. The structure has been established from crystals of $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{MB}_{9} \mathrm{O}_{23}(\mathrm{M}=\mathrm{Al}$ and Ga$)$ by single-crystal X-ray methods. Crystal data for $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{AlB}_{9} \mathrm{O}_{23}$ : $\mathrm{a}=12.728(1), \mathrm{c}=4.658(1)$ $\AA, V=754.7(1) \AA^{3}$, and $Z=2$. Crystal data for $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{GaB}_{9} \mathrm{O}_{23}: a=$ $12.7824(8), c=4.6576(9) \&, V=761.0(2) \AA^{3}$, and $Z=2$. Unit cell parameters for each of the other analogs have been determined by powder X-ray methods. The structure is a new type that exhibits an isolated polyborate ring $\left[\mathrm{B}_{8} \mathrm{O}_{20}\right]^{16-}$ built from triangular $\mathrm{BO}_{3}$ groups and tetrahedral $\mathrm{BO}_{4}$ groups. The rings are bridged by Y atoms occupying square antiprisms, resulting in the formation of channels that extend along the $c$ axis. These channels are occupied by 6-coordinate Li atoms and a crystallographically unique $\mathrm{BO}_{3}$ group. The 4-coordinate Al (Ga) atom occupies interchannel interstices.

## Introduction

From an investigation of phase equilibria in the systems $\mathrm{YAl}_{3}\left(\mathrm{BO}_{3}\right)_{4}-\mathrm{LiBO}_{2}$ and $\mathrm{YGa} \mathrm{B}_{3}\left(\mathrm{BO}_{3}\right)_{4}-\mathrm{LiBO} 2$ that was conducted to evaluate the use of $\mathrm{LiBO}_{2}$ as a flux for the crystal growth of the compounds $\mathrm{YAl}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ and $\mathrm{YGa}_{3}\left(\mathrm{BO}_{3}\right)_{4}(1)-(2)$, we isolated several small single crystals that exhibited tetragonai symmetry. Structure determinations on these crystals revealed the presence of a very unusual polyborate anion as well as a unique three-dimensionel framework. In this report we describe the preparation and structure of the tetragonal materials $\mathrm{Li}_{4} \mathrm{Ln}_{4} \mathrm{MB}_{9} \mathrm{O}_{23}$ where $\mathrm{Ln}=\mathrm{Y}, \mathrm{Er}$, and Gd and $\mathrm{M}=\mathrm{Al}$ and Ga .

## Experimental

## Synthesis

Homogeneous powders of the title compounds were prepared by treatment of the constituent oxides with concentrated $\mathrm{NH}_{4} \mathrm{OH}(\mathrm{aq})$. The reagents used in the syntheses were $\mathrm{LiNO}_{3}, 99.9 \%$, ALFA; $\mathrm{Y}\left(\mathrm{NO}_{3}\right)_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}, 99.9 \%$, ALFA; $\mathrm{Al}_{2} \mathrm{O}_{3}, 99.99 \%$, CERAC; $\mathrm{Ga}_{2} \mathrm{O}_{3}, 99.999 \%$, AESAR; $\mathrm{Gd}\left(\mathrm{NO}_{3}\right)_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}, 99.9 \%$, ALFA; $\mathrm{Er}_{2}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3} \cdot 10 \mathrm{H}_{2} \mathrm{O}, 99.9 \%$, ALFA; $\mathrm{B}_{2} \mathrm{O}_{3}, 99.99 \%$, ALFA; $\mathrm{NH}_{4} \mathrm{OH}(\mathrm{aq}), \mathrm{J} . \mathrm{T}$. Baker, $29.1 \% \mathrm{NH}_{3}$. Stoichiometric ratios of the reagents were initially heated at $600^{\circ} \mathrm{C}$ for 2 hours to decompose the nitrates and oxalates to the oxides. The resulting oxides were ground and placed into a tefion container; 3 mL of $\mathrm{NH}_{4} \mathrm{OH}(\mathrm{aq})$ for each gram of oxide was then added. The teflon container was covered, placed into a digestion bomb, and heated at $135^{\circ} \mathrm{C}$ for 24 hours. The container was then removed from the bomb and placed in a drying oven $\left(135^{\circ} \mathrm{C}\right)$ for one hour. The solid product was ground into a fine powder and heated at $700^{\circ} \mathrm{C}$ for 24 hours, then reground and fired at $800^{\circ} \mathrm{C}$ for 72 hours. Unit-cell parameters for each compound were refined from powder X-ray diffraction patterns. The patterns compare well to those calculated from the results of the singlecrystal structure determinations of the compounds $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{MB}_{9} \mathrm{O}_{23}$ ( $\mathrm{M}=\mathrm{Al}$ and Ga ).

Crystals of the compounds $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{MB}_{9} \mathrm{O}_{23}$ ( $\mathrm{M}=\mathrm{Al}$ and Ga ) used in the structure determinations were isolated from melts of composition 33 wt. \% $\mathrm{YM}_{3}\left(\mathrm{BO}_{3}\right)_{4}(\mathrm{M}=\mathrm{Al}$ and Ga$)$ and $67 \mathrm{wt} \.% \mathrm{LiBO}_{2}$. These melts were cooled in Pt crucibles from $975^{\circ} \mathrm{C}$ to $700^{\circ} \mathrm{C}$ at the rate $5.5^{\circ} \mathrm{Chr}{ }^{-1}$,
then cooled to ambient temperature at $100^{\circ} \mathrm{C} \mathrm{hr}^{-1}$. A number of crystals of maximum dimension 0.1 mm were physically isolated from the flux.

The crystals of $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{GaB}_{9} \mathrm{O}_{23}$ used for the SHG measurement were grown from a melt corresponding to the composition $31 \mathrm{wt}. \mathrm{\%}$ $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{GaB}_{9} \mathrm{O}_{23}, 7$ wt. $\% \mathrm{Ga}_{2} \mathrm{O}_{3}$, and 62 wt. $\% \mathrm{LiBO}_{2}$. The melt was heated at $875^{\circ} \mathrm{C}$ for 2 hours and cooled at $9^{\circ} \mathrm{Chr}{ }^{-1}$ to $500^{\circ} \mathrm{C}$. The crystals with an average edge length 0.8 mm were isolated by dissolution of the excess $\mathrm{LiBO}_{2}$ in boiling $\mathrm{H}_{2} \mathrm{O}$ followed by decantation to eliminate insoluble powders.

## X-ray Work

$X$-ray data for the compounds $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{MB}_{9} \mathrm{O}_{23}$ ( $M=\mathrm{Al}$ and Ga ) were collected on a Rigaku AFC6R diffractometer with Mo K $\alpha$ radiation. For each compound, the data were collected from rectangular block-shaped crystals of approximate dimensions $0.1 \times 0.05 \times 0.05 \mathrm{~mm}$. Accurate unit cell parameters were derived from least-squares analyses of the angle settings of 17 reflections in the range $30^{\circ} \leq 2 \theta \leq 45^{\circ}$ that had been automatically centered on the diffractometer. The crystals were determined to belong to Laue group $4 / \mathrm{mmm}$. Intensity data were collected with the $\omega-2 \theta$ scan technique; intensities of three standard reflections measured after every 199 reflections exhibited no significant fluctuations. For the compound $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{AlB}_{9} \mathrm{O}_{23}, 2795$ reflections were collected over the range of indices $-17 \leq h \leq 19$, $0 \leq k \leq 19,0 \leq 1 \leq 6$, corresponding to $2 \theta_{\max }=65^{\circ}$. For the compound $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{GaB}_{9} \mathrm{O}_{23}$, 2963 reflections were measured in the range of
indices $-18 \leq h \leq 20,0 \leq k \leq 20,0 \leq 1 \leq 6$, corresponding to $2 \theta_{\max }=$ $70^{\circ}$. Crystal data and experimental conditions are summarized in Table 6.1.

Each crystal structure was solved and refined with the use of computer programs from the Texray crystallographic software package (3). The systematic absence, OKO, $k=2 n+1$, that was observed for each crystal is consistent with the acentric space groups $\mathrm{P}-42_{1} \mathrm{~m}$ (No. 113) and $P 42_{1} 2$ (No. 90). The space group $P 42_{1} 2$ is favored on the basis of the successful solution and refinement of the structure; a satisfactory solution could not be achieved in space group $P-42_{1} \mathrm{~m}$. Patterson syntheses and direct methods were used to determine the positions of the atoms $Y, G a$, and $A 1$. The $B$ and $O$ atoms were located from ensuing electron density syntheses. At this point of the solution, the contents of the unit cell were 8 Y atoms, $2 \mathrm{Al}(\mathrm{Ga})$ atoms, 18 B atoms, and 500 atoms, indicating a large negative imbalance of formal charge. A drawing of the cell and analys is of distances and angles indicated an unreasoriable coordination environment for atom $B(3)$. A reasonble triangular environment resulted by reduction of the occupancy of atom $0(7)$ to $1 / 2$, affording an orientational disorder of the $\mathrm{BO}_{3}$ group. With this change in occupancy the number of 0 atoms was reduced to 46 and a negative charge that could be balanced by $8 \mathrm{Li}^{+}$ions resulted. These $8 \mathrm{Li}^{+}$ ions were placed from analysis of several drawings and subsequently refined. To remove the orientational disorder of the unique $\mathrm{BO}_{3}$ group, the structure was refined in the subgroup $P 2_{1} 2_{1} 2$. The residual exhibited a small but statistically insignificant increase and the

Table 6.1. Crystal Data and Experimental Conditions for the Compounds $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{MB}_{9} \mathrm{O}_{23}(\mathrm{M}=\mathrm{Al}$ and Ga$)$.

$$
\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{AlB}_{9} \mathrm{O}_{23} \quad \mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{GaB}_{9} \mathrm{O}_{23}
$$

formula wt., amu
875.65
918.38
space group
a, $\AA$
c, $\AA$
$V, \dot{A}^{3}$
Z
Pcalcd, $\mathrm{g} \mathrm{cm}^{-3}$
3.85
4.01
temperature, ${ }^{\circ} \mathrm{C}$
23
23
$\mu(\mathrm{MoK} \alpha), \mathrm{cm}^{-1}$
155.28
170.72
$R\left(\right.$ on F for $\mathrm{F}_{0}{ }^{2}>3 \sigma\left(\mathrm{~F}_{0}{ }^{2}\right)$ )
0.064
0.075
$R_{W}(F)$
0.099
0.114
bond distances and angles are equivalent. We, therefore, favor the higher symmetry group. We also carefully checked for weak superstructure reflections with the diffractometer that would indicate a doubling of the $\underline{\mathbf{c}}$ axis; none were found.

The final cycles of refinement following application of an absorption correction with the program Difabs (4) were performed on $F_{0}$ for $F_{0}{ }^{2} \geq 3 \sigma\left(F_{0}{ }^{2}\right)$. For the compound $L i_{4} Y_{4} A 1 B_{9} O_{23}$ the refinement with 595 unique reflections resulted in $R=6.4 \%$ and $R_{W}=9.9 \%$. For the compound $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{GaB}_{9} \mathrm{O}_{23}$ the refinement with 707 unique reflections converged to $R=7.5 \%$ and $R_{W}=11.4 \%$. The final difference electron density maps for both compounds exhibit no features with height greater than $1.3 \%$ of an $Y$ atom.

Final atomic positional parameters and isotropic thermal parameters for the compounds are listed in Table 6.2.

X-ray powder diffraction data for $\mathrm{Li}_{4} \mathrm{Ln}_{4} \mathrm{MB}_{9} \mathrm{O}_{23}$ ( $\mathrm{Ln}=\mathrm{Y}$, Er and Gd ; $M=A 1$ and Ga ) were obtained with $\mathrm{Cu} \mathrm{K} \alpha$ radiation on an automated Philips diffractometer. Values of $2 \theta$ were corrected with use of NBS Si powder (640b) as an internal standard (5). Unit cell parameters for each compound were refined by least-squares analys is of 11 reflections in the range $27^{\circ} \leq 2 \theta \leq 60^{\circ}$ with the use of the computer program Polsq. The results of these refinements appear in Table 6.3.

Table 6.2a. Atomic Parameters and Equivalent Isotropic Thermal Parameters for $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{AlB}_{9} \mathrm{O}_{23}$.

| atom | $x$ | $y$ | $z$ | $B(e q)$ |
| :---: | :---: | :---: | :---: | :---: |
| Y(1) | 0.3522 (1) | $0.3522(1)$ | 1/2 | 0.31(4) |
| $Y(2)$ | 0.1537(1) | 0.1537(1) | 1/2 | 0.45(4) |
| A1 | 0 | 0 | 0 | 0.5 (1) |
| O(1) | 0.3019(9) | 0.1889(9) | 0.718(2) | 0.4(1) |
| O(2) | $0.3850(7)$ | 0.5082 (8) | $0.792(2)$ | $0.3(1)$ |
| O(3) | 0.2985(8) | 0.499 (1) | 0.261(2) | 0.6(1) |
| O(4) | 0.276(1) | 0.1017(9) | 0.153(3) | 0.8(2) |
| O(5) | 0.2250(8) | 0.4134(7) | 0.849(3) | 0.0(2) |
| O(6) | 1/2 | 0 | 0.312(4) | 0.3(3) |
| $0(7)^{\text {a }}$ | 0.440(2) | 0.071(2) | 0.851(4) | 0.3(3) |
| $B(1)$ | 0.281(1) | 0.496(1) | 0.961(3) | 0.1(2) |
| $B(2)$ | 0.345 (2) | 0.164(2) | 0.982 (4) | 2.0(3) |
| $B(3)$ | 1/2 | 0 | 0.024(7) | 0.8(4) |
| Li | 0.148(2) | 0.514(3) | 0.507(8) | 2.0(6) |

$\mathrm{a}_{\text {Occupancy }}=0.50$

Table 6.2b. Atomic Parameters and Equivalent Isotropic Thermal Parameters for $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{GaB}_{9} \mathrm{O}_{23}$.

| atom | x | y | z | $B(e q)$ |
| :---: | :---: | :---: | :---: | :---: |
| $Y(1)$ | 0.3519(1) | $0.3519(1)$ | 1/2 | 0.19(4) |
| $Y(2)$ | 0.1545(1) | 0.1545(1) | 1/2 | 0.25(4) |
| Ga | 0 | 0 | 0 | 0.20(4) |
| O(1) | 0.302(1) | 0.190(1) | 0.717(2) | 0.4(1) |
| O(2) | $0.3808(7)$ | 0.5071(9) | 0.780 (2) | 0.0(1) |
| O(3) | 0.2981(8) | 0.497 (1) | 0.255(2) | 0.4(1) |
| O(4) | 0.2765(9) | 0.0982(9) | $0.157(3)$ | 0.1(2) |
| O(5) | 0.223(1) | 0.415(1) | 0.854(3) | 0.4(2) |
| $0(6)$ | 1/2 | 0 | 0.308(5) | 0.2(3) |
| $O(7)^{\text {a }}$ | 0.437 (2) | 0.069(2) | 0.848(4) | 0.4(3) |
| $B(1)$ | 0.280(1) | 0.500(2) | 0.960(3) | 0.2(2) |
| $B(2)$ | 0.348(2) | 0.165(2) | 0.987(5) | 1.8(3) |
| $B(3)$ | 1/2 | 0 | 0.024(8) | 0.3(4) |
| Li | $0.143(4)$ | 0.518(4) | 0.50(1) | 3(1) |

$a_{0 c c u p a n c y}=0.50$

Table 6.3. Unit Cell Parameters for $\mathrm{Li}_{4} \mathrm{Ln}_{4} \mathrm{MB}_{9} \mathrm{O}_{23}$.

| Ln | M | a ( $A$ ) | c ( ${ }^{\text {a }}$ ) |
| :---: | :---: | :---: | :---: |
| Y | A1 | 12.737(2) | 4.061(2) |
| Y | Ga | 12.780(1) | 4.665(1) |
| Er | A1 | 12.732(1) | 4.650(1) |
| Er | Ga | 12.754(1) | 4.658(1) |
| Gd | A) | 12.862(4) | 4.712(3) |
| Gd | Ga | 12.888(2) | 4.712(1) |

## Results and Discussion

## Crystal Structure

Selected bond distances and angles for the compounds $L \mathrm{i}_{4} \mathrm{Y}_{4} \mathrm{MB}_{9} \mathrm{O}_{23}$ ( $M=A 1$ and $G a$ ) are listed in Table 6.4. A drawing of the unit cell is provided in Figure 6.1. The two compounds are isostructural.

The structure is a new type exhibiting the isolated polyborate anion $\left[\mathrm{B}_{8} \mathrm{O}_{20}\right]^{16-}$ (Figure 6.2). It is comprised of four $\mathrm{BO}_{4}$ groups and four $\mathrm{BO}_{3}$ groups that are condensed in successive alternation to form a 16 -membered B-O ring. These rings are bridged by an intervening Al (Ga) atom to form a two-dimensional network that extends orthogonal to the $\underline{C}$ axis. Also present in the structure are rings of edgesharing square antiprisms, each approximately centered by an $Y$ atom (Figure 6.3). Unlike the isolated borate anions, these rings fuse by sharing edges to form a two-dimensional honeycomb-like framework. The borate and yttrate rings stack one over the other along the $\underline{c}$ axis to afford one-dimensional channels that extend parallel to the $\underline{c}$ axis (Figure 6.4 and Figure 6.5). Atoms Li, B, and 0 occupy the channels formed by stacking the two types of rings. A simple orthoborate $\mathrm{BO}_{3}$ rests in the center of each borate ring (Figure 6.6). This group is orientationally disordered such that its principal atomic plane may be orthogonal to either diagonal of the $\underline{a b}$ face of the unit cell. A cluster of Li and O atoms occupies each ring of Y -centered antiprisms, bridging the unique $\mathrm{BO}_{3}$ groups of adjacent layers.

The structure of the anion $\left[\mathrm{B}_{8} \mathrm{O}_{20}\right]^{16-}$ is unique among other known cyclic polyborates. The most common cyclic motif is the six-membered

Table 6.4. Selected Bond Distances ( $\AA$ ) and Bond Angles ( ${ }^{\circ}$ ) for $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{MB}_{9} \mathrm{O}_{23}$ ( $M=A 1$ and Ga ).

| $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{AlB}_{9} \mathrm{O}_{23}$ |  | $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{GaB}_{9} \mathrm{O}_{23}$ |  |
| :---: | :---: | :---: | :---: |
| $Y(1)-0(1)$ | 2.40(1) $\times 2$ | $Y(1)-0(1)$ | $2.39(1) \times 2$ |
| $Y(1)-0(2)$ | 2.44(1) $\times 2$ | $Y(1)-0(2)$ | $2.40(1) \times 2$ |
| $Y(1)-0(3)$ | 2.28(1) $\times 2$ | $Y(1)-0(3)$ | 2.28(1) $\times 2$ |
| $Y(1)-0(5)$ | 2.42(1) $\times 2$ | $Y(1)-0(5)$ | 2.46(1) $\times 2$ |
| $Y(2)-0(1)$ | $2.19(1) \times 2$ | $Y(2)-0(1)$ | $2.19(1) \times 2$ |
| $Y(2)-0(2)$ | $2.35(1) \times 2$ | $Y(2)-0(2)$ | 2.34(1) $\times 2$ |
| $Y(2)-0(3)$ | 2.34(1) $\times 2$ | $Y(2)-0(3)$ | $2.40(1) \times 2$ |
| $Y(2)-0(4)$ | 2.34(1) $\times 2$ | $Y(2)-0(4)$ | $2.35(1) \times 2$ |
| A1-0(2) | 1.75(1) $\times 4$ | Ga-0(2) | $1.84(1) \times 4$ |
| Li-O(1) | 2.55 (4) | Li-0(1) | 2.51(5) |
| Li-0(3) | 2.24 (3) | Li-0(3) | 2.31(5) |
| Li-O(4) | 2.17 (4) | Li-0(4) | 2.16(5) |
| Li-0(5) | 2.27 (4) | Li-0(5) | 2.36(5) |
| Li-0(6) | 2.07 (3) | Li-0(6) | 2.05(5) |
| Li-0(7) | 2.13(4) | Li-0(7) | 2.02 (6) |
| Li-0(7) | 2.15 (4) | Li-0(7) | 2.14(6) |
| $B(1)-O(2)$ | 1.55 (2) | $B(1)-0(2)$ | $1.54(2)$ |
| $B(1)-0(3)$ | 1.42 (2) | $B(1)-0(3)$ | 1.39 (2) |
| $B(1)-0(4)$ | 1.61(2) | $B(1)-0(4)$ | 1.54(2) |
| $B(1)-0(5)$ | 1.37(2) | $B(1)-0(5)$ | 1.40 (2) |
| $B(2)-O(1)$ | $1.38(2)$ | $B(2)-O(1)$ | 1.43(3) |
| $B(2)-0(4)$ | 1.43(2) | $B(2)-$ ( 4 ) | 1.48(2) |
| $B(2)-0(5)$ | 1.41(2) | $B(2)-0(5)$ | 1.36(3) |
| $B(3)-0(6)$ | 1.34(4) | $B(3)-O(6)$ | 1.33(4) |
| $B(3)-0(7)$ | 1.43(3) $\times 2$ | $B(3)-0(7)$ | 1.44(3) $\times 2$ |
| $O(1)-Y(1)-O(3)$ | 75.7(4) | $O(1)-Y(1)-O(3)$ | 75.1(4) |
| $0(1)-Y(1)-O(5)$ | 78.0 (3) | $0(1)-Y(1)-O(5)$ | 78.0 (4) |
| $0(1)-Y(1)-O(5)$ | 79.4(3) | $0(1)-Y(1)-O(5)$ | 79.8 (4) |
| $0(2)-Y(1)-O(3)$ | 80.3(3) | $0(2)-Y(1)-0(3)$ | 81.5(4) |
| $0(2)-Y(1)-0(5)$ | 58.6(3) | $0(2)-Y(1)-0(5)$ | 58.0(3) |
| $O(1)-Y(2)-O(3)$ | $74.2(4)$ | $0(1)-Y(2)-0(3)$ | $74.7(4)$ |
| $O(1)-Y(2)-O(4)$ | $77.7(4)$ | $0(1)-Y(2)-O(4)$ | $78.7(4)$ |
| $0(1)-Y(2)-O(4)$ | 78.8(4) | $0(1)-Y(2)-0(4)$ | $79.2(4)$ |
| $0(2)-Y(2)-O(3)$ | $75.7(3)$ | $O(2)-Y(2)-O(3)$ | 77.0 (3) |
| $0(2)-Y(2)-0(4)$ | 61.1(4) | $0(2)-Y(2)-0(4)$ | 60.0(3) |
| $0(2)-A 1-0(2)$ | 101.8(6) $\times 2$ | $0(2) \cdots \mathrm{Ga}-0(2)$ | 103.2(7) $\times 2$ |
| $0(2)-A 1-0(2)$ | $113.2(6) \times 2$ | $0(2)-\mathrm{Ga}-0(2)$ | $112.2(6) \times 2$ |
| $0(2)-A 1-0(2)$ | $113.7(7) \times 2$ | $0(2)-\mathrm{Ga}-0$ (2) | $113.2(7) \times 2$ |

Table 6.4. cont'd

| $O(1)-L i-O(3)$ | 69(1) | O(1)-Li-O(3) | 70(1) |
| :---: | :---: | :---: | :---: |
| O(1)-Li-O(4) | 75(1) | O(1)-Li-0(4) | 76(2) |
| $0(3)-L i-O(5)$ | 87(1) | $0(3)-L i-0(5)$ | 84(2) |
| O(4)-Li-O(5) | 65(1) | O(4)-Li-O(5) | 62(1) |
| O(6)-Li-O(7) | 82(1) | O(6)-Li-O(7) | 83(2) |
| $O(2)-B(1)-O(3)$ | 111(1) | $0(2)-3(1)-0(3)$ | 114(1) |
| $0(2)-B(1)-O(4)$ | 98(1) | $0(2)-3(1)-0(4)$ | 99(1) |
| $0(2)-B(1)-O(5)$ | 109(1) | $0(2)-B(1)-O(5)$ | 106(1) |
| $0(3)-B(1)-O(4)$ | 112(1) | $0(3)-3(1)-0(4)$ | 117(1) |
| $O(3)-B(1)-O(5)$ | 119(1) | $0(3)-B(1)-0(5)$ | 114(1) |
| $O(4)-B(1)-O(5)$ | 106(1) | $0(4)-B(1)-O(5)$ | 105(1) |
| $O(1)-B(2)-O(4)$ | 112(2) | $O(1)-B(2)-O(4)$ | 110(2) |
| $O(1)-B(2)-O(5)$ | 128(2) | $0(1)-B(2)-O(5)$ | 128(2) |
| $0(4)-B(2)-O(5)$ | 112(1) | $0(4)-B(2)-O(5)$ | 115(2) |
| $0(6)-B(3)-O(7)$ | 124(1) $\times 2$ | $0(6)-B(3)-0(7)$ | 125(1) |
| $0(7)-B(3)-O(7)$ | 112(3) | $0(7)-B(3)-0(7)$ | 111(3) |
| $B(1)-0(4)-B(2)$ | 123(1) | $B(1)-0(4)-B(2)$ | 125(1) |
| $B(1)-0(5)-B(2)$ | 123(1) | $B(1)-O(5)-B(2)$ | 126(2) |



Figure 6.1 Drawing of the unit cell of $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{MB}_{9} \mathrm{O}_{23}$ ( $\mathrm{M}=\mathrm{Al}$ and Ga ). The largest open circles represent $O$ atoms, the smallest open circles represent $B$ atoms, the open circles with shaded bonds represent $Y$ atoms, and the small filled circles represent Al (Ga) atoms.


Figure 6.2 Drawing of a 16 -membered $B-0$ ring $\left[\mathrm{B}_{8} \mathrm{O}_{20}\right]^{16-}$.


Figure 6.3 A ring comprised of eight $Y$-centered square antiprisms.


Figure 6.4 The packing of the borate and yttrate rings as viewed along the c axis. The small filled circles represent Al (Ga) atoms.


Figure 6.5 The packing of the borate and yttrate rings as viewed along the $\underline{\mathbf{a}}$ and $\underline{\mathbf{b}}$ axes.


Figure 6.6 A view of the crystallographically unique orthoborate and the polyborate ring.
ring typified by boroxine $\left[\mathrm{B}_{3} \mathrm{O}_{6}\right]^{3-}$, which is present in its simple isolated form in a variety of compounds, including the material $\mathrm{BaB}_{2} \mathrm{O}_{4}(6)$. We are unaware of any larger isolated rings that exist in anhydrous borates although portions of certain polymeric borates exhibit higher member rings; a 12-membered ring is observed in the compound $\mathrm{Ba}_{2} \mathrm{LiB}_{5} \mathrm{O}_{10}$ (7). Very large, macrocyclic rings have been reported for complex hydrated copper borates (8). The average tetrahedral and triangular $\mathrm{B}-\mathrm{O}$ distances of the anion $\left[\mathrm{B}_{8} \mathrm{O}_{20}\right]^{16-}$ in the Al compound are $1.4(1)$ and $1.40(3) \&$, respectively, while the corresponding values in the Ga compound are $1.46(8)$ and $1.42(6) \dot{A}$, respectively. These are in agreement with similar interactions, $1.46 \AA$ for the tetrahedral site and $1.37 \AA$ for the triangular site in the anion $\left[B_{3} \mathrm{O}_{6}\right]^{3-}$ observed in the compound $\mathrm{LaB}_{3} \mathrm{O}_{6}$ (9). The angles $B(1)-O(4)-B(2), 123(1)^{\circ}$, and $B(1)-O(5)-B(2), 123(1)^{\circ}$, for the A1 derivative and $\mathrm{B}(1)-\mathrm{O}(4)-\mathrm{B}(2), 125(1)^{\circ}$, and $\mathrm{B}(1)-\mathrm{O}(5)-\mathrm{B}(2), 126(2)^{\circ}$, for the $G$ derivative are typical values for the links between borate groups. For example, the $0-\mathrm{B}-0$ angles, $126-128^{\circ}$ and $117-123^{\circ}$, have been observed for the $\left[\mathrm{B}_{4} \mathrm{O}_{7}\right]^{2-}$ networ's in the compound $\mathrm{MgB}_{4} \mathrm{O}_{7}$ (10) and the $\left[\mathrm{B}_{3} \mathrm{O}_{6}\right]^{3-}$ rings in the compourid $\mathrm{BaB}_{2} \mathrm{O}_{4}$, respectively.

The irregular square antiprismatic sites for atoms $Y(1)$ and $Y(2)$ are drawn in Figure 6.7 and Figure 6.8, respectively. The distortions from a regular square antiprism afford a site with $\mathrm{C}_{2}$ symmetry. These distortions include the shorter $\mathrm{Y}(1)-\mathrm{O}(3)$ and $\mathrm{Y}(2)-\mathrm{O}(1)$ distances, 2.28(1) and 2.19(1) $\AA$, respectively, as well as several irregular bond angles (cf. Table 6.4). Bond distances range from 2.28(1) to 2.46(1) \& for the interactions $Y(1)-0$ and from $2.19(1)$ to


Figure 6.7 Square antiprismatic site of the atom $Y(1)$.


Figure 6.8 Square antiprismatic site of the atom $Y(2)$.
$2.40(1) \&$ for the interactions $Y(2)-0$. These distances compare to those, $2.21-2.41 \mathrm{~A}$, reported for the 8 -coordinate site in the compound $\mathrm{YBO}_{3}$ (11). The eight antiprisms centered by independent atoms $Y(1)$ and $Y(2)$ are 1 inked by sharing edges $O(1) \cdots O(1)$ and $O(2) \cdots O(3)$ to form the ring discussed earlier.

The Al (Ga) atom resides in a tetrahedral site that links the borate rings, sharing 0 atoms with the tetrahedral $B$ atoms of four adjacent $\left[B_{8} \mathrm{O}_{20}\right]^{16-}$ units. The A1-O distance, $1.75(1) \AA$, and the Ga-O distance, 1.84(1) A , compare favorably with those calculated from crystal radii (12), 1.77 A and $1.85 \&$, respectively.

The Li atom binds to six 0 atoms at the corners of a highly distorted polyhedron (Figure 6.9). The Li-O distances range from 2.02(6) to 2.55(4) \& and are similar to those reported for the compound $\mathrm{Sr}_{2} \mathrm{LiScB}_{4} \mathrm{O}_{10}(13), 1.97(1)-2.67(1) \mathrm{A}$. Four of these Licentered polyhedra share vertex $O(6)$ (Figure 6.10), which resides in the channel.

The atom $\mathrm{B}(3)$ coordinates to three 0 atoms in a triangular manner. The $\mathrm{BO}_{3}$ triangle that is linked by the Li-centered polyhedra through $O(6)$ and $O(7)$ is present in the center of the channel. The B-O distances, $1.33(4)-1.44(3) \mathrm{A}$, are similar to those observed in the orthoborate $\mathrm{NdAl}_{3}\left(\mathrm{BO}_{3}\right)_{4}(14)$ where B atoms are also coordinated in a triangular manner by 0 atoms, $1.35(2)-1.42(4) \mathrm{A}$.

Five of the seven 0 atoms are coordineted by four cations in approximate tetrahedral coordination. Atom $O(7)$ is present at the apex of a trigonal pyramid with atom $B(3)$ and two Li atoms at the base; atom $O(6)$ is located in a square pyramid with four Li atoms at


Figure 6.9 Distorted 6-fold site of the Li atom.


Figure 6.10 A cluster of four Li-centered polyhedra.
the base and atom $B(3)$ at the apex.

Synthesis
Attempts to prepare the compounds $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{MB}_{9} \mathrm{O}_{23}$ ( $\mathrm{M}=\mathrm{Al}$ and Ga ) by heating ground mixtures of the nitrates and $\mathrm{B}_{2} \mathrm{O}_{3}$ or mixtures obtained from precipitation of aqueous solutions of the reagents with oxalic acid dihydrate afforded only the compound $\mathrm{YBO}_{3}$ as a crystalline product. No evidence for the formation of the desired compounds was obtained, even after heating at $800^{\circ} \mathrm{C}$ for more than 5 days. In contrast, heating powders resulting from the treatment with $\mathrm{NH}_{4} \mathrm{OH}(\mathrm{aq})$ at $700^{\circ} \mathrm{C}$ for 24 hours affords primarily $\mathrm{YBO}_{3}$ with $\approx 20 \%$ desired products. Heating these samples at $800^{\circ} \mathrm{C}$ for 72 hours affords $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{MB}_{9} \mathrm{O}_{23}$ with $\approx 2 \% \mathrm{YBO}_{3}$ while heating them at $900^{\circ} \mathrm{C}$ affords decomposition and the appearance of strong diffraction peaks attributable to $\mathrm{YBO}_{3}$ in the X -ray patterns. Treatment of the oxides with $\mathrm{NH}_{4} \mathrm{OH}(\mathrm{aq})$ provides a favorable synthetic route for preparation of the title compounds. Because the phase $\mathrm{YBO}_{3}$ is observed to form initially in the reaction it seems likely that treatment with $\mathrm{NH}_{4} \mathrm{OH}(\mathrm{aq})$ primarily assists in the reduction of particle sizes as well as promoting some mixing of the reagents.

Unit-cell parameters derived from powder data for the compounds $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{MB}_{9} \mathrm{O}_{23}(\mathrm{M}=\mathrm{Al}$ and Ga$)$ are in agreement with those observed from the single-crystal structure determinations. As expected from crystal radii (12) $\left(\mathrm{Gd}^{3+}, 1.20, \mathrm{Er}^{3+}, 1.14\right.$, and $\left.\mathrm{Y}^{3+}, 1.16 \AA\right)$, unit-cell parameters for the Gd analogues are slightly larger than those observed for the Er and $Y$ analogues. We attempted to prepare La and

Nd analogues and found that the principal products of the syntheses to be the compounds $\mathrm{LaBO}_{3}$ and $\mathrm{NdBO}_{3}$, respectively. This result is consistent with the observation of 9 -coordinate La and $N d$ atoms in the compounds $\mathrm{LaBO}_{3}$ (15) and $\mathrm{NdBO}_{3}$ (16) and 8-coordinate Ln atoms ( $\mathrm{Ln}=\mathrm{Y}$, Er , and Gd ) in the compounds $\mathrm{LnBO}_{3}$ (11). The larger coordination number and accompanying greater coulombic interaction favor the formation of the simple La and Nd orthoborates under the high temperature conditions. A low-temperature method of synthes is could afford the quarternary borate.

SHG
Crystals of the compound $\mathrm{Li}_{4} \mathrm{Y}_{4} \mathrm{GaB}_{9} \mathrm{O}_{23}$ have been tested for their efficiency in generation of the second harinonic of the 1064 nm line of a $\mathrm{Nd}^{3+}$ :YAG laser. In a simple test, an efficiency of $10 \%$ of that of KDP (potassium dihydrogen phosphate) was found. This low efficiency may be consistent with the characteristics of the structure. The principal chromophores in the structure that contribute to the second harmonic generation are the triangular $\mathrm{BO}_{3}$ groups. Because of the presence of the $2_{1}$ screw axes parallel to the crystallographic $\underline{a}$ and $\underline{b}$ axes, $\mathrm{BO}_{3}$ groups in neighboring rings are orientated approximately antiparallel to one another (Figure 6.4). This alignment affords approximate cancellation of the components of the hyperpolarizability tensor and a small macroscopic nonlinearity for the crystals. Additional detailed studies of the optical conversion efficiency are planned.

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APPENDIX

## APPENDIX A

## ADDITIONAL NEW BORATES

Results on the synthesis and identification of additional new borates are summarized in this Appendix.
$\mathrm{GdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$. A powder sample of $\mathrm{GdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ was prepared by heating a stoichiometric ratio of the reagents $\mathrm{Gd}\left(\mathrm{NO}_{3}\right)_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}, \mathrm{Sc}_{2}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$, and $\mathrm{B}_{2} \mathrm{O}_{3}$ at $700^{\circ} \mathrm{C}$ for 6 hours. Crystals were grown from melts corresponding to the composition 33 wt. $\% \mathrm{GdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ and 67 wt. $\%$ $\mathrm{LiBO}_{2}$. Two melts were heated at $1000^{\circ} \mathrm{C}$ for 2 hours, one was cooled to $825^{\circ} \mathrm{C}$ and the other to $750^{\circ} \mathrm{C}$, at the rate $2.5^{\circ} \mathrm{Chr}^{-1}$, each was cooled to ambient temperature at $100^{\circ} \mathrm{Chr}^{-1}$. Crystals were isolated from the melts by dissolution of the excess $\mathrm{LiBO}_{2}$ in boiling $\mathrm{H}_{2} \mathrm{O}$. Unit-cell parameters were derived by single crystal X-ray methods. The phase obtained from the melt slowly cooled to $825^{\circ} \mathrm{C}$ afforded a rhombohedral cell of dimensions $a=9.718(1), c=7.892(1) \AA$, and $V=645.5(1) \AA^{3}$ and was determined to be isostructural to the compound $\mathrm{NdSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ (cf. Chapter 4). The crystal isolated from the melt slowly cooled to $750^{\circ} \mathrm{C}$ afforded a monoclinic cell of dimensions $a=7.662(3), b=9.757(3), c=11.954(3) \AA, \beta=105.3(1)^{\circ}$, and $V=$ 861.8(5) $\dot{A}^{3}$ and it was found to be isostructural to the compound $\mathrm{LaSc}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ (cf. Chapter 4).
$\mathrm{BiAl}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ and $\mathrm{BiAl}_{2 \cdot 07} \mathrm{~B}_{4} \mathrm{O}_{10 \cdot 6}$. Crystals of the compounds
$\mathrm{BiAl}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ and $\mathrm{BiAl}_{2.07} \mathrm{~B}_{4} \mathrm{O}_{10.6}$ were isolated from a melt composed of $16.5 \mathrm{~mol} \% \mathrm{Bi}_{2} \mathrm{O}_{3}, 11.4 \mathrm{~mol} \% \mathrm{Al}_{2} \mathrm{O}_{3}$, and $72.1 \mathrm{~mol} \% \mathrm{~B}_{2} \mathrm{O}_{3}$ during the course of an investigation of the system $\mathrm{Bi}_{2} \mathrm{O}_{3}-\mathrm{Al}_{2} \mathrm{O}_{3}-\mathrm{B}_{2} \mathrm{O}_{3}$. The melt was soaked at $750^{\circ} \mathrm{C}$ for one hour and cooled to $600^{\circ} \mathrm{C}$ at the rate $5^{\circ} \mathrm{Chr}^{-1}$.

X-ray data for each compound were collected on a Rigaku AFC6R diffractometer. The compound $\mathrm{BiAl}_{3}\left(\mathrm{BO}_{3}\right)_{4}$ is isostructural to the Huntite-type borate $\mathrm{NdSC}_{3}\left(\mathrm{BO}_{3}\right)_{4}$. Unit-cell parameters are $\mathrm{a}=$ $9.348(1) ~ \dot{A}, c=7.289(2) ~ \dot{A}$, and $V=551.7(3) \dot{A}^{3}$. The cell parameters and hexagonal lattice derived from a single crystal of the compound $\mathrm{BiAl}_{2.07} \mathrm{~B}_{4} \mathrm{O}_{10.6}$ suggest that it is isostructural to the compound $\mathrm{NdAl}_{2.07} \mathrm{~B}_{4} \mathrm{O}_{10.6}$ (Pushcharovskii, Karpov, Leonyuk, and Belov, 1978). The powder sample of this compound was prepared by heating a stoichiometric ratio of the oxides $\mathrm{Bi}_{2} \mathrm{O}_{3}, \mathrm{Al}_{2} \mathrm{O}_{3}$, and $\mathrm{B}_{2} \mathrm{O}_{3}$ at $800^{\circ} \mathrm{C}$ for 24 hours. The X-ray powder diffractogram of the product agrees well with a pattern calculated from use of the computer program LAZY-PULVERIX and the results of the aforementioned single crystal X-ray study.
$\mathrm{Na}_{3} \mathrm{SC}_{2}\left(\mathrm{BO}_{3}\right)_{3}$. The new compound $\mathrm{Na}_{3} \mathrm{Sc}_{2}\left(\mathrm{BO}_{3}\right)_{3}$ was identified from analysis of phase equilibria in the system $\mathrm{Na}_{2} \mathrm{O}-\mathrm{Sc}_{2} \mathrm{O}_{3}-\mathrm{B}_{2} \mathrm{O}_{3}$. A homogeneous powder of the compound was prepared by grinding stoichiometric amounts of the reagents $\mathrm{NaNO}_{3}, \mathrm{Sc}_{2} \mathrm{O}_{3}$, and $\mathrm{B}_{2} \mathrm{O}_{3}$ and heating them at $700^{\circ} \mathrm{C}$ for one hour. The resulting powder was reground, pressed into a pellet, and heated at $850^{\circ} \mathrm{C}$ for 24 hours. Identification of the phase was made by powder X-ray diffraction. The
peaks appearing in the X-ray pattern (Figure A.1) do not correspond to those of any known sodium or scandium borates; this result indicates that the phase is a new material. An endothermic signal at $1040^{\circ} \mathrm{C}$ in the DTA trace indicates decomposition of the sample. The appearance of diffraction peaks attributable to the compound $\mathrm{ScBO}_{3}$ in the X-ray pattern of a sample quenched from $1060^{\circ} \mathrm{C}$ indicates that the compound decomposes as follows:
$\mathrm{Na}_{3} \mathrm{Sc}_{2}\left(\mathrm{BO}_{3}\right)_{3} \longrightarrow \mathrm{Na}_{3} \mathrm{BO}_{3}+2 \mathrm{ScBO}_{3}$.
A suitable flux must be found to grow single crystals of this sample.


Figure A.1 X-ray powder pattern of the compound $\mathrm{Na}_{3} \mathrm{SC}_{2}\left(\mathrm{BO}_{3}\right)_{3}$.

