Structural and physical properties of undoped and nickel-doped $BaFe_{2-x}Ni_xAs_2$ ($x = 0$, 0.04) single crystals*

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Single crystals of undoped and nickel-doped $BaFe_{2-x}Ni_xAs_2$ ($x = 0$, 0.04) have been grown by FeAs self-flux method. The maximum dimension of the crystal is as large as ~ 1 cm along the ab plane. The crystalline topography of a cleaved crystal surface is examined by scanning electron microscope (SEM). By x-ray powder diffraction (XRD) experiments using pure silicon as an internal standard, precise unit cell parameters (tetragonal at room temperature) are determined: $a = 3.9606(4)$ Å (1 Å=0.1 nm), $c = 13.015(2)$ Å for $BaFe_{1.96}Ni_{0.04}As_2$ and $a = 3.9590(5)$ Å, $c = 13.024(1)$ Å for $BaFe_2As_2$. DC magnetization and transport measurements are performed to check superconducting transition ($T_c = 15$ K for $x = 0.04$) and other subtle anomalies. For $BaFe_{1.96}Ni_{0.04}As_2$ crystal, the resistance curve at normal state shows two distinct anomalies associated with spin and structure transitions, and its magnetization data above ~ 91 K exhibit a linear temperature dependence due to spin density wave (SDW) instability.

Keywords: $BaFe_{2-x}Ni_xAs_2$, single crystal, superconductivity, x-ray diffraction

PACC: 6110F, 7430C, 7430F, 7470

1. Introduction

Shortly after the discovery of the novel iron-based superconductor $La[O_{1-x}F_x]FeAs$ (so-called "1111" system) with $T_c \sim 26$ K,[1] a lot of attempts have been made to search for new iron-based superconductors and to understand the fundamental physical mechanism.[2−5] Now, it is well known that the crystal structure of this novel superconductor is analogous to that in copper-based high temperature superconductors, with FeAs plane as a charge carriers layer in place of CuO plane.[6−8] The early discovered "1111" system has single FeAs conductive layer. Before long ternary iron pnictide $BaFe_2As_2$ with the tetragonal (S.G.: $I4/mmm$) $ThCr_2Si_2$-type structure and double FeAs layers was proposed to be a parent compound for superconductor.[9] It has been found that $BaFe_2As_2$ compound becomes superconducting by K/Co/Ni-doping into it.[10−12]

At present, the superconductivity/magnetic phase diagram of iron-based superconductors has been widely studied.[13−16] Especially, it is found that magnetic state and superconductivity can coexist near the underdoped side of the phase diagram. For example, such coexistence region in $SmFeAsO_{1-x}F_x$ with $0.1 \leq x \leq 0.15$,[17] $Ba_{1-x}K_xFeAs_2$ with $0.2 \leq x < 0.4$,[18] and Co-doped $Ba(Fe_{1-x}Co_x)_2As_2$ with $x = 0.047$[19] can be clearly seen. Theoretically, it was proposed that the coexistence of magnetic state and superconductivity is possible and some experimental observations can be well explained.[20] So the carrier concentration plays an important role in the physical properties of this new class of iron-based superconductors. For this reason, we have tried and succeeded in growing a series of Ni-doped $BaFe_{2-x}Ni_xAs_2$ single crystals. The result of our collaborator P. C. Dai *et al.*[21] suggests that reduced dimensionality in spin excitations of iron arsenides is important for the separated structural/magnetic phase transition and the occurrence of high-T_c superconductivity in these superconducting materials. In this paper we report structural and physical properties of the lightly doped $BaFe_{1.96}Ni_{0.04}As_2$ and parent $BaFe_2As_2$. Especially their precise unit cell parameters are determined and the observations of linear temperature dependence of

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magnetization as well as distinct anomalies associated with spin and structure transitions in resistance data are discussed.

2. Experiments and results

Single crystals of $BaFe_{2-x}Ni_xAs_2$ (with nominal composition $x = 0$, 0.04) were grown using conventional high temperature solution technique with FeAs as self-flux.[22] Detailed description of our crystal growth procedure can be found elsewhere.[23] Composition analyses by ICP–AES indicate Ba:Fe:As=0.80:1.96:2 for nominal $BaFe_2As_2$ crystal and Ba:Fe:Ni:As= 0.82:1.9:0.04:2 for nominal $BaFe_{1.96}Ni_{0.04}As_2$. We use the nominal chemical formula in this paper for simplicity.

Figure 1(a) is a photo of grown $BaFe_{1.96}Ni_{0.04}As_2$ single crystal with the maximum dimension of ~ 1 cm. The layered structure feature can be clearly seen from the scanning electron microscopy (SEM) image shown in Fig. 1(b). The neutron diffraction rocking curve experiments on this crystal indicate the in-plane and out-of-plane mosaic is 1.74° and 2.20° (full width at half maximum), respectively.[21]

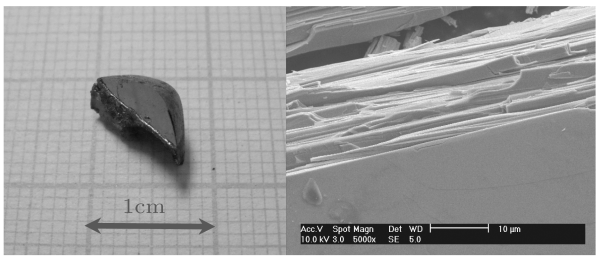


Fig. 1. (a) The photograph of cleaved crystal of the $BaFe_{1.96}Ni_{0.04}As_2$. (b) The SEM picture of $BaFe_{1.96}Ni_{0.04}As_2$ crystal where the layered structure feature can be clearly seen.

The magnetization measurement is carried out on a Quantum Design MPMS XL-1 system under a field of 1 and 1000 Oe (1 Oe=79.5775 A/m) parallel to *ab* plane in both zero-field cooling and field cooling modes. Figure 2 shows the enlarged plot of the temperature dependence of magnetization under 1000 Oe. The inset exhibits the whole profile of the data. The superconducting transition temperature determined from the ZFC curve under a field of 1 Oe is $T_c \sim 15$ K. From Fig. 2 we can see an increasing linear behaviour of magnetization with temperature from about 91 K up to room temperature. Although the linear regime depends on dopants, this linear temperature dependence of susceptibility is universal in iron-based superconductors.[22,24–27] Its origin has been interpreted as resulted from SDW instability within the frame of itinerant electron picture or by considering the possible coexistence and coupling of itinerant electrons with local moments.[28–30]

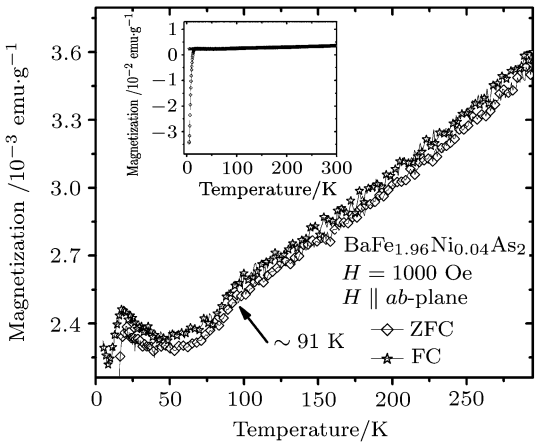


Fig. 2. An enlarged plot of temperature dependence of magnetization for $BaFe_{1.96}Ni_{0.04}As_2$ single crystal. The inset shows the whole profile of the data.

The electrical resistance in *ab* plane for $BaFe_{1.96}Ni_{0.04}As_2$ single crystal is measured by a standard four-probe method. Figure 3 shows the temperature dependence of electrical resistance. Two anomalies at $T_N \sim 91$ K and $T_S \sim 97$ K can be clearly seen, which are associated with spin and structure transitions, respectively, as has been discussed based on neutron scattering experiment.[21] One single antiferromagnetic/structural transition at ~ 135 K in undoped parent $BaFe_2As_2$ (see the inset) splits into two separate anomalies with the introduction of carriers. This behaviour is very similar to that in $Ba(Fe_{1-x}Co_x)_2As_2$.[31,32]

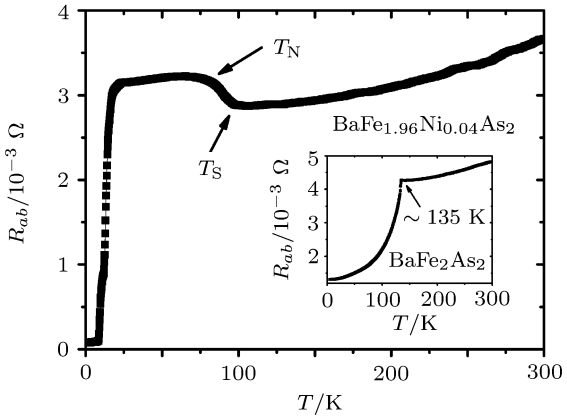


Fig. 3. Temperature dependence of electrical resistance in *ab* plane of $BaFe_{1.96}Ni_{0.04}As_2$ single crystal. The inset shows the *ab* plane data of $BaFe_2As_2$ crystal.

The XRD experiments of the single crystals $BaFe_{2-x}Ni_xAs_2$ ($x = 0$, 0.04) are performed on a diffractometer (MXP18A-HF) using Cu–Kα radiation. The data are collected at room temperature in the 2θ range from 10° to 92° by step scanning with a step of 0.02° and a count time of 2 sec/step. First the diffraction patterns are corrected for Kα_2 component in Cu–Kα spectrum by software Powder X.[33] It is noted that we use ground single crystals for powder diffraction experiments with Si powder (purity 99.999% from Alfa Aesar) added as an internal standard. The systematic error of the diffraction data is then corrected using parabolic least-squares refinement in reference to the standard Si peak positions (JCPDS No. 27-1402). In the data processing, we do not take into account the Si peaks overlapping with those of the main phase. Figures 4(a) and 4(b) plot the XRD patterns of powder $BaFe_{1.96}Ni_{0.04}As_2$ and $BaFe_2As_2$. The insets show the diffraction patterns of single crystal pieces cleaved from as-grown samples. Only (0 0 L) diffraction peaks are observed, it suggests that the crystallographic c-axis is perpendicular to the crystal plate. The preliminary cell parameters are obtained using program Treor90;[34] then they are least-squares refined using program Pirum.[35] The final refined tetragonal lattice parameters are: $a = 3.9606(4)$ Å, $c = 13.015(2)$ Å for $BaFe_{1.96}Ni_{0.04}As_2$ and $a = 3.9590(5)$ Å, $c = 13.024(1)$ Å for $BaFe_2As_2$. The results of the indexation, hkls and d values, are given in Table 1, with all peaks conforming to the reflection condition $h + k + l = 2n$. The data show that c-axis decreases while a-axis increases slightly when 4% Ni substitutes for Fe in the parent $BaFe_2As_2$.

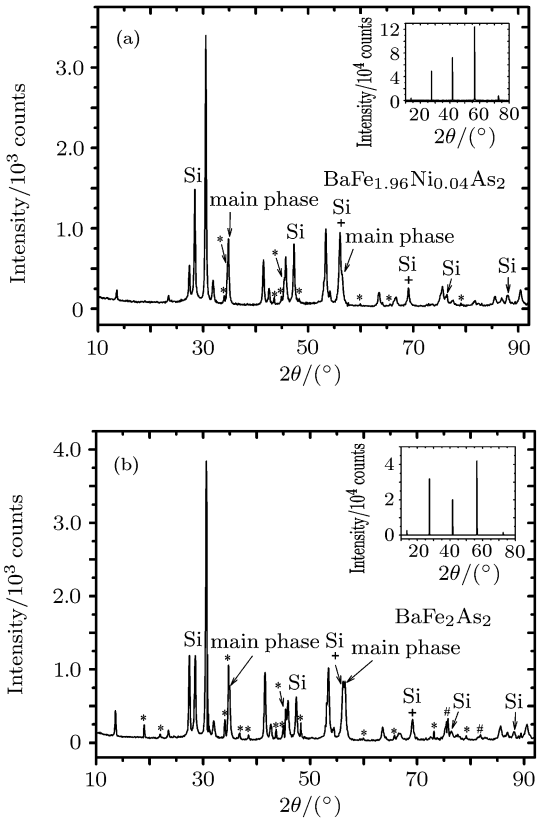


Fig. 4. The x-ray powder diffraction patterns for $BaFe_{1.96}Ni_{0.04}As_2$ (a) and $BaFe_2As_2$ (b). The insets show the single crystal diffraction patterns on ab plane (only 00L diffraction peaks are observed). Note: Si powder was added as an internal standard for powder XRD. Peaks marked with "∗" are contributed mainly from impurity FeAs (in excess as flux in crystal growth). Symbols "#" indicate the peaks of main phase overlapping with that of impurity phase. Peaks of main phase overlapping with Si standard are marked by "+". For clarity, some partially overlapped main phase peaks are also specially indicated.

Table 1(a). The indexation results at room temperature for $BaFe_{1.96}Ni_{0.04}As_2$ (a) and $BaFe_2As_2$ (b). Symbols "+" indicate the d values overlapping with those of Si standard (see Fig. 4).

$BaFe_{1.96}Ni_{0.04}As_2$				
lattice parameters/Å			$a = b = 3.9606(4)$	
			$c = 13.015(2)$	
h	k	l	d-obs./Å	I/I_0
0	0	2	6.5064	7
1	0	1	3.7946	5
0	0	4	3.2523	16
1	0	3	2.9252	100
1	1	0	2.8013	10
1	1	2	2.5727	26
1	0	5	2.1738	18
1	1	4	2.1215	8
2	0	0	1.9810	19
1	1	6	1.7150	29
2	0	4	1.6921	7
2	1	3	1.6388^+	28
0	0	8	1.6273	13
2	1	5	1.4639	6
2	2	0	1.4011	4
1	0	9	1.3581^+	8
3	0	3	1.2633	5
2	0	8	1.2573	8
3	1	2	1.2293	3
1	1	10	1.1802	3
2	2	6	1.1764	3
3	1	4	1.1687	2
1	0	11	1.1340	5
2	1	9	1.1201	4
0	0	12	1.0845	7

Table 1(b).

$BaFe_2As_2$				
lattice parameters/Å			$a = b = 3.9590(5)$	
			$c = 13.024(1)$	
h	k	l	d-obs./Å	I/I_0
0	0	2	6.5316	0.5
1	0	1	3.7930	5
0	0	4	3.2568	31
1	0	3	2.9264	100
1	1	0	2.8012	8
1	1	2	2.5707	28
1	0	5	2.1744	25
1	1	4	2.1211	6
2	0	0	1.9799	15
1	1	6	1.7152	7
2	0	4	1.6929	5
1	0	7	1.6850	6
2	1	3	1.6382^+	22
0	0	8	1.6284	22
2	1	5	1.4635	6
2	2	0	1.4002	3
1	0	9	1.3585^+	8
3	0	3	1.2627	6
3	1	2	1.2298	3
1	1	10	1.1814	2
2	2	6	1.1762	3
3	1	4	1.1686	2
1	0	11	1.1343	6
2	1	9	1.1205	4
0	0	12	1.0855	6

3. Summary

The structural and physical properties of single crystals $BaFe_{2-x}Ni_xAs_2$ (x = 0, 0.04) are characterized by various methods including XRD, magnetic and transport measurements. The precise room temperature tetragonal unit cell parameters are determined by powder XRD analysis using silicon as an internal standard, with a = 3.9606(4) Å, c = 13.015(2) Å for $BaFe_{1.96}Ni_{0.04}As_2$ and a = 3.9590(5) Å, c = 13.024(1) Å for $BaFe_2As_2$, and the indexation results are presented. We find that at normal state the *ab* plane resistance data of $BaFe_{1.96}Ni_{0.04}As_2$ displays two distinct anomalies associated with spin and structural transition, and that the temperature dependence of magnetization shows a linear behaviour from 91 K up to room temperature, indicating a common SDW fluctuation in the vicinity of the boundary between parent poor metal and superconductor in iron-based materials.

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