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Relationship Between Crystal Structures and Physical Properties in Iron Arsenides with Perovskite-type Layers

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Abstract

Effect of two-dimensionality of crystal structure on superconducting transition temperature(T_c) in iron arisenides with thick perovskite-type layer was investigated. Solid solutions of $(Fe_2As_2)(Ca_4(Sc,Ti)_3O_y)$ and $(Fe_2As_2)(Ca_4(Mg,Ti)_3O_y)$, as well as $(Fe_2As_2)(Ca_5(Sc,Ti)_4O_y)$ and $(Fe_2As_2)(Ca_5(Mg,Ti)_4O_y)$ were successfully fabricated. Lattice constants were systematically controlled by mixing ratio of Mg, Sc and Ti. All samples show bulk superconductivity at 30 – 40 K. Maximum T_c was achieved at a = 3.88 Å in both $(Fe_2As_2)(Ca_4M_3O_y)$ and $(Fe_2As_2)(Ca_5M_4O_y)$ compounds. T_c slightly decreases with increasing thickness of the perovskite-type layer. It indicates that the interlayer distance does not have positive effect on T_c in layered iron arsenides with thick blocking layers.

Keywords: iron-based superconductor; perovskite structure; crystal structure;

1. Introduction

Since the discovery of superconductivity in LaFeAs(O,F)[1], several families of iron-based superconductors have been discovered. Owing to these discoveries, several determining factors of superconducting transition temperature(T_c) were proposed, and anion height(h_{An}), distance from iron-plane to pnictogen or chalcogen, is regarded as one of the most important factor[2,3]. On the other hand, there is few systematic study between two-dimensionality of the crystal structure and T_c in iron-based superconductors, though emphasis of two-dimensionality by an increase of the interlayer distance of superconducting planes might be a promising way to enhance T_c, as in the case of the intercalated HfNCl by large amounts of lithium and tetrahydrofuran[4]. The problem is that there is a difficulty to control two-dimensionality of the structure without changing local structure at the FeAs layer.

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Meanwhile, large number of layered iron pnictides composed of antifluorite-type iron pnictide layers and perovskite-type oxide layers have been found[5-7]. The thickness of the perovskite-type layer can be controlled according to the composition and the synthesis conditions. In our previous study, we have discovered several homologous series of iron-based superconductors such as $(Fe_2As_2)(Ca_{n+1}(Sc,Ti)_nO_y)$ [$n = 3 \sim 5$][8], $(Fe_2As_2)(Ca_{n+1}(Mg,Ti)_nO_y)$ [$n = 3,4$][9,10] and $(Fe_2As_2)(Ca_{n+2}(Al,Ti)_nO_y)$ [$n = 2 \sim 4$][11]. These compounds have characteristic two-dimensional crystal structure and exhibit bulk superconductivity with T_c^{onset} around 30 ~ 40 K without intensive carrier doping. Figure 1 shows crystal structure of $(Fe_2As_2)(Ca_4M_3O_y)$[abbreviated as 22438], $(Fe_2As_2)(Ca_5M_4O_y)$[abbreviated as 225\underline{11}] and $(Fe_2As_2)(Ca_6M_5O_y)$[abbreviated as 226\underline{14}]. Blocking layer of these compounds are consisted by triple to quintuple perovskite-type layers, and

Fig.1 Crystal structures of $(Fe_2As_2)(Ca_4M_3O_y)$(a), $(Fe_2As_2)(Ca_5M_4O_y)$(b) and $(Fe_2As_2)(Ca_6M_5O_y)$(c).

interlayer Fe-Fe distance increases about 4 Å by adding one sheet of perovskite-type layer. In addition, 22438 and 225\underline{11} phases were obtained for M = (Sc,Ti) and (Mg,Ti). Therefore, by mixing (Mg,Ti) and (Sc,Ti), or changing number of perovskite-type sheet, local structure at FeAs layer and two-dimensionality of the crystal structure can be controlled independently.

In this paper, we have made solid solutions of $(Fe_2As_2)(Ca_4(Sc,Ti)_3O_y)$ and $(Fe_2As_2)(Ca_4(Mg,Ti)_3O_y)$, as well as $(Fe_2As_2)(Ca_5(Sc,Ti)_4O_y)$ and $(Fe_2As_2)(Ca_5(Mg,Ti)_4O_y)$ and investigated their physical properties.

2. Experimental

The samples were synthesized by solid-state reaction starting from FeAs(3N), CaO(2N), MgO(2N), Sc_2O_3(3N), Ti(3N) and TiO_2(3N). Powder mixture of starting materials was pelletized and sealed in evacuated quartz ampoules. Heat-treatments were performed at 1000-1200°C for 50 - 100 hours. Phase identification was carried out by X-ray diffraction (XRD) with RIGAKU Ultima-IV diffractometer and intensity data were collected in the 2θ range of 5° - 80° at a step of 0.02° using Cu-$K\alpha$ radiation. Silicon powder was used as the internal standard. Magnetic susceptibility measurement was performed by a SQUID magnetometer (Quantum Design MPMS-XL5s). Electric resistivity was measured by AC four-point-probe method using Quantum Design PPMS.

3. Results & Discussions

Figure 2(a) shows observed XRD pattern of $(Fe_2As_2)(Ca_4(Sc_{2-2x},Mg_{0.75x},Ti_{1+1.25x})_3O_{7.5})$ reacted at 1050°C for 72 h. Starting compositions were determined considering valence of the cations(Sc^{3+}, Mg^{2+} and Ti^{4+}) and results of previous experiments[8-10]. 22438 phase were obtained as main phase for all compositions with small amounts of impurities such as $CaFe_2As_2$ and CaO. Both a- and c-axis lengths of the compounds were decreased systematically with increasing x as shown in Fig.2(b). Similar results were obtained for 225\underline{11} phases starting from $(Fe_2As_2)(Ca_5(Sc_{2-2x},Mg_{0.8x},Ti_{2+1.2x})_3O_{10})$ sintered at 1100°C for
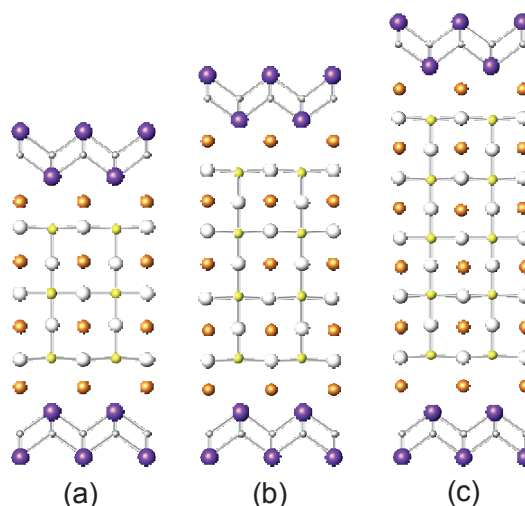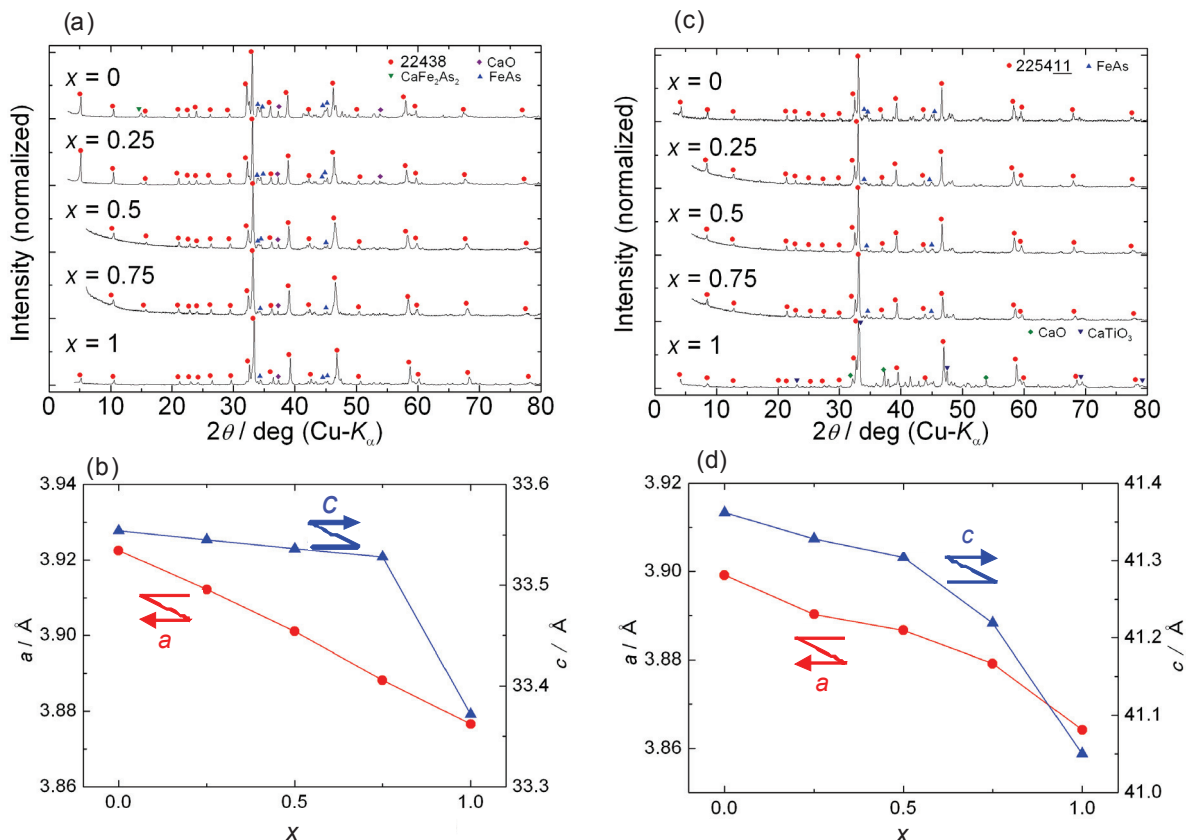
Fig.2 Powder XRD patterns(a) and lattice constants(b) of $(Fe_2As_2)(Ca_4(Sc_{2-2x},Mg_{0.75x},Ti_{1+1.25x})_3O_{7.5})$, and Powder XRD patterns(c) and lattice constants(d) of $(Fe_2As_2)(Ca_5(Sc_{2-2x},Mg_{0.8x},Ti_{2+1.2x})_3O_{10})$

72 h. 225411 phases were obtained as main phase for all compositions, and both *a*- and *c*-axis lengths of the compounds were decreased with increasing *x* as shown in Fig.2(c) and (d). Though *a*-axis lengths of the 225411 samples are similar to those for corresponding 22438 samples, there is large difference of *c*-axis lengths due to different numbers of perovskite-type sheet at the blocking layer.

The temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves of the 22438 and 225411 phases were measured under 1 Oe as shown in Fig. 3. All the compounds exhibited large diamagnetism due to bulk superconductivity. The onsets of T_c were systematically increased with increasing *x* for 22438 phases. On the other hand, the onsets of T_c for 225411 was maximized at *x* = 0.75. The reversible magnetization observed down to several K below the T_c onset was observed, similar to those of $(Fe_2As_2)(Ca_{n+1}(Sc,Ti)_nO_y)$ and $(Fe_2As_2)(Ca_{n+1}(Mg,Ti)_nO_y)$[8,9]. Figure 4 shows the temperature dependence of resistivity for the 22438 and 225411 phases. All samples exhibited metallic behavior in the normal state resistivity. Superconducting transitions were observed around 30-47 K depending on the compositions. The onset of T_c, determined by crossing point of the normal state resistivity and the transition part were systematically increased from 33 K to 47 K with increasing *x* for 22438 phases. On the other hand, maximum T_c of 46 K was observed at *x* = 0.75 in 225411 phases. The tendency was same with magnetization measurement.

Figure 5 shows relationship between T_c and *a*-axis lengths of each sample. T_c changes systematically with *a*-axis length in both 22438 and 225411 phases. In both phases maximum T_c is achieved when *a*-axis length is around 3.88 Å probably due to optimization of local structure at FeAs layer, because there is
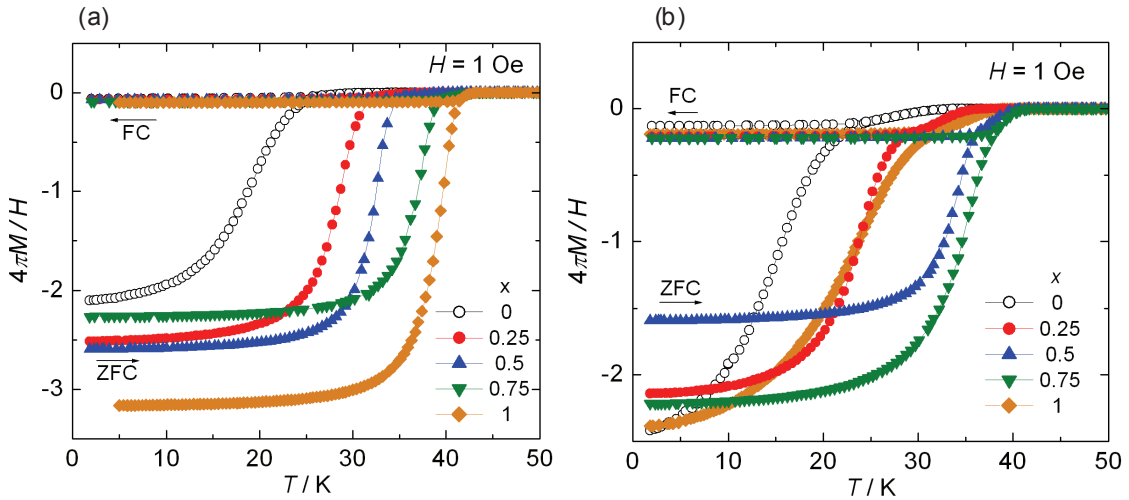
Fig.3 Temperature dependence of ZFC and FC magnetization curves of
$(Fe_2As_2)(Ca_4(Sc_{2-2x},Mg_{0.75x},Ti_{1+1.25x})_3O_{7.5})$(a) and $(Fe_2As_2)(Ca_5(Sc_{2-2x},Mg_{0.8x},Ti_{2+1.2x})_3O_{10})$(b)

correlation between *a*-axis length and h_{An}[12]. Maximum T_c of each phases are 47 and 46 K in 22438 and 225$\underline{11}$ phases, respectively. Taking into account that $(Fe_2As_2)(Ca_6(Sc,Ti)_5O_y)$ has T_c of 42 K with *a*-axis length of 3.884 Å, T_c of the samples with similar *a*-axis lengths slightly decreases with increasing interlayer Fe-Fe distances. From the result, it is clear that there is no positive effect on T_c from the two-dimensionality of crystal structure in iron-based superconductors with such thick blocking layers.

4. Conclusions

Two-dimensionality of the crystal structure and local structure at FeAs layer was independently controlled by making solid solutions of $(Fe_2As_2)(Ca_{n+1}(Sc,Ti)_nO_y)$ and $(Fe_2As_2)(Ca_{n+1}(Mg,Ti)_nO_y)$ with *n* = 3 and 4. Systematic decrease of lattice constants with increasing Mg content was observed. In both cases, T_c is maximized when *a*-axis lengths are around 3.88 Å. T_c slightly decreases with increasing thickness of the blocking layers. There is no positive effect on T_c from two-dimensionality of crystal structure in iron-based superconductors with thick blocking layers.
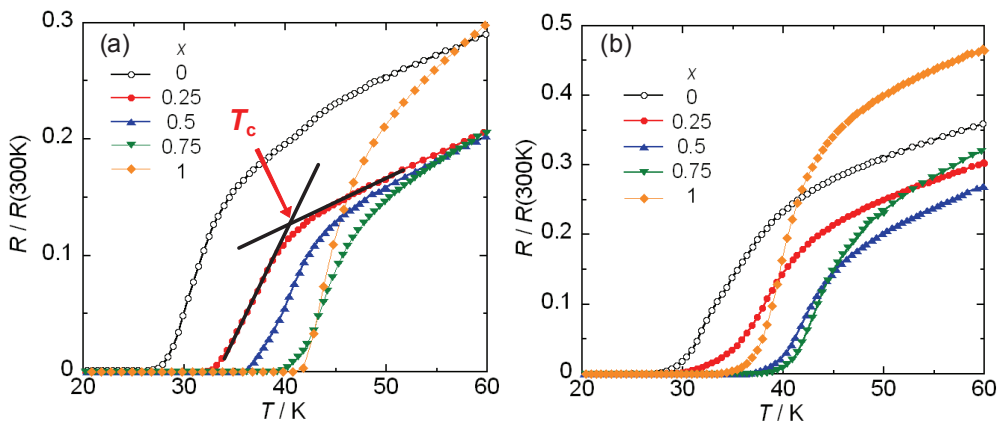

Fig.4 Temperature dependence of resistivity of $(Fe_2As_2)(Ca_4(Sc_{2-2x},Mg_{0.75x},Ti_{1+1.25x})_3O_{7.5})$(a) and
$(Fe_2As_2)(Ca_5(Sc_{2-2x},Mg_{0.8x},Ti_{2+1.2x})_3O_{10})$(b)

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Acknowledgements

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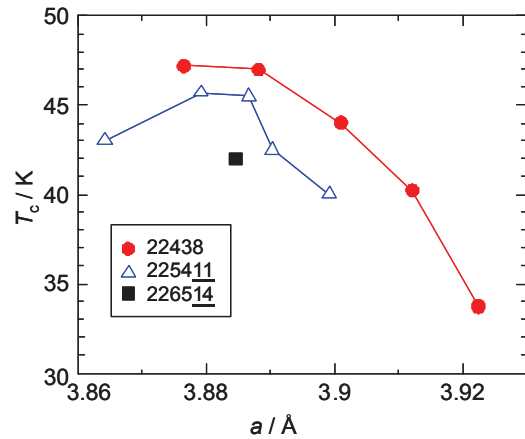

Fig.5 Relationship between T_c and a-axis length of 22438, 225411 and 226514 phases