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Synthesis and microstructural studies of iron oxypnictide LaO$_{1-x}$F$_x$FeAs superconductors

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Abstract

We report on the synthesis and structural/microstructural studies of iron-based fluorine doped LaOFeAs superconductors. We have successfully synthesized fluorine doped superconducting LaO$_{1-x}$F$_x$FeAs materials by choosing lower temperature ($\sim$1150 °C) and longer synthesis duration ($\sim$60 h) as compared to the standard values of these employed in the pioneering first contribution (Kamihara et al 2008 J. Am. Chem. Soc. 130 3296). A decrease of lattice parameters, as determined by x-ray diffraction, confirms the substitution of fluorine. The superconducting transition temperature is 27.5 K which is observed at a doping level of $x = 0.2$. This superconducting material LaO$_{1-x}$F$_x$FeAs exhibits interesting microstructural characteristics. These relate to the existence of another structural phase, besides the standard phase, having $c$ parameters of $\sim$12.67 Å. This suggests the existence of a modulated structure, similar to the cuprates, in these new oxypnictides. This phase may have new impact on this new high-$T_c$ family.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since the discovery of superconductivity at 3.2 K in iron-based LaOFeP compounds [1], extensive efforts have been devoted towards searching for new superconductors in this system. A team led by Hosono at the Tokyo Institute of technology (Japan) replaced a P atom by an As atom together with substitution of oxygen with fluorine. The resultant compound LaO$_{1-x}$F$_x$FeAs ($x = 0.11$) shows the superconducting transition temperature ($T_c$) at 26 K [2]. Subsequently, superconductivity at 25 K was also observed by partial substitution of an La atom by an Sr atom [3]. Shortly after this discovery, $T_c$ was surprisingly increased to more than 40 K when La in LaO$_{1-x}$F$_x$FeAs was replaced by other rare earth elements such as Ce [4], Pr [5], Nd [6], Sm [7] and Gd [8].

The compound LaOFeAs is an equiatomic quaternary of ZrCuSiAs type tetragonal layered structure with lattice parameter $a = 4.035$ Å, $c = 8.739$ Å [9] and its structure belongs to the $P4/nmm$ space group. The crystal is composed of a stack of alternating LaO and FeAs layers. The LaO layer is sandwiched between FeAs layers. It is thought that these two layers are positively and negatively charged respectively and that the La–O chemical bond in the LaO layer is ionic whereas the Fe–As has a predominantly covalent nature. Thus, the chemical formula may be expressed as (La$^{3+}$O$^{2-}$)$^{+1}$ (FeAs)$^{2-}$. The charge carriers have been increased by substitution of the O$^{2-}$ ion by an F$^{-}$ ion. The parent material LaOFeAs is non-superconducting but shows spin density wave instability in between 150 and 160 K in both resistivity and dc magnetic susceptibility [2, 8]. The spin density wave instability has been found to relate to a structural transition from tetragonal to monoclinic [10]. Doping the system with fluorine suppresses both the magnetic order and the structural distortion in favor of superconductivity. Another important characteristic associated with this new superconductor is its layered structure
and hence these types of superconductors possess a high value of upper critical field \([11–13]\). This leads to the possibility of high current carrying capacity. The structural and microstructural features of this new family of superconductors have not been investigated in detail so far. Understanding of structural features is expected to assist further tailoring of this oxypnictide. We have, therefore, focused our investigation on structural and microstructural studies.

2. Experimental details

In the present study the synthesis of F doped La\(_{1-x}\)F\(_x\)FeAs (0 \(\leq x \leq 0.4\)) high temperature superconductor has been carried out by a two-step solid state reaction at ambient pressure. In the first step, for preparation of LaAs, Fe\(_2\)As and FeAs, we mixed La (99.9% purity, 0.5–1 mm size, Leico), Fe (99.98% purity, 0.2–0.5 mm, Aldrich) and As (99.999% purity, Lump, Alfa-Aesar) in a ratio of 1:3:3 with the help of agate and pestle. The mixture powder was pelletedized and then sealed in an evacuated quartz tube in Ar atmosphere. The sealed silica tube was heated at 900°C for 12 h. In the second step, the mixture of LaAs, Fe\(_2\)As and FeAs were mixed with dehydrated La\(_2\)O\(_3\) (99.99% purity, 0.1–0.2 mm size, Aldrich), La and LaF\(_3\) (99.99% purity, 0.2–0.5 mm, Aldrich) and As (99.999% purity, Lump, Alfa-Aesar) in a ratio of 1:3:3:1 with the help of agate and pestle. The mixture powder was pelletedized and then sealed in an evacuated quartz tube in Ar atmosphere. The sealed silica tube was heated at 900°C for 12 h. In the second step, the mixture of LaAs, Fe\(_2\)As and FeAs was mixed with dehydrated La\(_2\)O\(_3\) (99.99% purity, 0.1–0.2 mm size, Aldrich), and As (99.999% purity, Lump, Alfa-Aesar) in a ratio of 1:3:3:1 with the help of agate and pestle. The mixture powder was pelletedized and then sealed in an evacuated quartz tube in Ar atmosphere. The sealed silica tube was heated at 900°C for 12 h. In the second step, the mixture of LaAs, Fe\(_2\)As and FeAs were mixed with dehydrated La\(_2\)O\(_3\) (99.99% purity, 0.1–0.2 mm size, Aldrich), La and LaF\(_3\) (99.99% purity, 0.1–0.2 mm size, Aldrich) in stoichiometric ratio. The final stoichiometry is \((1 + x)\)La + \((1 - x)\)La\(_2\)O\(_3\) + xLa\(_2\)Fe\(_3\) + 3FeAs, \(x = 0\) for pure and \(x = 0.05, 0.1, 0.2\), for fluorine doped samples. After the final grinding, the powder was again pelletized at a pressure of 4 tons inch\(^{-2}\). The quartz tube was evacuated up to 10\(^{-5}\) Torr and sealed. The sealed quartz tube was heated again at 1150°C for 60 h followed by furnace cooling to room temperature. We have chosen a comparatively low temperature (1150°C instead of 1250°C) and longer synthesis duration (60 h instead of 40 h) to avoid explosion. This is some what different to the standard synthesis temperature and duration so far adopted \([2]\). All the grindings have been carried out in a glove box containing P\(_2\)O\(_5\), NaOH and under argon atmosphere. All the samples in the present investigation were subjected to gross structural characterization by x-ray diffraction (XRD, PANanalytical X’Pert PRO, Cu K\(\alpha\) radiation), electrical transport measurements by the four-probe technique (Keithley Resistivity-Hall setup), surface morphological characterization by scanning electron microscope (SEM, Philips XL-20), and microstructural characterization by high resolution transmission electron microscopy (HRTEM, FEI, Tecnai 20G\(^2\)). The elemental analysis has been carried out by an energy dispersive analysis of x-ray (EDAX) microanalysis system which is attached with HRTEM.

3. Results and discussion

The as-synthesized samples, having various doping concentrations of fluorine, were subjected to gross structural characterization employing the x-ray diffraction technique. The XRD patterns of La\(_{1-x}\)F\(_x\)FeAs (\(x = 0.0, 0.1, 0.2\)) samples are shown in figure 1. These reveal that the pristine sample exhibiting a spin density wave anomaly marked by an arrow but no superconducting transition is shown by the upper curve.

Figure 2 shows the resistivity versus temperature behavior of pure and fluorine doped LaOFeAs samples. The superconducting transition temperature 27.5 K corresponds to the \(x = 0.2\) composition. The pristine sample exhibiting a spin density wave anomaly marked by an arrow but no superconducting transition is shown by the upper curve.

<table>
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<tr>
<th>LaO(_{1-x})F(_x)FeAs</th>
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<th>x=0.1</th>
<th>x=0.2</th>
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<tr>
<td>Resistivity (m(^2) cm)</td>
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<td>2.8</td>
<td>2.6</td>
<td>2.4</td>
<td>2.2</td>
<td>2.0</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Figure 1. XRD pattern of (a) LaOFeAs (b) \(x = 0.1\) fluorine doped LaOFeAs (c) \(x = 0.2\) fluorine doped LaOFeAs samples. All the indexed peaks corresponds to LaOFeAs and peaks marked by an asterisk (*) are impurity phases.

Figure 2. Resistivity versus temperature behavior of pure and fluorine doped LaOFeAs samples. The superconducting transition temperature 27.5 K corresponds to the \(x = 0.2\) composition. The pristine sample exhibiting a spin density wave anomaly marked by an arrow but no superconducting transition is shown by the upper curve.
shows an anomaly at 155 K, which is similar to that of other reports, where it has been shown to occur due to spin density wave instability [2, 6, 10]. The $T_C$ of the sample LaO$_{0.8}$F$_x$FeAs is 27.5 ($\pm$0.2) K which is reproducible and slightly higher ($\sim$5.8%) in comparison to other reports [2]. This may be explicable in terms of enhanced chemical pressure originating from shrinkage of the lattice, as demonstrated by the smaller lattice parameters of the phase synthesized in the present case.

The stoichiometry of various compositions of LaO$_{1-x}$FeAs was investigated by employing an EDAX microanalysis system at several points. It was found that samples were homogeneous and for the specific sample nearly the same stoichiometry was found at different regions. The representative example of LaO$_{0.8}$F$_0.2$FeAs stoichiometry, as determined and shown in figure 3, approximates quite reasonably to the synthesized composition. It can thus be said that the synthesis has actually led to the envisaged composition.

Although several studies have been made in regard to the occurrence of superconductivity in fluorine doped LaOFeAs (i.e. LaO$_{1-x}$F$_x$FeAs), hardly any of the studies have focused on the microstructural aspect. Similarly, variations of microstructural details for optimally doped LaOFeAs have not been studied earlier. This communication is centered on the studies of the microstructural characterization of the above type of LaO$_{1-x}$F$_x$FeAs superconductors. As is known, the microstructural and related structural characteristics have considerable effect on the superconducting behavior. In view of this, present studies are devoted to investigations of microstructural and related structural characteristics of the new superconducting material (LaO$_{1-x}$F$_x$) (FeAs).

Investigations of microstructural characteristics employing TEM (imaging and diffraction modes) explorations have revealed interesting microstructural features. The specimens for transmission electron microscopy (TEM) have been prepared by (a) scrapping particles from the surface of the (LaO$_{1-x}$F$_x$) (FeAs) pellets (b) turning pellets into fine particles and mounting such particles which floated on benzene. These particles were mounted on porous carbon grids. The broad microstructural/structural details for the sample prepared by (a) and (b) were found to be the same. Thus it can be said that the microstructural features observed through TEM are representative of the superconducting phase (LaO$_{1-x}$F$_x$) (FeAs). TEM exploration studies were employed for several samples of the superconducting material. Representative transmission electron micrographs of superconducting specimens are shown in figure 4.

In order to explore the structural aspects of the as-grown phase, selected area diffraction patterns (SAD), particularly with the electron beam along the [001] direction, were taken. Representative examples of the (hkl) diffraction patterns from the (LaO$_{1-x}$F$_x$) (FeAs) with $x = 0.2$ are depicted in figure 4(b). This diffraction pattern is in (hkl) orientation and the corresponding microstructure is shown in figure 4(a). As can be seen from figure 4(b) the diffraction spots are arranged on a square grid corresponding to (100) and (010) spots. The indexing should be a spacing of 4.03 Å which is the expected spacing of the lattice parameter $a$ of the LaOFeAs material. Further, we have taken SAD patterns with the electron beam along the [100] or [010] direction. A representative diffraction pattern is shown in figure 4(d). This figure reveals some interesting characteristics. These are (a) strong 00c type diffraction spots whose indexing is outlined in the figure and (b) comparatively weak spots indicative of different c lattice parameters than those represented by strong diffraction spots. The analysis of bright 00c spots revealed the standard c spacing of $\sim$8.73 Å. However, the faint spots in conjunction with bright spots, some of which are marked by arrows, exhibited spacing, this invariably was found to be $\sim$12.67 Å. A spacing of this type is shown by vertical arrows in figure 4(c). In order to get further insights relating to the occurrence of new $\sim$12.67 Å spacing, HRTEM micrographs were taken. A typical HRTEM micrograph is shown in figure 4(c). Careful analysis of lattice fringes has shown dominantly the presence of a regular c lattice parameter of $\sim$8.73 Å. However, the lattice fringes with the $\sim$12.67 Å lattice parameter were also visible. Some such fringes revealing a c lattice parameter of $\sim$12.67 Å are marked by arrows in figure 4(c). Together with the existence of new local structure with a c spacing of $\sim$12.67 Å, staking faults were also found to be present. Some of these are

![Figure 3. EDAX spectra of LaO$_{0.8}$F$_0.2$FeAs composition (crystal is shown in inset).](image-url)
Figure 4. TEM micrographs of LaO$_{0.8}$F$_{0.2}$FeAs sample. (b) SAD pattern corresponding to the microstructure (a) with the electron beam along the [001] direction. (d) SAD pattern corresponding to the microstructure (c) with the electron beam along the [100] or [010] direction. The lattice fringe width $\sim$12.67 Å is marked by vertical arrows in (c).

marked by SF in figure 4(c). It is interesting to find that the spacing $\sim$12.67 Å is equal to the $c$ parameter ($\sim$8.73 Å) of the known phase of the superconductor (LaO$_{1-x}$F$_x$) (FeAs) plus the thickness of FeAs block (3.94 Å). It can thus be taken that in addition to the known structure another structure with a $c$ parameter of $\sim$12.67 Å, representing a new phase with $c_{new} \sim$ 12.67 Å also exists. The existence of this phase has been confirmed by SAD and HRTEM. The observations suggest an interesting feature of the new superconducting material (LaO$_{1-x}$F$_x$) (FeAs). This relates to the existence of a new structural phase in (LaO$_{1-x}$F$_x$) (FeAs) where the $c$ parameter is equal to the standard $c$ parameter plus the thickness of the block containing charge carriers. This is similar to a cuprate where Bi, Tl and Hg bearing cuprates exhibit such structural phases [14, 15]. For cuprates, this block is CuO$_2$ and for the new (LaO$_{1-x}$F$_x$) (FeAs), it is FeAs. A schematic figure exhibiting the new structural phase as suggested has been shown in figure 5. If the phase (LaO$_{1-x}$F$_x$) (FeAs) is represented by the numerical symbol 11, the new phase with two FeAs layers corresponds to 12. It should be pointed out that similar to the cuprates, for these new superconductors the transition temperature may vary for the above said different structural phases. Further investigations on this aspect are required.

4. Conclusion

Based on the present investigations it can, therefore, be concluded that the new superconducting material (LaO$_{1-x}$F$_x$) (FeAs) exhibits interesting microstructural features. These relate to the existence of another structural phase, besides the standard phase, having $c$ parameters of $\sim$12.67 Å. This is equal to the standard $c$ parameter of $\sim$8.73 Å and width of FeAs block ($\sim$3.94 Å). This modified structural phase may affect the superconducting transition temperature. The existence of this new structural phase with extended $c$ parameter ($\sim$12.67 Å) may throw new light on the superconducting characteristics of the oxypnictide family of superconductors.
Acknowledgments

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References