

Rapid Microwave Synthesis of the Iron Arsenides NdFeAsO and NdFe_{0.9}Co_{0.1}AsO.

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ABSTRACT: The future of iron pnictide superconductors in technology is still undecided. While these materials are now known to possess high critical temperatures and critical magnetic fields processing methods for these materials are still in their infancy. Recently we have been investigating possible ways to speed up the synthetic process for obtaining polycrystalline iron arsenide superconductors and other transition metal pnictides. Here we report the synthesis of NdFeAsO and NdFe_{0.9}Co_{0.1}AsO in less than one hour total exposure to microwave radiation using a secondary microwave susceptor to surround the reaction ampoule. Magnetic susceptibility and electronic resistivity measurements reveal the Co doped sample to be of high quality with a narrow transition range.

It has been almost 4 years now since layered iron arsenide materials, such as LaFeAsO and BaFe₂As₂, were ‘reborn’ and a new surge of superconductor research began.^{1,2} At 4 years old the iron arsenide superconductors are still young and have not yet proven themselves worthy of industrial application. They are certainly off to a good start by virtue of possessing high critical temperatures and large critical magnetic fields. It still has to be determined however whether all the aspects important to application can be optimized; these include basic material parameters such as grain connectivity and more general factors such as ease of manufacturing.³

Recently we have been working to extend the well known field of solid state microwave synthesis to iron arsenide superconductors and other transition metal pnictides such as skutterudites.⁴ Microwave energy has been used to rapidly make polycrystalline samples of many different functional materials; from the high T_c superconductors such as YBa₂Cu₃O_{7-x} and Bi₂Sr₂CaCu₂O_{8+x} to high K dielectrics such as CaCu₃Ti₄O₁₂.^{5,6,7}

Many inorganic metal powders and metal oxides will heat extremely fast when exposed to 2.45 GHz radiation, the common frequency of domestic and research grade multimode microwaves. The thermal energy dissipated by these materials upon exposure can be harnessed to drive atomic diffusion and solid state reactions. If none of the reactants is a microwave susceptor than an additional susceptor may be used to surround the reaction vessel or may be placed in direct contact with the reactants, so long as there are no possible susceptor-reactant side reactions. For more general information on these techniques see the reviews and references given by Rao *et al.* or Mingos and Baghurst.^{8,9}

We have been interested in rapid solid state microwave reactions for two reasons primarily. One is that the speed at which samples can be produced allows for more rapid trial and error analysis of potentially interesting compositions. The second is

that if high quality polycrystalline materials are needed, perhaps for sputter target manufacturing or powder in tube wire production, then a rapid microwave synthesis method may prove economical. Here we report the synthesis of the iron arsenide compounds NdFeAsO and NdFe_{0.9}Co_{0.1}AsO, using microwave radiation and copper oxide, CuO, as an additional microwave susceptor. Due to their stoichiometry these materials are often called the 1111-type iron arsenides. Currently the 1111-type materials have demonstrated the highest critical temperatures out of all the iron arsenides classes now known. At room temperature these materials adopt a tetragonal structure with P4/nmm (#129) symmetry. The structure is often described a Nd₂O₂ and Fe₂As₂ layers stacked along the *c*-axis, wherein the former adopts a fluorite style arrangement (anion in tetrahedral coordination) and the later adopts an anti-fluorite coordination (metal cation in tetrahedral coordination). Figure 1 details the 1111-type structure and *c*-axis stacking.

Elemental Fe and As were used along with Nd and Nd₂O₃ as starting reagents, all were of 3N purity or better and from Alfa Aesar. Stoichiometric amounts were ground and pressed into pellets (0.5 grams) within an Ar glove box. The pellets were subsequently sealed inside fused silica ampoules (OD 11 mm, ID 9 mm, approx. 90 mm length) evacuated to approximately 1 x 10⁻⁴ torr. The sealed ampoule was then placed inside an alumina combustion boat crucible and buried within 110-115 grams of CuO. The reaction vessel was then surrounded by microwave transparent high-temperature fire bricks and placed in the microwave oven cavity, see figure 2. The microwave used was a CEM MDS-81D (2.45 GHz multi-mode oven). If continuously exposed to microwaves the temperature of the CuO can reach its melting point (1474 K) and cause softening of fused silica ampoules, so care must be taken to limit the maximum temperature. For this reason microwave exposure was limited to 5 minute intervals at 100% power (750 Watts). The

temperature was estimated to be approximately 1170-1220 K by placing a thermocouple in the surrounding CuO immediately after exposure. Ten 5 minute heating cycles was sufficient to produce high quality samples of NdFeAsO and NdFe_{0.9}Co_{0.1}AsO. The total microwave exposure time was thus only 50 minutes.

Recently a 20 minute low temperature (1173 K) synthesis of iron arsenide superconductors such as SmFeAsO_{0.85}F_{0.15} has been reported but the reactants were ball-milled for 4 hours to enhance reaction kinetics.¹⁰ It is interesting to note that even without ball milling the speed of microwave synthesis appears to be on par with that of the ball milled samples. Cobalt and iron powders are both excellent microwave susceptors and have been reported to achieve temperatures around 1000 K after about 3 - 7 minutes exposure.⁸ It is possible that this coupling to the microwave energy allowed for enhanced interdiffusion of the Fe and Co; however, the small batch size used here meant that the energy dissipated by the Co and Fe reactants alone was not enough to drive the reaction. By using an additional susceptor we are in essence creating a miniature furnace around our sample with an extremely high ramp rate. The radiative heat from this susceptor material then becomes the main driving force for the reaction.

After microwave synthesis, powder x-ray diffraction (PXRD) patterns were collected from 20-60° 2θ, using a Rigaku MiniFlex 2, with stepsize of 0.02° 2θ, and 2 second dwell time. Least squares refinement of the PXRD data within the *P4/nmm* (#129) space group reveals the lattice parameters of NdFeAsO to be *a*=3.9612(9) Å and *c*=8.583(2) Å. The lattice parameters of NdFe_{0.9}Co_{0.1}AsO are found to be *a*=3.9656(6) Å and *c*=8.554(1) Å. PXRD patterns for each are shown in figure 1; very small peaks identified as FeAs are labeled, (*). The refined cell lengths for both compositions agree well with previously reported lattice parameters.¹¹ The interplay between metal-metal bonding and metal-arsenide bonding interactions means that standard ionic radii considerations are not easily applied to these materials. The *a*-parameter of NdFe_{0.9}Co_{0.1}AsO undergoes a slight expansion as Fe is replaced with Co while the *c*-parameter contracts more sharply. Refinements of the NdFe_{1-x}Co_xAsO system have shown that Co substitution is accompanied by a shift in the As *z*-position towards the Fe/Co layer and a decrease in the average M-As bond length.¹¹

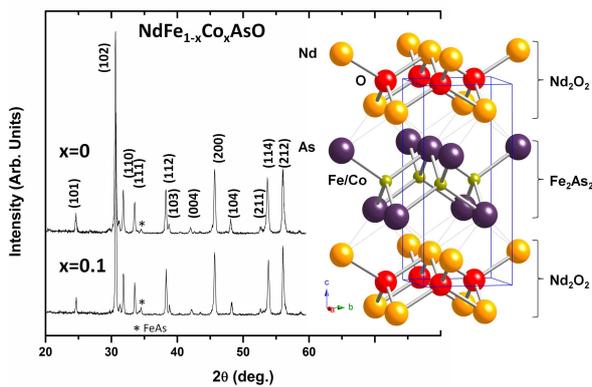


Figure 1. X-ray powder diffraction patterns for NdFeAsO and NdFe_{0.9}Co_{0.1}AsO synthesized using microwave radiation and an additional susceptor, CuO, surrounding the reaction ampoule. Shown right is the structure of Nd(Fe/Co)AsO materials depicted as layers of Nd₂O₂ and Fe₂As₂ stacked along the *c*-axis.

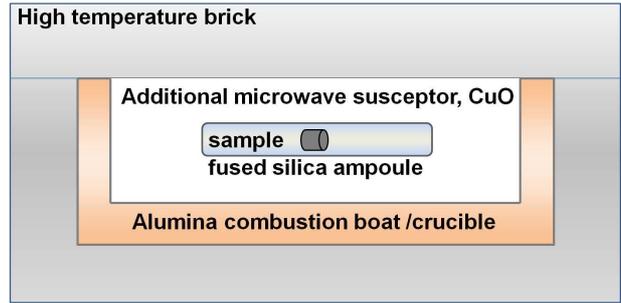


Figure 2. Schematic of the setup used to synthesize NdFeAsO and NdFe_{0.9}Co_{0.1}AsO using reaction ampoules surrounded by an additional susceptor within a 2.45 GHz multi-mode microwave cavity.

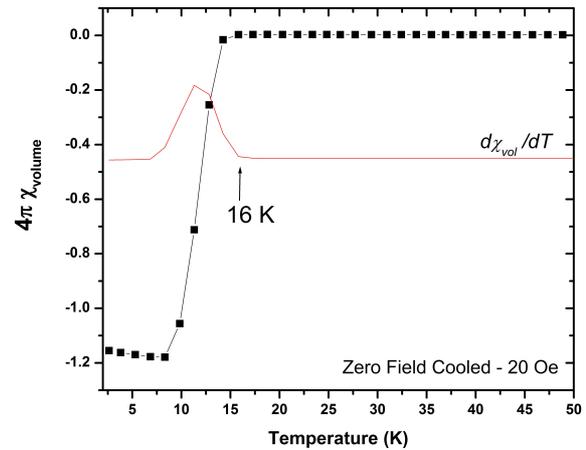


Figure 3. Magnetic susceptibility of NdFe_{0.9}Co_{0.1}AsO collected under zero field conditions and a magnetic field of 20 Oe; shown plotted as $4\pi\chi_{vol}$. The critical temperature, T_c , as determined by the $d\chi_{vol}/dT$ plot is 16 K; shown overlaid for comparison.

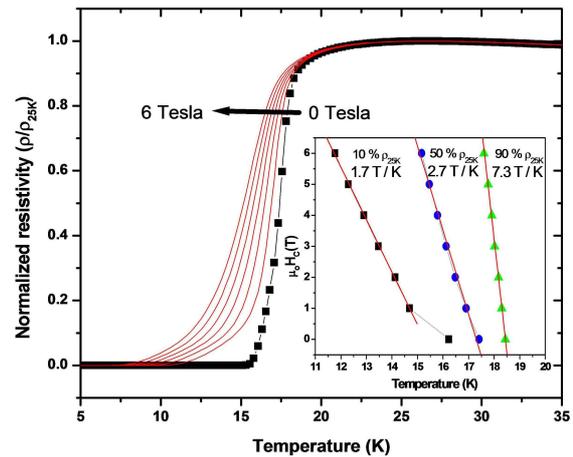


Figure 4. Normalized resistivity (ρ/ρ_{25K}) of NdFe_{0.9}Co_{0.1}AsO collected under magnetic fields from 0 - 6 Tesla (T). The inset details how the critical temperatures for 10%, 50%, and 90% of the normal state resistivity change with increasing magnetic field; the rate of the change for each is listed below the label.

Magnetization and resistivity data for $\text{NdFe}_{0.9}\text{Co}_{0.1}\text{AsO}$ was collected using a Quantum Design PPMS from 2 K - 300 K. Magnetic susceptibility for the composition $\text{NdFe}_{0.9}\text{Co}_{0.1}\text{AsO}$, plotted as $4\pi\chi_{\text{vol}}$, indicates the susceptibility onset critical temperature, $T_c(\chi_{\text{onset}})$, is 16 K and the value at 2 K demonstrates that the superconductivity is a of a bulk nature, figure 3. The critical temperature as determined by resistivity, $T_c(\rho_{\text{onset}})$ is found to be 18.4 K, when using the 90% normal state resistivity criterion. Both critical temperature values are in excellent agreement with those previously reported. Figure 4 shows the normalized resistivity, $(\rho/\rho_{25\text{K}})$, for $\text{NdFe}_{0.9}\text{Co}_{0.1}\text{AsO}$ from 5-35 K at various magnetic field strengths. The inset of figure 5 details the temperature of 10%, 50%, and 90% normal state resistance as a function of magnetic field strength. The slope, $(dH_{c2}/dT)_{T-T_c}$, is found to be -1.7, -2.7, -7.3 T/K for the 10%, 50%, and 90% normal states resistances respectively. The Werthamer-Helfand-Hohenberg model can then be used to estimate the upper critical field at zero Kelvin as $H_{c2}(0) = 0.693(T_c)(dH_{c2}/dT)_{T-T_c}$. Using the 50% normal resistance value for $(dH_{c2}/dT)_{T-T_c}$ the upper critical field is calculated to be 32 T.

In summary we have synthesized NdFeAsO and $\text{NdFe}_{0.9}\text{Co}_{0.1}\text{AsO}$ using microwave radiation in conjunction with an additional microwave susceptor, CuO . The total exposure time needed to produce the samples is 50 minutes. Properties such as lattice parameters, T_c , and $H_{c2}(0)$ agree well with those reported in the literature and show this method to be capable of producing high quality samples of iron pnictide superconductors. The ability for iron arsenides to make inroads to the industrial market place will depend on a large number of factors, one of them being ease of manufacturing. We believe microwaves offer a rapid and efficient means of producing bulk polycrystalline materials such as the layered iron arsenides.

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A rapid method for synthesizing NdFeAsO and $\text{NdFe}_{0.9}\text{Co}_{0.1}\text{AsO}$ is reported. This method uses 2.45 GHz microwave radiation and an additional microwave susceptor to drive the reaction. The superconducting properties $\text{NdFe}_{0.9}\text{Co}_{0.1}\text{AsO}$ of microwave synthesized materials match well with those reported previously.

