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Superconductors of $SmFe_{1-x}Co_xAsO$ synthesized by mechanical alloying

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ABSTRACT

The $SmFe_{1-x}Co_xAsO$ ($x = 0 - 0.25$) superconductors were synthesized by mechanical alloying (MA) and rapid sintering method with Co atoms doped into FeAs layers to replace the Fe sites. The phase purity and superconducting properties of the samples were characterized by X-ray diffraction, electrical resistivity, magnetic susceptibility and Hall coefficient. All the samples belong to the tetragonal ZrCuSiAs structure type with the grain size in 1–3 μm. The superconducting critical temperature T_c of $SmFe_{0.9}Co_{0.1}AsO$ was 12.5 K, and the structure/SDW transition was suppressed by Co doping. The negative Hall coefficient of $SmFe_{0.9}Co_{0.1}AsO$ indicated the electron conduction in the sample. The charge carrier density is about 2×10^{20} cm^{-3} at the temperature lower than 150 K, larger than that of SmFeAsO.

1. Introduction

Since the F-doped LaFeAsO sample with T_c up to 26 K discovered in 2008 [1], many Fe-based oxypnictide superconductors of LnFeAsO (Ln = rare earth element, Y) [2–5], AFe_2As_2 (A = alkali metal, earth-alkali metal) [6], AFeAsF (A = alkali metal) [7], and $Ca_{n+1}(Sc,Ti)_nFe_2As_2O_y$ ($n = 3,4,5$) [8], etc., have been prepared, and their doped superconducting derivative with T_c's up to 55 K [9]. Compared with the cuprate superconductors, the new type of Fe-based superconductors has a remarkable characteristic of accommodating dopants. Superconductivity is induced by doping impure elements not only into LnO (Ln = rare earth element) charge reservoir layers but also into FeAs conducting layers, such as Co into the Fe sites in the LnFeAsO compounds [10–14]. In contrast, the superconductivity of cuprate is always damaged by small amount of dopants into the CuO_2 conducting planes [15].

The phase purity and superconducting properties of LnFeAsO compounds are related to the sample preparation history [16–18]. The conventional solid-state synthesis of F-doped LnFeAsO often suffered from the fluorine loss during long sintering time (about 40 h) at high temperature (1433–1523 K) [19]. In order to overcome the disadvantage of this conventional method, the phase-pure F-doping SmFeAsO samples were sintered at 1173 K for only 2 h by employing high-energy ball-milled starting materials of SmAs and FeO [20]. As it is well known, mechanical alloying (MA) method has been successfully used in the preparations of alloys [21–23], ceramics, and some superconductors such as MgB_2 and $YBa_2Cu_3O_{7-\delta}$ [24,25]. Considering the complicated preparation of individual starting materials, the mechanical alloying may be a simpler method to form a homogeneous precursor to obtain the high-quality product. In this paper, mechanical alloying method was used to prepare the $SmFe_{1-x}Co_xAsO$ samples. The obtained samples were characterized by powder X-ray diffraction, electrical resistivity, magnetic susceptibility, and Hall coefficient measurements. The results proved that the mechanical alloying method is a rapid, reliable and effective method to synthesize $SmFe_{1-x}Co_xAsO$.

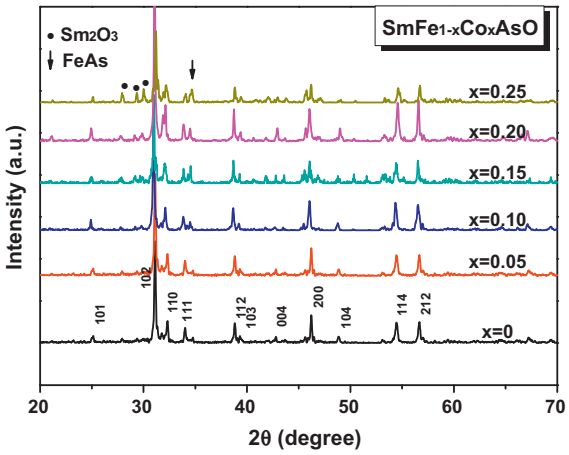

Fig. 1. Powder XRD patterns of $SmFe_{1-x}Co_xAsO$ samples.

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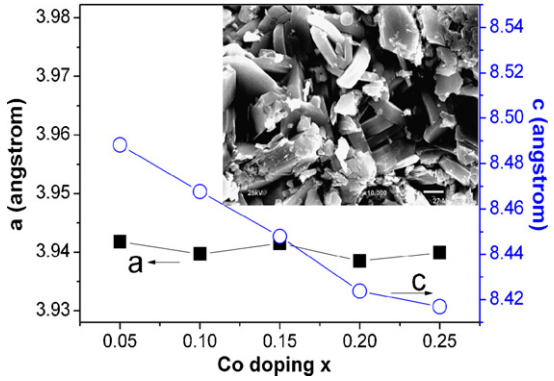

Fig. 2. Lattices parameters (a and c) as functions of Co-doping content. The inset is SEM image of $SmFe_{0.9}Co_{0.1}AsO$ sample.

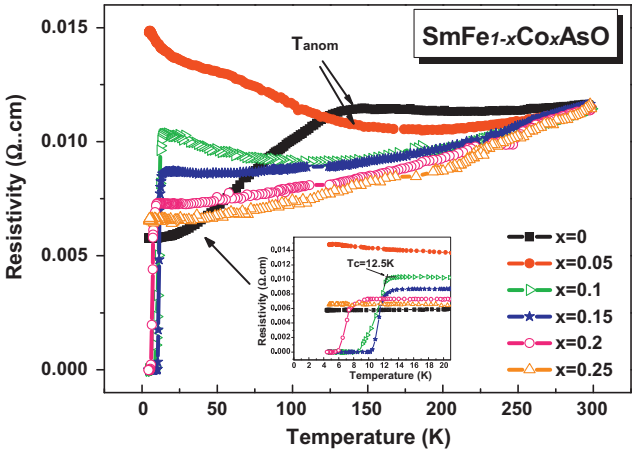

Fig. 3. Temperature dependant resistivity of $SmFe_{1-x}Co_xAsO$ samples, the inset is the enlarged view of resistivity curve near T_c.

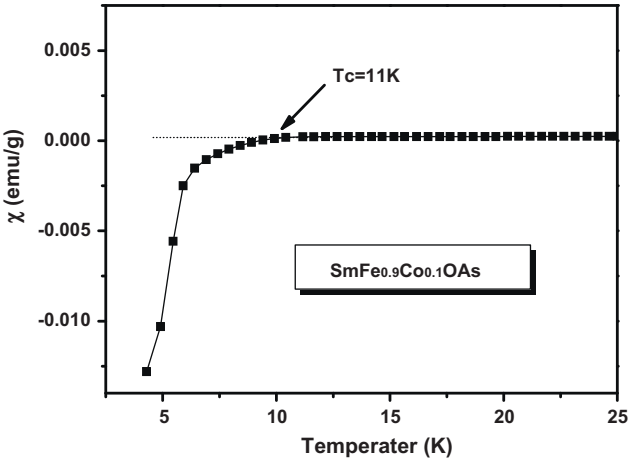

Fig. 4. Temperature dependence of the real component of the AC magnetic susceptibility for $SmFe_{0.9}Co_{0.1}AsO$ sample.

2. Experimental details

SmAs, Co_2O_3, Fe, and Fe_2O_3 were selected as starting materials and well mixed in an agate mortar according to $SmFe_{1-x}Co_xAsO$ (x = 0–0.25). The precursors were loaded into a cylindrical steel vial in diameter of 10 cm together with a batch of activation balls in diameter of 5 mm, 8 mm and 11 mm (ratio: 5:7:15). The weight ratio of milling balls to raw materials was about 8:1. The vial was evacuated, back filled with high pure argon gas and sealed with "O" ring to avoid atmospheric contamination. Mechanical alloy processing was carried out on a high-energy shaker mill (GN-2, Shenyang Xinke Instrument & Equipment Co. Ltd., China) at 480 rpm for 2 h. The resulted precursors were pressed into pellets with 10 mm in diameter and 2 mm in thickness under a uniaxial pressure of 8 MPa. The pellets were sealed, annealed at 1433 K for 3 h in evacuated silica tubes and then cooled at room temperature to obtain final samples.

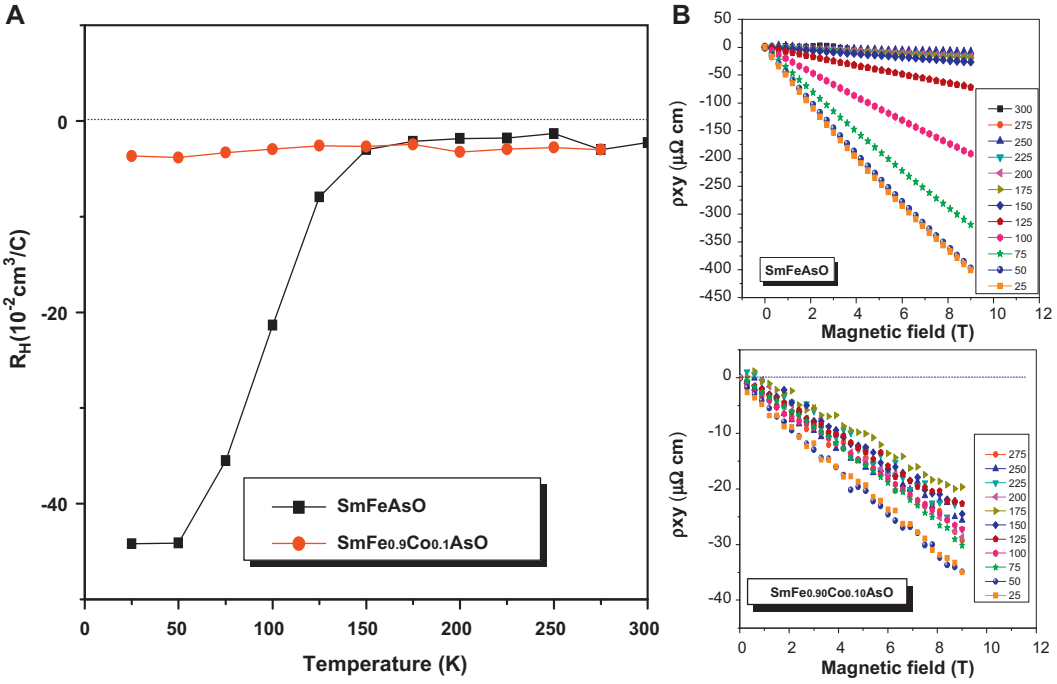

Fig. 5. (A) The temperature dependant Hall coefficient R_H of the SmFeAsO and $SmFe_{0.9}Co_{0.1}AsO$ samples, (B) Hall resistivity ρ_{xy} as a function of magnetic field at different temperatures for these two samples.

Phase purity was determined on a powder X-ray diffractometer (Bruker D8 Focus) using Cu Kα radiation (λ = 0.15418 nm). The microstructure was examined by a scanning electron microscope (SEM, JSM6390, JEOL). The electrical resistivity, magnetism and Hall resistivity were measured on Physical Property Measurement System (PPMS-9T, Quantum Design Company).

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction (XRD) patterns of the $SmFe_{1-x}Co_xAsO$ samples. The main peaks are well indexed to the ZrCuSiAs structure type with the space group of P4/nmm. Some impurities of Sm_2O_3 and FeAs were observed, especially in the $x = 0.20$ and 0.25 samples due to the Co doping limit in SmFeAsO. The lattice parameters (a and c) were refined using least squares fitting method using MDI Jade 5.0 package, as shown in Fig. 2. The value of a axis is almost unchanged, and the value of c axis decreases linearly in the doping range of $x < 0.2$, consistent with the reported values of the Co-doped LnFeAsO samples [10–12]. This linear reduction of the lattice volume upon the Co doping content (x) indicates the successful substitution of Fe^{2+} by smaller Co^{3+}. The SEM image of $SmFe_{0.9}Co_{0.1}AsO$ with typical plate-like crystal grains in 1–3 μm, as shown in the inset of Fig. 2.

The temperature dependant resistivity of the $SmFe_{1-x}Co_xAsO$ samples is displayed in Fig. 3. The parent SmFeAsO sample exhibits a clear anomalous transition near $T_{anom} = 140$ K. The resistivity of $SmFe_{1-x}Co_xAsO$ decreases with the increasing Co doping content x due to the enhanced carrier concentration. Most of the samples are superconducting except for the semiconducting $SmFe_{0.95}Co_{0.05}AsO$ and metallic $SmFe_{0.75}Co_{0.25}AsO$. The onset superconducting transition temperature T_c^{onset} are 12.5 K, 12 K and 9.5 K for $x = 0.1$, 0.15 and 0.20, respectively. The temperature dependence of the real component of the AC magnetic susceptibility for $SmFe_{0.9}Co_{0.1}AsO$ sample

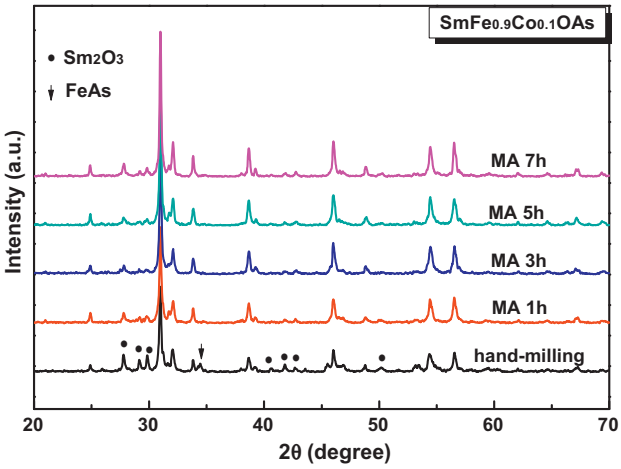

Fig. 6. Powder XRD patterns of $SmFe_{0.9}Co_{0.1}AsO$ samples sintered from raw powders mechanical alloyed for different time ranged from 0 h to 7 h.

in 10 Oe AC field amplitudes with a frequency of 333 Hz is shown in Fig. 4. The bulk superconductivity was indicated by the obvious diamagnetic transition at temperature of 11 K [26].

Fig. 5 shows the Hall resistivity and related Hall coefficient R_H of $SmFe_{0.9}Co_{0.1}AsO$ and SmFeAsO samples, and the R_H was derived from the slopes of curves of Hall resistivity ρ_{xy}. The electron conduction behavior in both of the samples was confirmed by the negative R_H. The R_H of SmFeAsO was found quickly drop below 140 K, which was supposed to be ascribed from the structure/SDW transition, and the similar phenomenon was reported in [27]. The R_H value of $SmFe_{0.9}Co_{0.1}AsO$ is much smaller than SmFeAsO below 140 K. The resulted charge carrier density of $SmFe_{0.9}Co_{0.1}AsO$ is

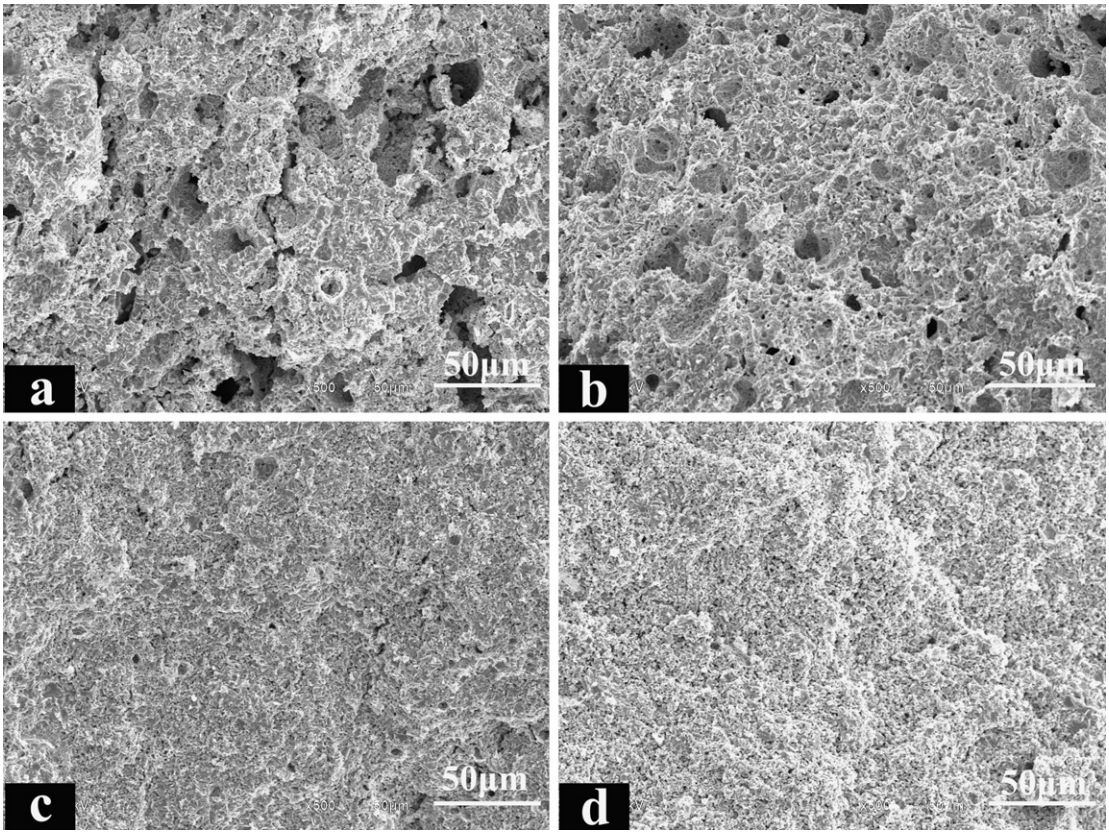

Fig. 7. Cross sectional SEM images of $SmFe_{0.9}Co_{0.1}AsO$ samples sintered from raw powders mechanical alloyed for different time. (a) Hand-milled, (b) 1 h, (c) 3 h, (d) 5 h.

larger than that of the parent compound SmFeAsO according to the single band approximation $n = 1/R_H e$, which strongly indicated that the Co atoms were successfully doped into SmFeAsO.

The phase purities and superconducting properties of the MA samples are similar to those samples synthesized by conventional solid-state reactions [10–12]. The reaction time of the MA sample was significantly reduced. The high-energy milled fine powders with large surface areas and mechanical deformation energy can significantly enhance the reaction kinetics and reduce the reaction time. Furthermore, LnAs and FeO as the starting materials can induce a displacement reaction to form the requisite layered compound (Ln_2O_2–Fe_2As_2).

The effects of MA time on the phase evolution were further investigated from a series of sample preparation. The raw materials were mixed and mechanical alloyed for 1 h, 3 h, 5 h, and 7 h, respectively, and then sintered at 1433 K for 3 h. For comparison, the hand-milled sample was sintered at the same condition. Fig. 6 shows the XRD patterns of the relevant samples. The impurities of Sm_2O_3 and FeAs in the hand-milled sample were much higher than the other samples. Starting from 1 h-milled raw materials, the lattice ordering of FeAs and Sm_2O_3 diminished tremendously, which indicated that the mechanical alloying improved the crystallization of the SmFeAsO main phase by increasing the reactivity of reagents. However, these impurities slightly decreased in the samples with a longer MA time. Fig. 7 shows the SEM cross-section images of the hand-milled sample (Fig. 7a) and the MA samples for 1 h (Fig. 7b), 3 h (Fig. 7c) and 5 h (Fig. 7d), respectively. The sample density increases with prolonging the MA time. Numerous large cavities were observed in the hand-milled sample, and became smaller and fewer after 1 h mechanical alloying. It is ascribed to the finer powders and higher reactivity of the high-energy MA raw materials with longer time.

4. Conclusions

In summary, the mechanical alloying method was successfully introduced to synthesize the $SmFe_{1-x}Co_xAsO$ superconductors. The carrier concentration of $SmFe_{0.9}Co_{0.1}AsO$ is larger than that of the parent compound SmFeAsO because of the successful substitution of Fe^{2+} by Co^{3+}. The superconductivity was induced in the middle doping content x ranging from 0.10 to 0.20 by only sintering the raw materials at 1433 K for 3 h. Considering our earlier research, the mechanical alloying and rapid sintering method is effective to synthesize the LnFeAsO-based superconductors by different elements substitution, such as Ln sites, Fe sites, and O site.

Acknowledgments

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