New iron-based arsenide oxides
(Fe\textsubscript{2}As\textsubscript{2})(Sr\textsubscript{4}M\textsubscript{2}O\textsubscript{6})(M = Sc, Cr)

Hiraku Ogino\textsuperscript{1,2}, Yukari Katsura\textsuperscript{3}, Shigeru Horii\textsuperscript{2,4}, Kohji Kishio\textsuperscript{1,2} and Jun-ichi Shimoyama\textsuperscript{1,2}

\textsuperscript{1} Department of Applied Chemistry, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
\textsuperscript{2} JST-TRIP, Sanban-cho, Chiyoda-ku, Tokyo 102-0075, Japan
\textsuperscript{3} Magnetic Materials Laboratory, RIKEN, 2-1 Hirosawa, Wako-shi, Saitama 351-0106, Japan
\textsuperscript{4} Department of Environmental Systems Engineering, Kochi University of Technology, Kami-shi, Kochi 782-8502, Japan

E-mail: tuogino@mail.ecc.u-tokyo.ac.jp

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Abstract
We have discovered new arsenide oxides (Fe\textsubscript{2}As\textsubscript{2})(Sr\textsubscript{4}M\textsubscript{2}O\textsubscript{6})(M = Sc, Cr: M-22426). These materials are isostructural with (Fe\textsubscript{2}P\textsubscript{2})(Sr\textsubscript{4}Sc\textsubscript{2}O\textsubscript{6}), which was found in our previous study. The new compounds are tetragonal with a space group of \textit{P4}/\textit{nmm} and consist of the anti-fluorite-type FeAs layer and a perovskite-type blocking layer. These compounds have long interlayer Fe–Fe distances corresponding to the \textit{c}-axis length; the 15.8 Å in Sc-22426 is the longest in the iron-based pnictide oxide systems. Chemical flexibility of the perovskite block in this system was probed by chromium-containing (Fe\textsubscript{2}As\textsubscript{2})(Sr\textsubscript{4}Cr\textsubscript{2}O\textsubscript{6}). Different trends were found in bond angle and bond length of the new pnictide oxides compared to the reported systems, such as REFePnO. The absence of superconductivity in these compounds is considered to be due to insufficient carrier concentration as in the case of undoped REFeAsO.

1. Introduction

High-\textit{T}_c superconductivity in iron-based pnictide oxide systems [1] has proposed new guidelines for the development of superconducting materials. Several types of iron-based superconductors are discovered such as LiFeAs [2], AEFe\textsubscript{2}As\textsubscript{2} (abbreviated as 122, AE = alkaline earth metals) [3], REFeAsO (abbreviated as 1111, RE = rare earth elements) [4], AEFeAsF [5] and related phosphide oxide and chalcogenide materials. Meanwhile, there are still continuous demands for new materials containing iron tetragonal lattices, particularly for achieving higher \textit{T}_c.

Several discussions have been already given for determining factors of \textit{T}_c in iron-based pnictide oxides. High symmetry in Fe\textsubscript{nPn} tetrahedra is pointed out to be an important factor for high \textit{T}_c. Actually, the highest \textit{T}_c for 1111 and 122 phases were achieved by compounds with angles between As–Fe–As of \textdegree109.5°, which is the desirable value for perfect symmetry. In addition, from a chemical point of view, the high \textit{T}_c exceeding 30 K under ambient pressure was achieved only in compounds having an FeAs layer. Combination of iron and arsenic might be one of the key factors to achieve high \textit{T}_c. In our recent study [6], we have discovered a new superconducting pnictide oxide (Fe\textsubscript{2}P\textsubscript{2})(Sr\textsubscript{4}Sc\textsubscript{2}O\textsubscript{6}) with \textit{T}_c \sim 17 K. This material has an alternate stacking of a perovskite (K\textsubscript{2}NiF\textsubscript{4}-type) oxide layer and an anti-fluorite pnictide layer. Flexibility of the perovskite-based structure in sulfide oxide and pnictide oxide systems has already been investigated and several structural types and a variety of constituent transition metals in the perovskite layer including FeAs-based material have been reported [7–14]. These motivated us to search for new iron pnictide oxides with perovskite-type oxide layers. In this study, we have extended the previous discovery of (Fe\textsubscript{2}P\textsubscript{2})(Sr\textsubscript{4}Sc\textsubscript{2}O\textsubscript{6}) to the arsenide oxide system. New iron arsenide oxides (Fe\textsubscript{2}As\textsubscript{2})(Sr\textsubscript{4}M\textsubscript{2}O\textsubscript{6}) (M = Sc, Cr) (abbreviated as M-22426) have been successfully synthesized and their structural and physical properties were characterized.

2. Experimental details

All samples were synthesized by solid-state reaction starting from FeAs(3N), SrO(2N), Sr(2N), Cr(3N), Sc\textsubscript{2}O\textsubscript{3}(4N) and Cr\textsubscript{2}O\textsubscript{3}(3N). Nominal compositions were fixed according to
Figure 1. Rietveld refinement of powder XRD and the crystal structure of Sc-22426 (a): dashed line indicates calculated fit pattern and solid line indicate difference of observed and calculated pattern. Bars show diffraction peak positions of Sc-22426. Rietveld refinement of powder XRD of the Cr-22426 (b): upper and lower bars show diffraction peak positions of FeAs and Cr-22426, respectively. (This figure is in colour only in the electronic version)

3. Results and discussions

Bulk samples of Sc-22426 with a single phase were obtained by sintering at 1200°C. On the other hand, phase purity of isostructural Cr-22426 samples was relatively poor even after sintering at 1200°C for a long time, though the target compound was formed as a main phase. Small amounts of FeAs, SrO and other unknown impurities were included in the samples. The powder XRD patterns of Sc-22426 and Cr-22426 reacted at 1200°C for 40 h are shown in figure 1. Lattice constants were determined to be \(a = 4.050\) Å and \(c = 15.809\) Å for Sc-22426 and \(a = 3.918\) Å and \(c = 15.683\) Å for Cr-22426. The space group of both compounds is \(P\bar{4}nmm\).

Similar to an Sc-22426 compound with an FeP layer [6], the interlayer Fe–Fe distance of Sc-22426 with an FeAs layer is very long \(\sim 15.8\) Å, which is the longest value ever reported in the iron pnictide oxide systems.

Rietveld refinement was carried out for powder XRD patterns of Sc-22426 and Cr-22426. In the case of Sc-22426, there are no traces of impurity or other phases, such as \((\text{Fe}_2\text{As}_2)(\text{Sr}_3\text{M}_2\text{O}_6)\) (abbreviated as Sc-22325), which was found by Zhu et al [14]. The difference in Sc-22426 and Sc-22325 is the stacking pattern of the perovskite structure. In the refinement for Cr-22426, diffraction peaks derived from impurity phases were excluded. The results of the refinement are summarized in table 1, while \(R\) factors of Cr-22426 were rather poor because of several coexisting impurities. It was found that the \(a\)-axis length of Sc-22426 is slightly shorter and the \(\alpha\) angle is slightly smaller than those of Sc-22325. Meanwhile, Cr-22426 has a short \(a\) axis and small \(\alpha\) angle compared to Sc-based iron pnictide oxides. XRD measurements were performed down to 15 K to investigate structural changes: however, no structural change was observed for either compound.

Figure 2 shows a bright-field TEM image and an electron diffraction pattern taken from the [110] direction.

Figure 2. Bright-field TEM images and corresponding electron diffraction patterns of an Sc-22426 crystal viewed from the [110] direction.

In this general formula: \((\text{Fe}_2\text{As}_2)(\text{Sr}_3\text{M}_2\text{O}_6)\) (M = Sc, Cr). Since the starting reagents, Sr and SrO, are sensitive to moisture in air, manipulations were carried out under an inert gas atmosphere. A powder mixture of the reagents was pelletized and sealed in evacuated quartz ampoules. Heat treatments were performed in the temperature range from 1000 to 1200 °C for 24–50 h.

Phase identification was carried out by x-ray diffraction (XRD) with a Rigaku Ultima-IV diffractometer and intensity data were collected in the 2\(\theta\) range of 5°–80° at steps of 0.02° using Cu K\(\alpha\) radiation. Silicon powder was used for the internal standard. Structural refinement was performed using the analysis program RIETAN-2000 [15]. High-resolution images were taken by JEOL JEM-2010F field emission TEM. Magnetic susceptibility measurement was performed by a SQUID magnetometer (Quantum Design MPMS-XL5s). Electric resistivity was measured by the AC four-point-probe method using a Quantum Design PPMS.
Figure 3. Temperature dependence of ZFC and FC magnetization curves of the Sc-22426 and Cr-22426 bulk samples measured under 10 kOe.

Table 1. Fitting parameters, bond lengths and bond angles for (Fe$_2$As$_2$)(Sr$_4$M$_2$O$_6$).

| Atom | x     | y     | z (Sc) | z (Cr) |
|------|-------|-------|--------|--------|
| Sc   | 0.250 | 0.250 | 0.3071 | 0.3116 |
| Fe   | 0.250 | −0.250| 0.0000 | 0.0000 |
| Sr1  | −0.250| −0.250| 0.1887 | 0.1947 |
| Sr2  | −0.250| −0.250| 0.4153 | 0.4157 |
| O1   | 0.250 | 0.250 | 0.2857 | 0.2945 |
| O2   | 0.250 | 0.250 | 0.4301 | 0.4250 |
| As   | 0.250 | 0.250 | 0.0854 | 0.0898 |

$R_{wp} = 9.32$ $R_p = 6.48$ $R_e = 9.70$ $S = 0.5436$ $R_F = 2.21$ (Sc) $R_{wp} = 13.68$ $R_p = 9.99$ $R_e = 9.98$ $S = 1.3709$ $R_F = 2.71$ (Cr)

Fe–As 2.433 Å 2.414 Å
Fe–Fe 2.863 Å 2.770 Å

Figure 4 shows the temperature dependence of resistivity for Sc-22426 and Cr-22426. As in the case of Sc-22325 [14], any anomaly was not found in the resistivity curve. In contrast, Cr-22426 showed metallic behavior above 130 K and an anomalous drop below 60 K. Although origins of the anomaly are not clear at the present stage, it is interesting that the temperature of the anomaly in resistivity is slightly different from that in magnetization.

In order to clarify structural features of the perovskite-based pnictide oxides, $\alpha$ angles of the FePn layer and distances coincide well with a corresponding value obtained from XRD patterns. It should be noted that any stacking faults were not found in the observed crystals, whereas the perovskite block has a large variety in layer stacking patterns, such as Sr$_3$Sc$_2$O$_5$. Furthermore, the absence of satellite spots probes commensurate stacking between Fe$_2$As$_2$ and Sr$_4$Sc$_2$O$_6$ layers.

Temperature dependences of magnetization of Sc-22426 and Cr-22426 measured under 10 kOe are shown in figure 3. Curie–Weiss-like behavior without anomaly was observed for the Sc-22426, while Cr-22426 showed a broad magnetization peak around 80 K. This behavior is similar to that of a sulfide analogue (Cu$_2$S$_2$)(Sr$_4$Cr$_2$O$_6$) [9]. In the case of (Cu$_2$S$_2$)(Sr$_4$Cr$_2$O$_6$), this behavior is explained by antiferromagnetic ordering of Cr$^{3+}$ in the perovskite-type layer derived from spin 3/2 at the Cr site. Both compounds did not exhibit any signs of superconductivity down to 1.7 K, possibly due to insufficient carrier concentration as in the case of the undoped REFeAsO compounds.

Figure 5 shows the relationship between $\alpha$ angle and $a$-axis length (a) and Fe–Pn distance and $a$-axis length (b) at room temperature except for NdFeAsO (at 175 K). The values are obtained by undoped samples except TbFeAsO$_{0.9}$F$_{0.1}$. Closed symbols indicate iron pnictide oxides with perovskite-type oxide layer. Solid and dashed lines are guideline for the eyes.
between Fe and Pn of reported phases are arranged by their a-axis length as shown in figure 5. Both α angles and Fe–Pn distances tend to increase with increasing a-axis length to maintain the crystal structures. On the other hand, there are differences in trends derived from structural groups. For example, the α angle of Sc-22426 is similar to that of Ce-1111 while the a axis of the compound (4.050 Å) is much longer than that of Ce-1111 (4.000 Å). This result is due to a longer Fe–As distance in Sc-22426 than that of LaFePO owing to its longer Fe–Pn distance. These facts suggest that the perovskite-based iron pnictide oxides have different nature from the local iron pnictide structure. Suggested by Lee et al. [20], the compounds with the less distorted FeAs$_4$ tetrahedron tend to exhibit higher $T_c$. The different trend in angles and bond length of the pnictide layer in perovskite-based pnictide oxides will bring new ways to control local structures.

The discovery of a new pnictide oxide having chromium-containing perovskite block showed the B site cation in the perovskite layer is not limited to Sc. This fact vastly expands the possibility of new materials in pnictide oxide systems having a perovskite-type oxide layer. We have already noticed structural similarity between copper sulfide oxides and iron pnictide oxides. In fact, as many as ten ions of the B site cation in the perovskite-type oxide layer are reported in copper sulfide oxides. Therefore, there must be other elements, which can occupy the B site of the perovskite-type layer in the pnictide oxides, if they satisfy the following restrictions. First, the cation must have appropriate valence and ionic radius. For example, the valence of the B site cation should be basically trivalent in the 22426 compounds and divalent in the hypothetical (Fe$_2$Pn$_2$)(Sr$_2$MO$_3$) compounds. Concerning ionic radii, ions with radii from 61.5 pm (Cr$^{3+}$, 6 coordination) [9] to 83.0 pm (Mn$^{2+}$, 6 coordination, high spin) [8] are reported in copper sulfide oxides. Existence of Cr$_2$-22426 and (Mn$_2$As$_2$)(Ba$_2$MnO$_4$) [7] indicates the restriction of ionic radii is almost the same in copper sulfide oxides and pnictide oxides. Second, the appropriate valence of the B site cation and Fe$^{2+}$ at the pnictide layer should coexist under the synthesis conditions. Finally, the B site cation should be introduced to the oxide layer prior to the pnictide layer to form the iron pnictide layer. Narrow stable conditions of Fe$^{2+}$ compared to that of Cu$^{1+}$ and the last limitation might severely restrict the candidate elements. Further investigations of the novel system will be needed to clarify the actual criteria for these restrictions.

4. Conclusions

New layered iron pnictide oxides M-22426; (Fe$_2$As$_2$)$_2$(M$_x$M$_{1-x}$O$_{6y}$) (M = Sc, Cr) have been synthesized and their crystal structures were determined. Both materials consist of alternate stacking of anti-fluorite Fe$_2$As$_2$ and perovskite Sr$_3$M$_2$O$_6$ layers with the space group of $P4/nmm$. The interlayer Fe–Fe distance of 15.809 Å for Sc-22426 is the longest among the reported values for iron pnictides. In both magnetization and resistivity measurements, these new compounds did not exhibit superconducting transitions, probably due to insufficient carrier concentration. Further attempts to introduce effective carriers to these materials must be promising for achieving high-$T_c$ superconductivity. On the other hand, existence of (Fe$_2$As$_2$)$_2$(Sr$_2$Cr$_2$O$_6$) suggested a large variety of constituent elements in the perovskite-type oxide layer. Moreover, trends of the local pnictide layer in pnictide oxides with a perovskite-type oxide layer are different from other structural systems, such as 1111. Structural and chemical variations in the perovskite layer will make this type of pnictide oxide as a reservoir of new functional materials including superconductors.

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