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Growth and annealing effect of Co-doped $BaFe_2As_2$ single crystals

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ABSTRACT

A series of Co-doped $BaFe_{2-x}Co_xAs_2$ ($0 \le x \le 0.32$) single crystals have been grown by self-flux method. Study of X-ray diffraction indicates that the lattice parameter c of the crystals decrease linearly with the increase in Co-content added to the initial mixtures. The segregation coefficient of Co related to Fe is determined to be ~0.78. The values of superconducting transition temperature T_c are found to increase to about 1–3 K by post growth annealing at high temperature, which should result from the improved crystallinity due to the release of residual strain in the samples. In addition, we demonstrate that the annealing atmosphere of Ar, air or vacuum has an identical effect on the enhancement of T_c. Due to inhomogeneous Co distribution, a broad transition temperature width ΔT_c is observed and discussed for the over-doped samples.

1. Introduction

The discovery of new $LaO_{1-x}F_xFeAs$ [1] family has stimulated great interest in the field of high temperature superconductors. After two decades of the study of cuprate superconductors, these iron-based compounds open a new field of vision and allow for the further exploring and understanding of the high T_c superconducting mechanism. Up to now, there are four types of crystallographic structures found in the iron-based compounds. The oxide system ROFeAs (R=La, Pr, Sm, Ce, Nd, Gd), i.e., (1 1 1 1), which the highest T_c~55 and 25 K have been found in the electron-doped $SmO_{0.9}F_{0.1}FeAs$ [2] and the hole-doped $La_{0.87}Sr_{0.13}OFeAs$ [3] polycrystalline samples, respectively. In the phase of oxygen-free system AFe_2As_2 (A=Ba, Sr, Ca, Cs), i.e., (1 2 2), which T_c ~38.5 and ~25 K have been obtained in the hole-doped $Ba_{0.68}K_{0.32}Fe_2As_2$ [4] and the electron-doped $BaFe_{1.87}Co_{0.13}As_2$ [5,6] single crystals, respectively. In the system AFeAs (A=Li, Na), i.e., (1 1 1), the T_c of LiFeAs and NaFeAs [7] have been reported to be ~18 and 25 K, respectively. Hsu et al. [8] were first to report that the T_c for the phase of As-free FeSe (11) can reach 8 K . The structure of the 122 phase is commonly recognized as charge reservoir block of the A layer, and the FeAs conducting layer alternatively stacks along the c-axis. By the out-of-plane doping with aliovalent ions in the A layer, namely hole doping, the charge carriers can be introduced into the FeAs layer and lead to superconductivity. In addition to doping in the A layer, superconductivity can also be induced by the in-plane doping aliovalent ions in the FeAs conducting layer, namely electron doping, such as $BaFe_{2-x}Co_xAs_2$ and $BaFe_{2-x}Ni_xAs_2$. The parent phases 122 show no superconductivity but it appears under high pressure conditions [9]. However, all these crystals with dimension less than 1 mm can be obtained using NaCl, NaAs or Sn as flux [10–14], but comparatively, it is feasible to grow Co and Ni doped 122 phase single crystals with large dimension and high quality [15]. Very recently, many efforts for exploring the fundamental physical properties by such approaches of neutron scattering [16], scanning tunneling microscopy [17], and angel resolved photoemission [18], have been focused on the 122 phase single crystals. In addition, Liu et al. [15], Ni et al. [19] and Chu et al. [20] have reported the phase diagrams of $BaFe_{2-x}Co_xAs_2$ single crystals; Baumbach et al. [21] have also reported the effect of annealing on the superconducting properties of $SrFe_{2-x}Ni_xAs_2$ single crystals. However, to improve the quality of the single crystals and accurate characterizations concerning the segregation of Co related to Fe and the effect of annealing on the properties of $BaFe_{2-x}Co_xAs_2$ crystals, are also required.

In this work, we present the growth of large single crystals of Co-doped $BaFe_{2-x}Co_xAs_2$ using self-flux method. A systematical investigation was carried out for the crystal structure, segregation behavior of Co-ions and annealing effect on the superconducting property.

2. Experimental

The electron-doped $BaFe_{2-x}Co_xAs_2$ single crystals were grown by self-flux method. The starting materials such as Ba pieces

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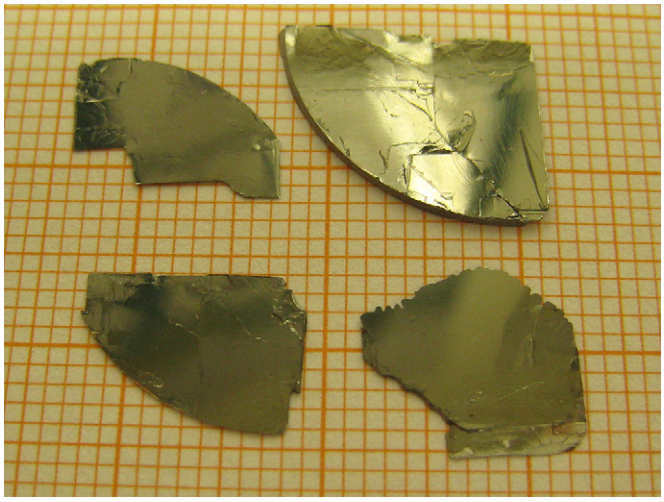

Fig. 1. As-grown optimal doped $BaFe_{1.87}Co_{0.13}As_2$ single crystals.

(Alfa Aesar, 4 N purity), Fe powders (4 N), Co powders (4 N) and As pieces (4 N) were weighted and mixed in mole ratio of Ba:Fe:Co:As=1:(5-y):y:5. The relationship $y=3.2x$ is defined and described in Section 3.2. Based on this starting composition, the concentration of Co in the single crystals of $BaFe_{2-x}Co_xAs_2$ is expected to be approximately proportional to that in the initial melt. The whole procedure was performed in a glove box with argon atmosphere. The mixtures were placed in an Al_2O_3 crucible, and a nucleation pole with an Al_2O_3 stick of $\phi 1\times 70$ mm was introduced through the hole of crucible lid. The crucible was sealed in a quartz ampoule with 250 mbar argon atmosphere. The ampoule was loaded in a furnace and heated up to 1190 °C for 10 h, and then the furnace was cooled at an average rate of 2 °C/h, followed by decanting FeAs flux at 1090 °C for 1 h and finally cooled down to room temperature at 100 °C/h. The crystals were found to grow and gather at the bottom of the crucible. Fig. 1 shows the typical as-grown optimal doped $BaFe_{1.87}Co_{0.13}As_2$ single crystals with dimensions of $10\times 10\times 0.1$–1 mm^3. The crystal was cleaved and displayed a shiny surface with the [0 0 1] direction. The annealing treatment for the crystals was carried out in a quartz ampoule at 750 °C for 7 days in 300 mbar argon atmosphere, 10^{-5} mbar vacuum and 1 atm air, respectively.

The X-ray diffraction (XRD) measurements of crystal powders were carried out with the X-ray diffractometer (Philips PW 3710) using Cu Kα radiation. Energy dispersive X-ray spectroscopy (EDX) analyses were employed to determine the crystal composition. DC magnetization measurements were carried out using a superconducting quantum interference device-vibrating-sample magnetometer (SQUID-VSM) (Quantum Design).

3. Result and discussion

3.1. Structural characterization

The phases of the $BaFe_{2-x}Co_xAs_2$ single crystals were identified by powder XRD measurements, as shown in Fig. 2. The indexed space group of these crystals was $I_{4/mmm}$ and no obvious impurity phases were observed. Fig. 3 plots the lattice parameters derived from the program of TOPAS 2.1, which is a general profile and structure analysis software for powder diffraction data treatment (Karlsruhe, Germany, 2002). Compared to the undoped $BaFe_2As_2$ with $a=3.9635(5)$ Å, $c=13.022(2)$ Å, the a-axis lattice constants of the $BaFe_{2-x}Co_xAs_2$ exhibit nearly invariant within

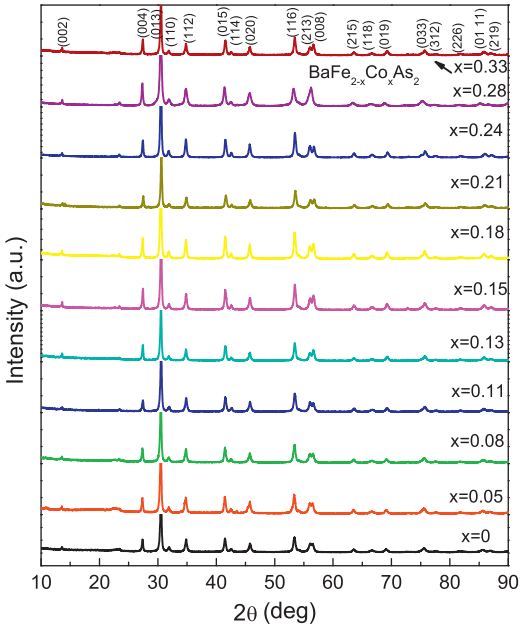

Fig. 2. XRD patterns of $BaFe_{2-x}Co_xAs_2$ single crystals.

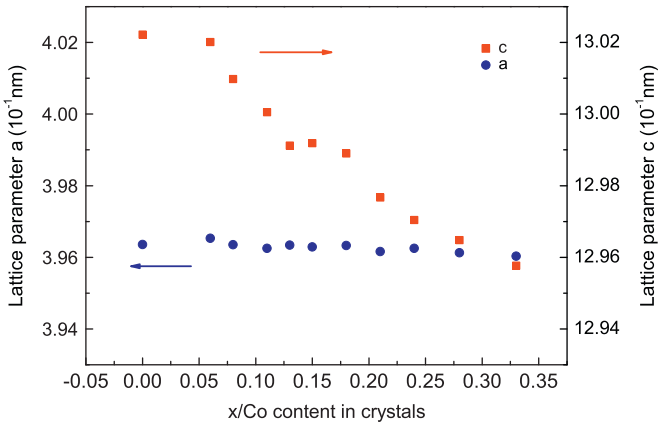

Fig. 3. Variation of lattice parameters of single crystals as a function of Co concentration x in $BaFe_{2-x}Co_xAs_2$.

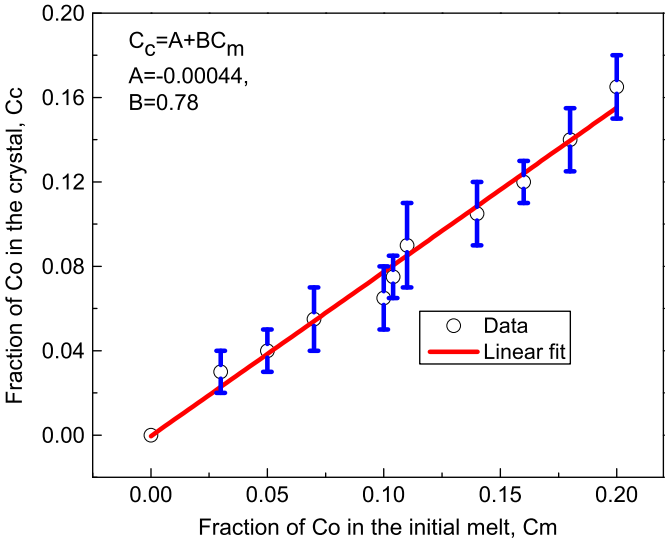

Fig. 4. Plot of Co concentrations as a fraction of total Fe and Co atoms present in crystals versus those in the melt.