The synthesis and magnetic structure of the iron selenide Ba$_{0.8}$Fe$_2$Se$_2$

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Abstract. The Ba$_x$Fe$_{2-y}$Se$_2$ ($x=0.8$) single crystal has been synthesized by using the one step technique at relatively lower temperatures. We have investigated structural properties of samples by using the XRD, SEM-EDX and magnetic properties. The SEM results clearly demonstrate that Ba ions are intercalated in the FeSe lattice. XRD result shows that the sample prepared has multi-phase structure. According to our $M$-$H$ measurements perfect diamagnetism has been observed only in low field at 5 K. In addition, those curves indicate that the high field value and some impurities reveal ferromagnetic interactions. The superconducting transition was observed at around $T_c \approx 10.9$ K.

1. Introduction

After the discovery of superconductivity in iron chalcogenides, FeSe having the critical temperature of $T_c = 8$ K, with the layered anti $PbO$- tetragonal structure at room temperature was followed and activated considerable interest in studying these compounds in more detail because of their having the simplest crystal structure among various iron based superconductors [1]. Subsequently, alkali metal intercalated FeSe superconductor [2] around the transition temperature $T_c \approx 30$ K was reported and then, a chalcogenide analog to the 122 iron pnictide superconductors [3, 4] was found as very interesting topic for the researchers.

Later on the first announced synthesis [2] of K$_{0.8}$Fe$_2$Se$_2$, different compounds with the formula A$_x$Fe$_{2-y}$Se$_2$ intercalated with A= Cs [5], Rb [6], Ti/K [7] and Ti/Rb [8] were successfully prepared. The critical temperatures of all these superconductors were reported around 30 K. A$_x$Fe$_{2-y}$Se$_2$ compounds exhibit several distinctive features comparing to other iron-based superconductors: (i) Fe deficiencies in the FeSe layer, proximity to an anti-ferromagnetic semiconducting state [9], (ii) an extremely high Neel transition temperature [10], and (iii) the absence of hole pockets [11]. The barium transition metal chalcogenides Ba$_M$X$_z$ (where M=3d metal, X= Se or S), compounds having different stoichiometries (x:y:z of 2:1:3, 1:1:2, 1:4:3, 1:2:2 and 1:2:3) could be synthesized [13]. For all these compounds, it is known that there are nine different structure types. It has been found that all these structures were based on columns of face-sharing BaX$_6$ tetrahedral. In Ba112 and Ba122, sheets are created by edge sharing of the neighboring columns. But, both in Ba123 and in Ba143, the columns are isolated [13]. In particular, Ba123 seems to be an interesting analog to K122, as the
additional charge of the alkaline earth metal is balanced by the additional chalcogenide anion in the formula [14]. For growing of the single crystals of $A_xFe_2ySe_2$, the Bridgman has typically been used. As it is well-known, this synthesis technique is performed at high temperatures above the melting point of the reactants and through a long growth process. In this work, we have synthesized the $Ba_{0.8}Fe_2Se_2$ sample by using the one-step-method at lower temperatures [12,22] and investigated the structural properties by using the XRD, SEM- EDX and magnetic properties with $M-T$ and $M-H$ measurements under the low and high magnetic fields. We have also calculated the critical current density, $J_c$ by using Bean Critical State Model formula [20]. The critical current density data have been used to obtain the volume pinning force $F_p$, originating from the interactions between the vortex lattices and pinning defects per unit volume in the $Ba_{0.8}Fe_2Se_2$ single crystal.

2. Experimental procedure
$Ba_{0.8}Fe_2Se_2$ was synthesized by a one step technique. First, $BaSe$ (99.9%), Fe (99%) powders and Se grains (99.999%) were put into an alumina crucible and sealed into an evacuated quartz tube. All preparation steps were carried out in argon filled glove box with $O_2-H_2O$ content less than 0.1 ppm. The quartz tube was heated to 930 °C and kept constant for 12 hours. Following this, the tube was cooled down to 550 °C temperature followed by quenching to room temperature. The obtained samples were characterized by Scanning Electron Microscopy (SEM) together with energy dispersive X-ray (EDX) spectrometer (LEO Evo-40 VPX), X-ray diffraction (XRD) (Rigaku D/max-B powder diffractometer system working with $CuK\alpha$ radiation), magnetization and magnetic hysteresis techniques (PPMS, Quantum Design magnetometer).

3. Results and discussions
The X-ray powder diffraction patterns of $BaFe_{2-y}Se_2$ sample is presented in Fig.1. Among the XRD patterns the six strong peaks appear at about $2\theta \approx 24.638, 29.533, 48.276, 50.376, 52.129$ and $76.652$ degrees. These peaks correspond to the reflected intensity from the $(202), (311), (321), (323), (024), (307)$ planes of the orthorhombic structure having space group $Pnma$ with the lattice parameters of $a = 11.85(4)$ Å, $b = 5.47(1)$ Å, $c = 9.15(8)$ Å and $V = 593.92(5)$ Å$^3$ [15]. Calculation of the unit cell parameters were done by using Jade 6.0+ crystal refinement program.
The uncertainty of the calculation remained in the ±0.0001 range. In addition to the above mentioned intensity peaks, sample has also shown some very weak additional peaks corresponding to impurity phase. These new impurity peaks in the XRD spectra may be due to different Fe-Se phases (Fe3Se4 or Fe7Se8) remains in the compound during the formation of BaFeSe. It may be concluded that the solubility of the Fe in the BaFeSe compound has been decreased by the annealing process. These results are in agreement with literature [14,15].

The SEM images 20.000 and 10.000 times magnified are shown in Fig 2. It is quite clear that the surface morphology of the sample is the terrace like formations together with well connected small rectangular bars. It may be argued that these structures are responsible from superconductivity. Fig. 2 also shows the corresponding energy dispersive x-ray (EDX) spectra of the Ba0.8Fe2Se2 sample. From the similarity of the Fe, Ba and Se peak intensity line traces in the EDX spectra of the sample, it is concluded that after the synthesis process, Fe, Ba and Se have been almost homogeneously distributed throughout the sample. All the locations in the matrix contain the expected elements (Fe, Ba, Se) pointing out no other impurity elements. In addition, the nominal chemical compositions of the sample determined by the EDX analyses are Ba0.69Fe1.83Se2. Namely, the EDX line traces indicate that Ba element integrated into the structure of FeSe. In addition it is said that instead Ba122 structure, almost Ba123 one has formed.

The magnetic properties of the Ba0.8Fe2Se2 sample have been also investigated. The temperature dependences of zero field cooled (ZFC) and field cooled (FC) magnetization at 10 Oe for sample are shown in Fig. 3. Above \( T_c \) sample has shown a Pauli paramagnetic type behavior without changing down to \( T_c \). But a sharp drop to diamagnetic phase was obtained after \( T_c \). The zero field cooled (ZFC) magnetization shows that the superconducting shield begins to emerge at superconducting transition temperature and then show a clear transition.

Figure 2. SEM images and EDX spectrums of the Ba0.8Fe2Se2 sample
The sample shows onset of diamagnetism at temperature, $T_{c_{\text{mag}}}$, 10.9 K. As seen in figure, the field cooled (FC) magnetization is very small below the $T_{c_{\text{mag}}}$ temperature for the sample. This is not imply the superconducting volume fraction is very small (around <3%) , since the diamagnetic signal at FC mode is very small even in $\text{Ba}_{0.8}\text{Fe}_2\text{Se}_2$ where bulk superconductivity is confirmed to exist from the specific heat measurements, as reported in previous papers [16,17]. This is probably due to the strong vortex-pinining effect in $\text{Ba}_{0.8}\text{Fe}_2\text{Se}_2$ [18]. In addition, this extremely small magnetic moment in the FC measurements is possibly a result of the local lattice distortions caused by the substitution with relatively large ionic radius of Ba ions, introducing effective pinning centers [19].

The two types of magnetic hysteresis measurements were performed on the samples: the magnetizations as a function of low and high magnetic fields for different temperatures. The results are plotted in Figs. 4 and 5.

**Figure 3.** FC and ZFC magnetizations against temperature for 10 Oe

**Figure 4.** Magnetization against low values of applied field for different temperatures

**Figure 5.** Magnetization against high of applied field for different temperatures
The M-H curves have revealed the existence of ferromagnetism as seen in Fig. 4 for temperatures 10, 15 and 20 K. The small amount of impurities may be the reason of the ferromagnetic components in M-H curves. It further supports the fact that the weaker coupling between each plane reveals in more layer-like transport characteristics as the distance between neighboring Fe-occupied planes increases. As can be seen from Fig. 4, the superconducting behavior is found at the lower magnetic fields for the temperature of 5 K. At this temperature, the sample behaves a type-II superconductor and shows nearly perfect diamagnetism. The area of the M-H loops indicate the ferromagnetic (nearly paramagnetic above ≈ H > 3 Tesla) behavior in the high magnetic fields (see Fig 5). This suggests that the co-existence of both magnetism and superconductivity in our sample due to ferromagnetic nature of Fe and impurity phase, as seen in the XRD analysis.

The critical current at 5 K for the lower magnetic fields can be obtained from the magnetic hysteresis curve by using the Bean’s Critical State Model [20] given as:

\[ J_c = \frac{20\Delta M}{a(1-a/3b)} \]  

where \( \Delta M = M^+ - M^- \) is measured in electromagnetic units per cubic centimeter, \( a \) and \( b \) are the dimensions of the cross section of the sample perpendicular to the applied field. We have estimated the critical current density of the sample at temperatures of 5K, and plotted in Fig.6 against applied magnetic field for the fields in the range \( 0 \leq H \leq 130 \) Oe.

![Figure 6](image1.png) **Figure 6.** Calculated critical current density against low magnetic field at 5K

![Figure 7](image2.png) **Figure 7.** Variation of pinning forces against applied low magnetic fields

It is clear that \( J_c \) increases in low fields region, and then decreases in high fields. Generally, \( J_c \) is composed by inter-granular and intra-granular parts of crystal [21]. As can be understood, the weak links exist for inter-granular. In case of existence of large numbers of weak links, for higher fields, \( J_c \) from the inter-granular part should be much more sensitive to magnetic field, which thus causes a decrement at \( J_c \). The critical current density data have been used to obtain the volume pinning force \( F_p \), originating from the interactions between the vortex lattices and pinning defects per unit volume in the Ba\(_{0.8}\)Fe\(_2\)Se\(_2\) sample, studied at temperature 5 K by using the formula:

\[ F_p = J_c \times B \]  

The plot of \( F_p \) versus \( H \) is given in Fig.7. The maximum value of \( F_p \) is found around 50 Oe.
4. Conclusions
We have systemically studied the structure and magnetic properties of Ba$_{0.8}$Fe$_2$Se$_2$. From XRD patterns multiphase structure was found. SEM images show that the surface morphology of the sample is the terrace like formations together with well connected small rectangular bars. The nominal stoichiometries of Ba, Fe and Se in the sample are determined as 0.69, 1.83, 2, respectively. This indicates that the Ba123 structure has formed in the matrix together with a small part of superconducting volume fraction (around <3%). The diamagnetic onset temperature obtained from the ZFC magnetization is 10.9 K. $J_c$ value calculated from low field $M$-$H$ curve measured at 5 K decreases by increasing the applied magnetic field, suggesting the weak-link behavior in the sample.

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