Single crystal growth and characterizations of iron arsenide superconductor $BaFe_{2-x}Ni_xAs_2$ $(0.0 \leq x \leq 0.12)$*

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A series of big single crystals of $BaFe_{2-x}Ni_xAs_2$ have been prepared by the FeAs self-flux method, with nominal nickel doping $x = 0$–0.12. The dimensions of the cleaved crystals are over 10 mm along ab plane and ~ 2 mm in maximum along the c direction. The measurements of x-ray diffraction, electrical resistance and magnetic property are carried out on the crystals. For the undoped parent compound $BaFe_2As_2$, both resistance and magnetization data display an anomaly associated with spin density wave and/or structural phase transition, with the transition temperatures at ~ 138 K. For Ni-doped $BaFe_{2-x}Ni_xAs_2$ crystals, the superconducting critical temperature T_c ranges from 4.3 K for $x = 0.06$ sample to 20 K for the optimally doped $x = 0.10$ crystal.

Keywords: FeAs self-flux crystal growth, $BaFe_{2-x}Ni_xAs_2$ single crystals, superconductivity

PACC: 6150C, 7430C, 7430F, 7470

1. Introduction

Since the discovery of $La[O_{1-x}F_x]FeAs$ superconductor with superconducting critical temperature T_c near 26 K,[1] superconductivity in this new iron pnictide family has attracted tremendous attention in the condensed matter community. Soon after that, the superconducting transition temperature was promoted to 55 K by substituting Sm for La.[2] Similar to the cuprates, such iron-based compounds adopt layered structure and Fe–As layer is thought to be responsible for superconductivity.

Recently, much attention has been paid to the $BaFe_2As_2$ (Ba-122) system and colourful results obtained. For example, a structural and magnetic phase transition occurs at $\sim$ 140 K in undoped $BaFe_2As_2$,[3] the maximum T_c of $Ba_{1-x}K_xFe_2As_2$ is 38 K near $x = 0.4$,[4] the co-existence of antiferromagnetic and superconductivity has been found in $BaFe_{2-x}Co_xAs_2$,[5] and the neutron scattering studies illustrate that electron-doping in the $BaFe_2As_2$ system plays an important role in transforming three-dimensional (3D) anisotropic spin waves into two-dimensional (2D) spin excitations.[6] Electron pairing in Fe-based superconductors is deduced to be relative to magnetic excitations.[7] The most interesting point is that sizable crystal growth is possible for this Ba-122 system, in comparison with other members in the iron arsenide superconductor family. There is no doubt that preparing serial samples, especially single crystals of $BaFe_{2-x}Ni_xAs_2$, is indispensable for giving an insight into the mechanism of superconductivity. In particular, crystal samples of large quantity and size are highly demanded by some important experiments such as neutron scattering. In this paper, we report the work on the growth of a series of sizable $BaFe_{2-x}Ni_xAs_2$ crystals, as well as their property characterizations by x-ray diffraction (XRD), resistance and magnetic measurements.

2. Experimental

Single crystals with nominal formula $BaFe_{2-x}Ni_xAs_2$ $(0 \leq x \leq 0.12)$ were prepared by the FeAs self-flux method.[8] The starting materials were commercially available Ba pieces (purity 99.2%),

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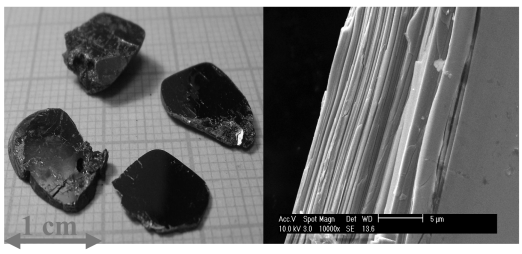
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Fe powders (99.5%) and As pieces (99.999%). First, FeAs binary was synthesized by reacting the mixture of Fe and As powders in an evacuated quartz tube at 900 °C for 12 hours; and NiAs was prepared by heating Ni and As powders in an evacuated quartz tube at 800 °C for 12 hours. Second, Ba pieces and ground FeAs/NiAs powders were mixed together at a ratio of Ba:$[(FeAs)_{2-x}(NiAs)_x]/2$=1:5. In order to avoid the reaction between the chemicals and the quartz tube, the mixture was loaded in an alumina crucible. This process was done in a glove box filled with high purity protective argon atmosphere. Then, the crucible was sealed in an evacuated quartz tube. Third, the quartz tube filled with all the starting materials was placed in a vertical furnace and was slowly heated up to 700 °C dwelled for 4 hours, and then heated to 1120–1190 °C for 10 hours followed by slowly cooling down to 850 °C−900 °C at a rate of 2 °C/h. Finally, the sample was cooled down to room temperature slowly. Pieces of $BaFe_{2-x}Ni_xAs_2$ single crystals were obtained by cleaving the as-grown bulks.

The x-ray diffraction analysis was made on an MXP18A-HF diffractometer using Cu–Kα radiation, with 2θ ranging from 10° to 80° and a 2θ scanning step of 0.01°. The electrical resistance was measured by a standard four-probe method. The magnetic measurements were carried out on a Quantum Design MPMS XL-1 system.

3. Results and discussion

Figure 1(a) is a photo of obtained single crystals. The dimensions of the cleaved crystals are over 10 mm along *ab* plane and ∼ 2 mm in maximum along the *c* direction. The layered structure feature can be clearly seen from the SEM image as shown in Fig. 1(b).



(a) (b)

Fig. 1. (a) A photograph of cleaved crystals of $BaFe_{1.9}Ni_{0.1}As_2$; (b) The SEM picture of $BaFe_{1.9}Ni_{0.1}As_2$ crystal.

The XRD patterns given in Fig. 2 are measured on the *ab*-plane of the crystals. All the diffraction peaks are sharp and no impurity diffraction is observed. The inset presents the nominal doping dependence of calculated *c*-axis lattice parameter of the $BaFe_{2-x}Ni_xAs_2$ crystals with x = 0–0.12. In consistence with the previous report,[9] the *c*-axis gradually decreases with increased Ni doping.

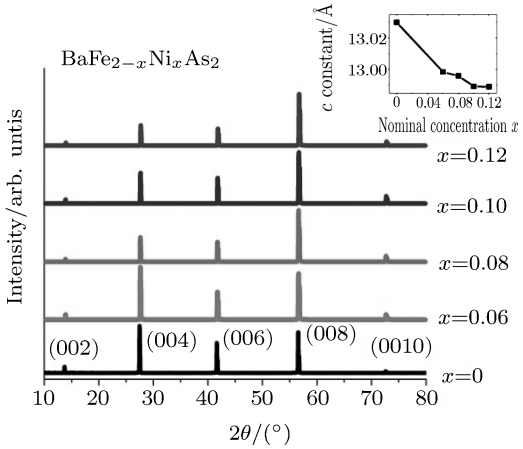


Fig. 2. The *ab* plane x-ray diffraction patterns at room temperature for $BaFe_{2-x}Ni_xAs_2$ single crystals. The inset shows the nominal doping dependence of *c*-axis lattice parameter (1 Å=0.1 nm).

Plotted in Fig. 3 is DC magnetization curves for the undoped $BaFe_2As_2$ single crystal under a field of 1 Tesla along both *ab*-plane and the *c* direction. An abrupt drop in the magnetic moment at ∼ 138 K is a signature of a spin density wave (SDW) and/or structural transition as pointed out previously.[3,8,10,]

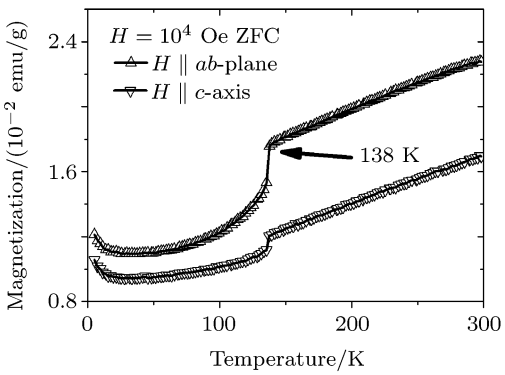


Fig. 3. Temperature dependence of DC magnetization under the field H = 1 Tesla for undoped parent compound $BaFe_2As_2$ along both *ab*-plane and *c* direction. The abrupt drop at 138 K is related to SDW/structure phase transition.

It is clear that there is a significant anisotropy in the magnetization throughout the entire temperature

range from 4.9 K to 300 K. As the temperature decreases from 300 K, the magnetic moment has a linear temperature dependence until the SDW transition sets in at $\sim$ 138 K. The magnetic measurements for Ni-doped $BaFe_{2-x}Ni_xAs_2$ crystals were performed under a magnetic field of 1 Oe (1 Oe=1 Gb/cm) in zero field cooling (ZFC) process. The data are shown in Fig. 4. As expected, the doping dependence of T_c exhibits the highest T_c of $\sim$ 20 K at optimal doping level of $x = 0.10$ as shown in the inset. Moreover, the sharp superconducting transition (ΔT = 0.8–1.3 K, except for $x = 0.06$) displayed in the magnetic curves suggests the good quality of our crystals.

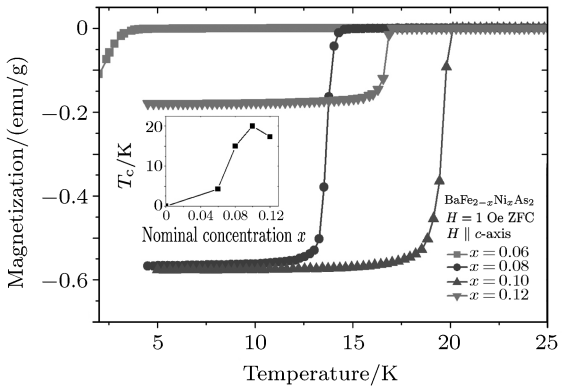


Fig. 4. The temperature dependence of magnetization for $BaFe_{2-x}Ni_xAs_2$ crystals. The inset shows the nominal Ni doping dependence of superconducting critical temperature.

Figure 5 plots the *ab*-plane electrical resistance data of the crystals as a function of temperature. The T_c values obtained from the resistance measurements are close to the ones from the magnetic data. The inset is the result for undoped $BaFe_2As_2$ sample, with a remarkable drop in the resistance curve which is related to the SDW/structure transition as observed in magnetic measurement (see Fig. 3). For the underdoped $BaFe_{2-x}Ni_xAs_2$ crystals, their resistance curves exhibit an upturned behaviour started at $\sim$ 81 K for $x = 0.06$ and $\sim$ 57 K for $x = 0.08$. A similar upturn was reported to occur at 91–97 K for $x = 0.04$ $BaFe_{2-x}Ni_xAs_2$ crystal, being attributed to magnetic/structural phase transition.[6] Given the fact that undoped parent $BaFe_2As_2$ displays the anomaly at $\sim$ 138 K, it can be suggested that magnetic/structural phase transition is suppressed to lower temperatures as the carriers were introduced into the FeAs layer due to the competition between antiferromagnetic long range order and superconductivity. Similar phenomena were also observed in Co- and K-doped $BaFe_2As_2$ systems.[11–14] For the optimal- and over-doped $BaFe_{2-x}Ni_xAs_2$ such anomaly disappears. The superconducting transition of slightly doped $BaFe_{1.94}Ni_{0.06}As_2$ crystal is rather broad according to both resistance and magnetization measurements, maybe there exists stronger inhomogeneity in the crystal.

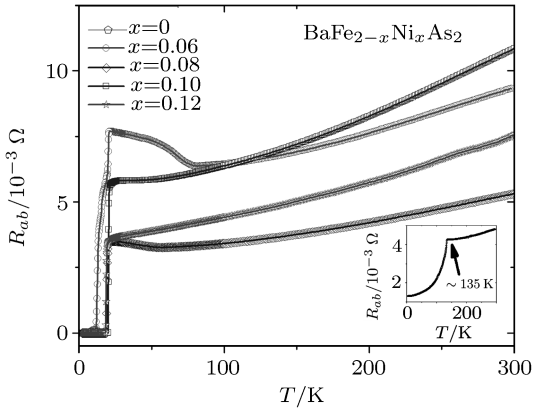


Fig. 5. The temperature dependence of *ab*-plane resistance for $BaFe_{2-x}Ni_xAs_2$ crystal. The inset is the R_{ab}–T data for undoped parent compound $BaFe_2As_2$, an anomaly associated with SDW/structure phase transition is also observed.

4. Summary

We have successfully grown a series of large $BaFe_{2-x}Ni_xAs_2$ single crystals with Ni doping $x = 0 - 0.12$ using the FeAs self-flux method. The grown crystals are of good quality, the dimensions of the crystals after cleavage are over 10 mm along *ab* plane and $\sim$ 2 mm in maximum along the *c* direction. The physical properties of the crystal samples are characterized using x-ray diffraction, electrical resistance and magnetic measurements. The results are consistent with previous reports. Also the doping dependence of the anomaly observed in resistance and magnetic experiments is discussed.

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