Journal of Alloys and Compounds 745 (2018) 460–466

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Cr doping effects on structure and superconductivity of $Ba_2Ti_2Fe_2As_4O$

C.C. Hsieh [a], C. Ke [a, **], D.J. Zhou [b], C.H. Cheng [a, c], H. Zhang [d], Y. Zhao [a, b, *]

[a] Key Laboratory of Levitation Technology and Maglev (Ministry of Education of China), Superconductivity R&D Center (SRDC), Mail Stop 165#, Southwest Jiaotong University, Chengdu, Sichuan 610031, China
[b] College of Physics and Energy, Fujian Normal University, Fuzhou, Fujian, 350117, China
[c] School of Materials Science and Engineering, University of New South Wales, Sydney, 2052, NSW, Australia
[d] School of Physics, Peking University, Beijing 100871 China

ARTICLE INFO

Article history:
Received 23 August 2017
Received in revised form
12 February 2018
Accepted 13 February 2018
Available online 23 February 2018

Keywords:
Transition metal alloy and compound
Solid state reaction
Iron-based pnictide
Electrical resistivity
Magnetic magnetization
Superconductivity

ABSTRACT

Chemical doping effects on structure and superconductivity were studied by introducing Cr at Fe sites in $Ba_2Ti_2Fe_2As_4O$, where Cr^{2+} can play dual role as impurities and hole dopants. $Ba_2Ti_2(Fe_{1-x}Cr_x)_2As_4O$ ($0 \leq x \leq 8\%$) compounds are synthesized by a solid-state reaction and characterized with x-ray diffraction, electric resistivity and magnetization measurements. It is observed that the Cr dopants induce lattice expansion and local structure distortion, and significantly suppress the superconducting transition temperature T_c. In the meantime, the residual resistivity is found steadily increased with Cr doping. Comprehensive analyses show that T_c suppression is strongly correlated with the impurity-induced scattering to electrons, which can be fitted with the Abrikosov-Gor'kov-like scaling function.

1. Introduction

After the discovery of high-T_c superconductivity in the iron-based pnictide [1], many new iron-based superconductors have been successively discovered. The crystallographic phase of them can be classified as FeSe (11-phase) [2], LiFeAs (111-phase) [3], $BaFe_2As_2$ (122-phase) [4], $K_xFe_{2-y}Se_2$ (122^*-phase) [5], and LaFeAsO (1111-phase) [1], where the abbreviations in numbers correspond to their chemical compositions. Recently, a new iron-based pnictide superconductor $Ba_2Ti_2Fe_2As_4O$ with T_c~21 K was discovered by Sun et al. [6]. Crystallographically, $Ba_2Ti_2Fe_2As_4O$ is the intergrowth consisted of $BaFe_2As_2$ (122-phase) and $BaTi_2As_2O$ (1221-phase) along the *c*-axis direction, and is denoted as 22241-phase hereinafter. As we know, the 122-phase is a superconductor after doping with carriers [4,7], but the 1221-phase is a spin density wave material [8]. This unique feature makes the 22241-phase to exhibit some interesting phenomena, e.g., the coexistence of superconductivity and spin density wave as revealed by Raman scattering [9], optical study [10], and inelastic neutron scattering [11]. Different from most other iron-based pnictide superconductors, the 22241-phase is a so-called self-hole-doping system in which the electrons are transferred from the FeAs layers to the Ti_2As_2 layers, leaving a self-hole-doped state in the FeAs layers [12]. This means the FeAs layers remain responsible for the superconductivity whereas the Ti_2As_2 layers take the responsibility for the density wave transition with $T^* \approx 125$ K in the 22241-phase [1,10].

Chemical doping is a common way of introducing carriers into the high-T_c superconductors [1,4,7] to manipulate their long-range antiferromagnetic order and/or superconductivity. For the hole-doped 122-phase superconductors by partially replacing Ba with K, a superconducting transition temperature of T_c as high as 38 K can be achieved, as in the $Ba_{0.6}K_{0.4}Fe_2As_2$ [4], whereas the T_c is only around 21.5 K for the self-hole-doped 22241-phase superconductor [6]. The mechanism behind the phenomena is unclear to date. One of the possible reasons is that the carrier concentration has not been optimized in this self-hole-doped 22241-phase system. Therefore, it is interesting to clarify the possible mechanisms for this and explore ways of enhancing the superconductivity of the 22241-phase system. In addition, chemical dopants are also a source of impurities. The study of impurity effects is very important

---

* Corresponding author. Superconductivity R&D Center (SRDC) Southwest Jiaotong University Chengdu, Sichuan 610031, China.
** Corresponding author.
E-mail addresses: cke@swjtu.edu.cn (C. Ke), yzhao@swjtu.edu.cn, zhaoyong@fjnu.edu.cn (Y. Zhao).

https://doi.org/10.1016/j.jallcom.2018.02.175
0925-8388/

to the understanding of superconductivity, which may provide insights on the underlying pairing symmetry and superconducting mechanism. Usually, the impurity-induced suppression of superconductivity provides some early hint of the unconventional pairing state [13]. The conventional s-wave superconductors are very sensitive to magnetic impurities while robust to nonmagnetic impurities, which could be explained by Anderson's theory [14]. The superconductivity of high-T_c cuprates with a d-wave pairing symmetry is fragile to both magnetic and nonmagnetic impurities [15]. The iron-based superconductors exhibit a quite complicated pairing state [16–21] which also shows little tolerance to impurities. To date, many researches have been performed on the impurity-induced suppression of superconductivity in the iron-based superconductors [22–26], however, further studies are clearly desired to elucidate the existing controversies in the previous studies. The newly discovered 22241-phase superconductor does offer a new and unique system for such a purpose.

The chemical doping effects on superconductivity have not yet been investigated intensively for the 22241-phase system to date. Similar to the 122-phase system, there are at least two ways to dope holes into the FeAs layers of this intergrowth system: (1) by partially substituting Ba with K; and (2) by directly doping hole dopants in the FeAs layer. However, for studying the impurity-induced suppression on superconductivity, a more efficient way is to directly dope the FeAs layers where the superconductivity occurs. In this paper, we partially substitute Cr for Fe in the 22241-phase superconductor since Cr^{2+} can play dual roles as impurities and hole dopants when doped in the Fe sites. A series of $Ba_2Ti_2(Fe_{1-x}Cr_x)_2As_4O$ samples were synthesized using a solid-state reaction method, and were characterized with X-ray diffraction (XRD), DC resistivity and magnetization measurements. Structure refinement analysis reveals that the local structures of the unit cell of the 22241-phase are slightly manipulated by doping Cr, leading to a minute decrease of the As-Fe-As angle and a moderate increase of the As-height above Fe plane. However, the superconductivity of the 22241-phase is drastically depressed. The experimental data can be fitted with the Abrikosov-Gor'kov-like scaling theory, which indicates that the impurity-induced pair-breaking effect is a possible mechanism for the suppression of superconductivity induced by doping Cr.

2. Experimental

Polycrystalline samples with a nominal composition of $Ba_2Ti_2(Fe_{1-x}Cr_x)_2As_4O$ ($x = 0$, 1%, 2%, 3%, 4%, 5%, 6%, and 8%) were synthesized by a solid-state reaction method. The preparation procedures are similar to what were described in Ref. [6]. Quality raw materials of Ba, Ti, Fe, Cr, As, TiO_2 and CrO_3 (≧99.9%, Alfa Aesar) were precisely weighed according to the stoichiometric ratio, well mixed and then sealed in an evacuated quartz ampule. All these procedures except for the ampule sealing were performed in a glove box filled with high-purity argon. The samples were slowly heated to 900 °C and kept at this temperature for 1 day, and then cooled to room temperature in the furnace. After being reground and pressed into pellets in a glove box filled with high-purity argon, the samples were sintered at 1050 °C in a vacuum for 3 days, and then cooled to room temperature in the furnace. Finally, all these samples were annealed at 500 °C for 2days in a vacuum.

The crystal structures of $Ba_2Ti_2(Fe_{1-x}Cr_x)_2As_4O$ were characterized by powder X-ray diffraction using a PANalytical diffractometer (Empyrean Series 2) with Cu Kα1 radiation in ambient condition. The XRD data were collected at room temperature and detailed structural were analyses by Rietveld refinements. The “goodness of fit” parameter was determined to be less than 2, demonstrating good reliability of the crystal structure. The microstructural and compositional analyses for the samples were studied using scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometry (EDX) instrument.

Standard 4-probe method was used to measure the electrical resistivity between 2 and 300 K using a Quantum Design PPMS-9. The testing current is 0.1 mA. The sample for resistivity measurement was shaped to a typical dimension of 4.0*1.5*1.0 mm^3. DC magnetic susceptibility was measured on a Quantum Design MPMS (MPMS-7) under a low field of 10 Oe. The T_c value was determined according to the onset transition temperature on the $M(T)$ curve.

3. Results and discussion

The powder XRD patterns are shown in Fig. 1(a), for two representative samples with $x = 0$, 4%, and 6% along with the Rietveld fits. The refinements were performed using the GSAS program with the pseudo-Voigt function as the peak profiles. It is evident from the difference plot shown in the figures that the fits are very good. Only the reflections whose index (h k l) satisfies $h + k + l =$ an even number were observed. This indicates that $Ba_2Ti_2(Fe_{1-x}Cr_x)_2As_4O$ possesses a body-centered lattice indexed with the space group $I4/mmm$, same as that reported in Ref. [6]. The typical values of the lattice constants a and c are around 0.403 nm and 2.73 nm, respectively. A long c-axis of the unit cell with $c \approx 2.73$ nm implies a layered structure, which is the intergrowth of $Ba(Fe_{1-x}Cr_x)_2As_2$ and $BaTi_2As_2O$ along the c-axis. As shown in Fig. 1(b), there are two unit cells of $BaTi_2As_2O$ and one unit cell of $Ba(Fe_{1-x}Cr_x)_2As_2$ in one $Ba_2Ti_2(Fe_{1-x}Cr_x)_2As_4O$ unit cell, where the (Fe,Cr)As double-layer is split and separated by intercalating a $BaTi_2As_2O$ unit cell.

The lattice constant variations as a function of Cr doping level, obtained from the Rietveld fits of the XRD data, are presented in Fig. 2(a). It is seen that with the increase of Cr doping level, both a and c lattice constants increase. No any evidence of structural phase transitions was observed to accompany with the lattice expansion, which is very similar to the previous report for Cr-doped $BaFe_2As_2$ [27]. For a Cr ionic state of “+2”, since the ionic radius of Cr^{2+}(0.8 Å) is bigger than that of Fe^{2+}(0.74 Å), it is understandable that both lattice constants a and c increase with Cr doping. It is also interesting to note that the a lattice constant does not change significantly compared to the changes of the c lattice constant, which is similar to that observed in Cr-doped $BaFe_2As_2$ system [27]. Such a similarity hints that Cr dopant mainly occupy the Fe site rather than Ti site because Cr doping in the Ti site may cause a shrink of the unit cell [28]. Fig. 2(b) displays the variation of some local structural parameters with the Cr doping level, viz. α, the As-Fe-As bond angle, and h_{As}, the As-height. Here the As-height, h_{As}, is defined as the distance of the As from the Fe plane, as described in Ref. [29]. The α and h_{As} are presented in the enlarged schematic of FeAs layers (*cf.* the Fig. 1(b)), and their values are extracted from the results of the Rietveld refinements. It is seen that with the increase of Cr doping level, α exhibits a slight decrease but h_{As} shows a slight increase. The systematic decrease of α with the Cr doping level is associated with the increase of the As-height, which is indicative of a distortion of the $FeAs_4$ tetrahedra caused by the Cr doping.

As shown in Fig. 3, with the increase of the Cr doping level, the superconductivity temperature, T_c, is found systematically depressed instead of increased, with an average depression rate of ΔT_c/Cr-1% = −2.6 K. Here, the T_c value is determined from the onset transition temperature of the magnetic measurements in the10 Oe field using zero field cooling (ZFC) process (see the inset (a) of Fig. 3). The magnetic measurement in the field cooling (FC) process also shows superconducting transition with the same T_c value (here, we only present the result for the sample with $x = 6\%$ and 8%, see the inset (b) of Fig. 3). The undoped $Ba_2Ti_2Fe_2As_4O$ shows a