

# Synthesis of Oxygen-Deficient LaFePO Oxypnictides

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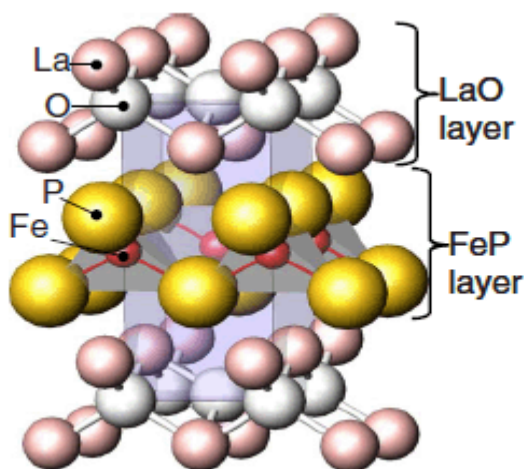
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A procedure was developed to synthesize oxygen-deficient polycrystalline LaFePO based on modifications to Miyasaka's procedure for synthesizing LaFePO [1]. To test its efficacy, the procedure was used to synthesize two oxygen-deficient LaFePO samples. Powder x-ray diffraction showed that the procedure failed to synthesize superconducting LaFePO crystals, but indicated that some LaFePO was successfully formed. This procedure is not yet perfected but shows promise for future work in synthesizing oxygen-deficient polycrystalline LaFePO oxypnictide crystals.

## I. INTRODUCTION

Oxypnictides were first produced in 1995. This class of compounds has the same crystal structure of ZrCuSiAs [2]. The name 'oxypnictides' refers to the constituent atoms of the compound. 'Oxy' refers to the oxygen, and 'pnictide' refers to the anionic form of a 'pnictogen,' a general name for Group 15 elements (excluding N) – P and As. LaFePO is a layered compound with chemical formula  $(\text{La}^{3+}\text{O}^{2-})^+(\text{FeP})^-$ . The material is made of alternating stacks of LaO and FeP layers, as shown in Figure 1. The FeP layer acts as the conduction layer, providing charge carriers, while the surrounding insulating LaO layers confine the charge carriers inside the conduction layer, leading to strong electron-electron coupling, which in turn can lead to superconductivity [3].

Stoichiometrically-balanced LaFePO is nonconducting down to temperatures as low as 0.35 K [4]. Consequently, work has focused on doping studies of LaFePO. Some examples of doping studies that have been carried out include F doping to create charge carriers and Ca doping to create holes in the conduction layer [5]. This work is similar to studies of LaFeAsO, a similar oxypnictide that was naturally insulating but achieved superconductivity at 26 K following 5-12% doping with F [6]. (Though with 5-10% F doping, the  $T_c$  for LaFePO was 5 K).



**Figure 1.** LaFePO has a ZrCuSiAs-type structure. The LaO and FeP form stacked layers.

In 2008, Hamlin et. al conjectured that the superconductivity in LaFePO might be caused by defects like oxygen vacancies, which dope the compound or one of its

layers [4]. Since no relevant data appeared to be in the literature, we attempted to synthesize LaFePO<sub>0.8</sub> and LaFePO<sub>0.9</sub> and then prepared powder X-Ray diffraction and magnetic susceptibility samples to characterize the superconducting properties of these materials.

## II. EXPERIMENT

The oxygen deficient samples of LaFePO were synthesized using two solid-state reactions. The method used was based on the one used by Miyasaka et. al [1]. The starting materials were elemental La, Fe, P, and Fe<sub>2</sub>O<sub>3</sub>. Of these compounds La, Fe, and P are highly reactive in atmosphere so they were measured under Ar. In the first reaction La and P were measured out in stoichiometric proportions to form LaP. The La and P were placed in a carbon coated quartz tube in Ar, closed using a balloon, and then evacuated then sealed in atmosphere. During this process it was important to not heat the materials too much or the P would react and escape the quartz tube.

The sealed La and P were then heated from room temperature to 300 °C at 25 °C/hour. The sample was then kept at 300 °C for 10 hours. It was then heated slowly to 700 °C at 10 °C/hour. It was then kept at that temperature for 10 hours. Finally the sample was cooled at a rate of 25 °C. It was important to heat the sample up slowly or the materials would react and destroy the quartz tube.

[Inexplicably the amount of LaP recovered after the heating was only 1/3 of what was expected from the materials placed in the quartz tube initially.]

The LaP created was divided into two samples. The LaP was combined stoichiometrically with Fe and Fe<sub>2</sub>O<sub>3</sub> to produce the desired 20% and 10% oxygen deficiency. The Fe was weighed out under Ar and then mixed with the LaP and dried out Fe<sub>2</sub>O<sub>3</sub> in atmosphere. The 20% O deficient sample was pressed at 3000 lb into a 0.25" pellet. The 10% sample was pressed at 10,000 lb into a 0.375" pellet. The pellets were sealed in a quartz tube and heated to 1100 °C at 10°C/hour. The samples were sintered at 1100 °C for 48 hours and then cooled at 25 °C.

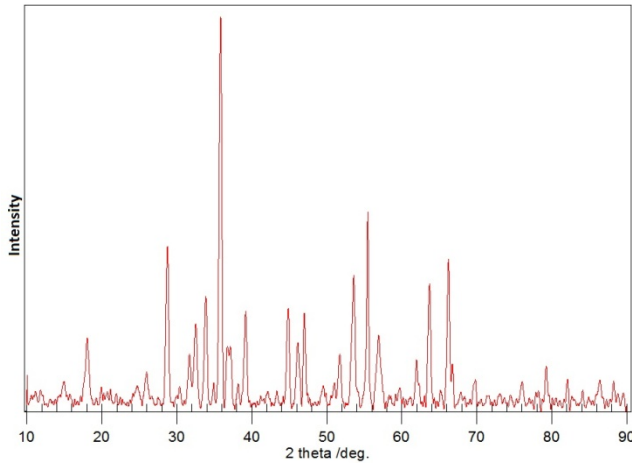
The final material was analyzed using powder x-ray diffraction and a Quantum Design MPMS. For the powder x-ray measurement the powder was mixed with petroleum jelly and placed on a piece of silicon. The MPMS was used to perform susceptibility measurements on the samples. The materials were held at 800 Oe and then zero-field cooled. Then the temperature was increased and then decreased in

the presence of a 10 Oe field.

During the synthesis of the two  $\text{LaFePO}_x$  samples the amount of LaP that was produced during the first reaction was inexplicably only 1/3 of the amount expected. After the final samples were created, the 20% sample was exposed to atmosphere for several hours causing it to oxidize, disintegrating into a gray powder.

### III. RESULTS

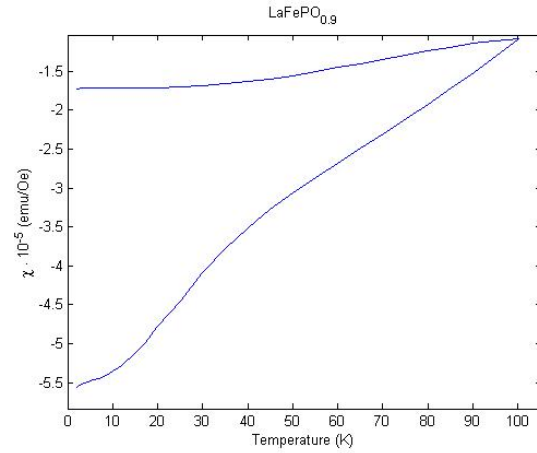
Figure 2 shows the x-ray diffraction pattern for the 10% sample of  $\text{LaFePO}$ . The diffraction pattern shows that the sample was not a single phase. The pattern indicates notable amounts of  $\alpha\text{-Fe}_2\text{O}_3$ , Fe,  $\text{La}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ , FeP, and some  $\text{LaFePO}$ .  $\text{Fe}_2\text{O}_3$  is the most abundant compound in the final sample. It is clear that during processing there was considerable oxygen contamination, despite attempts to work under Ar during the most critical steps. Most likely the La and P did not react completely during the solid-state reaction producing the LaP.



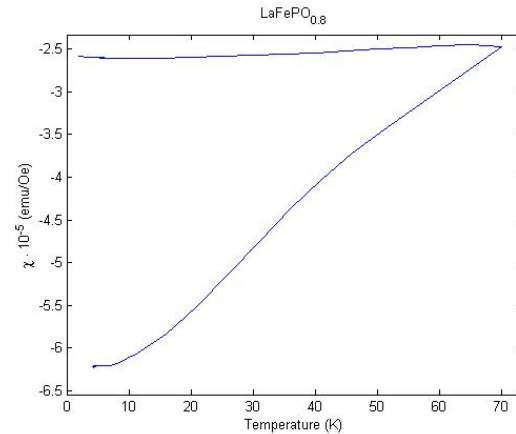
**Figure 2.** Powder x-ray diffraction measurement for the  $\text{LaFePO}_{0.9}$  sample. The largest peak corresponds to  $\text{Fe}_2\text{O}_3$  with several other binary compounds present.

Figures 3 and 4 show the DC magnetic susceptibility measurements for the 10% oxygen deficient sample and the 20% oxygen deficient sample. Neither sample demonstrated superconductivity down to 2 K. In fact the samples displayed strange hysteretic behavior during cooling and heating. The negative susceptibility of the results could be attributed to ferromagnetic components in the powder remaining magnetized after the zero-field cooling. These moments could point opposite to the applied field, producing a negative measure net moment. As the sample heated up, ferromagnetic grains gained enough energy to switch their moment to align with the small applied field. These moments would cancel the fixed moments, causing an increase in the measured moment of the sample. When the sample was field cooled the switched grains were frozen in place producing the hysteretic behavior.

Of the materials determined to be in the 20% oxygen deficient sample  $\alpha\text{-Fe}_2\text{O}_3$  is ferromagnetic and abundant in the sample. Additionally  $\text{La}_2\text{O}_3$  is diamagnetic and could be partially responsible for the decrease in susceptibility during field cooling. It is unlikely to be the sole factor, however, because diamagnetic behavior is weak.



**Figure 3.** Measured DC magnetic susceptibility of  $\text{LaFePO}_{0.9}$  versus temperature in a 10 Oe applied field. The sample was zero-field cooled to 2 K then heated to 100K and then field cooled back to 2 K. The material showed unexpected hysteretic behavior and a negative moment in a positive applied field.



**Figure 4.** Measured DC magnetic susceptibility of the  $\text{LaFePO}_{0.8}$  sample versus temperature in a 10 Oe applied field. The sample was zero-field cooled to 4 K and then heated to 70 K and then cooled in the presence of the field back to 4 K.

### IV. CONCLUSION

The attempt to prepare the  $\text{LaFePO}$  was largely unsuccessful. From the powder x-ray diffraction measurement it was apparent that many of the constituents had oxidized. Specifically it seemed as though the LaP was not formed and so the La and P reacted when the compound was exposed to air. The final reaction also did not complete. The sample was heated to 1100 °C but perhaps it needed to be heated to a higher temperature. Kamihara et. al successfully created polycrystalline  $\text{LaFePO}$  at 1200 °C so perhaps the material was not heated enough [5].

### V. ACKNOWLEDGEMENTS

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## VI. REFERENCES

- [1] Miyasaka, S., et. al, J. Phys: Conf. Ser. **150**, 1-4 (2009).
- [2] Zimmer, B., et. al, Journal of Alloys and Compounds. **229**, 238-242 (1995).
- [3] Ozawa, T. C. and Kauzlarich, S. M., Sci. Technol. Adv. Matter. **9**, 1-12 (2008).
- [4] Hamlin, J. J., et. al, J. Phys.: Condens. Matter. **20**, 1-6 (2008).
- [5] Kamihara, Y., et. al, Phys. Rev. B. **77**, 214515-1-214515-9 (2008).
- [6] Kamihara, Y., et. al, J. Am. Chem. Soc. **130**, 3296-3297 (2008).