Superconductivity at 17 K in \((\text{Fe}_2\text{P}_2)(\text{Sr}_4\text{Sc}_2\text{O}_6)\): a new superconducting layered pnictide oxide with a thick perovskite oxide layer

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Abstract
A new layered pnictide oxide \((\text{Fe}_2\text{P}_2)(\text{Sr}_4\text{Sc}_2\text{O}_6)\) has been synthesized by solid-state reaction. This material has an alternating layer stacking structure of anti-fluorite \(\text{Fe}_2\text{P}_2\) and perovskite-based \(\text{Sr}_4\text{Sc}_2\text{O}_6\) oxide layers. The space group of the material is \(P4/nmm\) and the lattice constants \(a\) and \(c\) are 4.016 and 15.543 Å, respectively. The interlayer \(\text{Fe}–\text{Fe}\) distance corresponding to the \(c\)-axis length is the longest ever reported in the iron-based pnictides. In both magnetization and resistivity measurements, the present compound exhibited superconductivity below 17 K; this temperature is much higher than that for \(\text{LaFePO}\) and the highest in arsenic-free iron-based pnictide systems under ambient pressure.

1. Introduction
Since the discovery of high \(T_c\) in \(\text{LaFeAs(O, F)}\) [1], new superconductors containing anti-fluorite iron pnictide layers have been eagerly searched for and several groups of superconducting materials, such as \(\text{LiFeAs}\) [2], \(\text{AEFe}_2\text{As}_2\) (abbreviated as 122; \(\text{AE}\) = alkaline earth metals) [3], \(\text{REFeAsO}\) (abbreviated as 1111; \(\text{RE}\) = rare earth elements) [4], \(\text{AEFeAsF}\) [5] and related phosphide oxide and chalcogenide materials, have been discovered thus far.

Empirically, a high \(T_c\) exceeding 50 K has been achieved in the fluorine-doped or oxygen deficient \(\text{REFeAsO}\) [6–8] or \(\text{RE}\)-doped \(\text{AEFeAsF}\) systems [9]. Crystal structures of these materials can be regarded as layer stackings of anti-fluorite-type \(\text{FeAs}\) layers and fluorite-type oxide or fluoride layers. Several discussions have already appeared as regards determining factors for \(T_c\) for iron-based pnictide oxides. Lee et al has pointed out, from a structural viewpoint for superconducting iron pnictide layers, that high symmetry in the \(\text{FeAs}_4\) tetrahedra is crucial for high \(T_c\) [10]. Actually, the highest \(T_c\) values for 1111 and 122 phases were achieved for compounds with \(\text{As}–\text{Fe}–\text{As}\) angles of \(\sim 109.5\,^\circ\), which is the desirable value for perfect symmetry. On the basis of this idea, relatively low \(T_c\) values for \(\text{LaFeP(O, F)}\) and \(\text{FeSe}\) are reasonably well explained.

On the other hand, materials with similar stacking structures of perovskite-type oxide layers and anti-fluorite chalcogenide or pnictide layers have already been found in several pnictide oxide [11] and chalcogenide oxide systems [12]. Because of the flexibility in the perovskite-based structure, several structure types and a variety of constituent transition metals in the perovskite block have been reported [12–18]. In our previous study [14], several new sulfide oxides, including a scandium-based sulfide oxide \((\text{Cu}_2\text{S}_2)(\text{Sr}_3\text{Sc}_2\text{O}_5)\) (abbreviated as Sc-22325), were discovered. Recently an isostructural compound with an...
FeAs layer was reported by Zhu et al. [19], while it did not show superconductivity, probably due to an insufficient carrier concentration. These facts indicate structural similarity between layered iron pnictide oxides and layered copper sulfide oxides. Because of the structural and chemical variety of the copper sulfides, pnictide with a perovskite oxide layer is expected to provide new functional materials including superconductors.

In the present study, an iron pnictide oxide with a new structure \((\text{Fe}_2\text{P}_2)(\text{Sr}_4\text{Sc}_2\text{O}_6)\) (abbreviated as Sc-22426) has been successfully synthesized. This material has a perovskite-related \(\text{Sr}_4\text{Sc}_2\text{O}_6\) layer (\(\text{K}_2\text{NiF}_4\)-type), which results in the longest interlayer Fe–Fe distance of \(\sim 15.5\) Å, and showed bulk superconductivity with a \(T_c\) (onset) of 17 K.

### 2. Experimental details

All samples were synthesized by solid-state reaction starting from FeP, \text{SrO}(2N), Sr(2N), \text{Sc}_2\text{O}_3 (4N). The precursor FeP was obtained by the chemical reaction of Fe(3N) and P(2N) with a molar ratio of 1:1 at 700°C for 12 h. The nominal composition was fixed according to the general formula \((\text{Fe}_2\text{P}_2)(\text{Sr}_4\text{Sc}_2\text{O}_6)\). 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 FeP, SrO, Sr and \text{Sc}_2\text{O}_3 was pelletized and sealed in evacuated quartz ampoules. Heat treatments were performed in the temperature range from 900 to 1200°C for 12–40 h.

Phase identification was carried out using x-ray diffraction with a RIGAKU Ultima-IV diffractometer and intensity data were collected in the 2\(\theta\) range of 5–80° at steps of 0.02° (Cu Ka), and Si was used as the internal standard. Structural refinement was performed using the analysis program Rietan-2000 [20]. High resolution images were taken using a JEOL JEM-2010F field emission TEM. Magnetic susceptibility measurement was performed using a SQUID magnetometer (Quantum Design MPMS-XL5s). The electrical resistivity was measured by an AC four-point-probe method using a Quantum Design PPMS under fields up to 9 T.

### 3. Results and discussion

Samples containing Sc-22426 as a main phase were obtained by sintering above 1100°C for more than 24 h. The color of the samples was dark black; however, they expanded during sintering, resulting in low bulk density less than 40%. This is possibly due to the anisotropic grain growth of Sc-22426 crystals or intermediate products during the ramping up process before the sintering process.

Figure 1(a) shows calculated and observed XRD patterns of the Sc-22426 sample reacted at 1200°C for 40 h. This compound consists of a stacking of anti-fluorite \(\text{Fe}_2\text{P}_2\) layers and perovskite-type \(\text{Sr}_4\text{Sc}_2\text{O}_6\) layers as presented in figure 1(b). Sc-22426 was obtained as the main phase by optimizing the sintering conditions, while formation of the secondary phase \(\text{SrFe}_2\text{P}_2\) is inevitable at the present stage. All peaks were indexed with Sc-22426 or \(\text{SrFe}_2\text{P}_2\). The Sc-22426: \(\text{SrFe}_2\text{P}_2\) ratio was estimated to be \(\sim 9:1\). The space group of the Sc-22426 was \(P4/mnm\) and its lattice constants were determined as \(a = 4.016(1)\) Å and \(c = 15.543\) Å. The interlayer Fe–Fe distance of the material is extremely long compared to the 8.5 Å for \(\text{LaFePO}\) and even longer than the recently reported 13.4 Å for Sc-22325 with an FeAs layer [19]. Although the Rietveld refinement was not well fitted, probably...
due to the coexistence of unidentified impurities, the Fe–P–Fe angles calculated using the tentative values of the coordinates (table 1) were 75° and 118°, which are closer to the ideal angles of highly symmetric tetrahedra compared to those of LaFePO [8]. The Fe–Fe distance of 2.840 Å is also close to that of LaFeAsO rather than that of LaFePO. These facts suggest that the new system has a nature of the local iron pnictide structure different from that in the 1111 system. In addition, it would be possible to optimize the local structure of the pnictide layer by changing the size of the perovskite subunit. Figure 2 shows a bright-field TEM image and an electron diffraction pattern taken from the [110] direction of a Sc-22426 crystal. Both the TEM image and the electron diffraction patterns indicated a tetragonal cell with $a \sim 4.0$ and $c \sim 16$ Å; these coincide well with corresponding values obtained from the XRD patterns. It should be noted that no stacking faults were found in the observed crystals, whereas the perovskite block has a large variation in layer stacking pattern. Furthermore, the absence of satellite spots probes the commensurate stacking between the Fe$_2$P$_2$ and Sr$_4$Sc$_2$O$_6$ layers.

The temperature dependences of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization of Sc-22426 measured under 1 Oe are shown in figure 3. As is clearly seen, Sc-22426 showed large diamagnetism due to superconductivity with $T_{c\text{(onset)}}$ of $\sim 17$ K. The superconducting volume fraction estimated from the ZFC magnetization at 2 K was much larger than the perfect diamagnetism one. This extremely large diamagnetism is due to the porous microstructure having a large amount of closed pores and a demagnetization effect of the sample. The reversible region, where the ZFC and FC magnetization curves overlap each other, down to $\sim 12$ K suggested that both the grain coupling and the intragrain pinning are relatively poor.

Figure 4 shows the temperature dependence of the resistivity for Sc-22426. The resistivity under 0 T was measured up to 300 K as shown in the inset. Although the metallic behavior was observed in the normal state resistivity, the absolute value of $\rho$ is approximately two orders of magnitude higher than that reported for the 1111 compounds. The superconducting transition was observed at a $T_{c\text{(onset)}}$ of 17 K, while zero resistivity was achieved at 9.8 K. Under magnetic fields, the superconducting transition became extremely broad and determination of $T_{c\text{(onset)}}$ for estimating the upper critical fields was difficult. The observed high resistivity and broad superconducting transition under magnetic fields are explained by the porous microstructure and the poor grain connectivity of the sample. In addition, high electromagnetic anisotropy due to a thick perovskite layer, i.e., a blocking layer, might contribute a broad resistivity transition in fields.

The newly found Sc-22426 with an FeP layer shows clear superconductivity below 17 K. This $T_c$ is much higher than that of LaFeP(O, F) and even higher than that of FeSe under ambient pressure [21, 22]. To our knowledge, the $T_c$ of the present compound is the highest found among the arsenic-free iron-based systems under ambient pressure. Its high $T_c$ might partially be attributed to the local structure of the FeP layer.
having relatively high symmetry. Further investigation will be needed to clarify the essential effects of the very long Fe–Fe interlayer distance on the electronic and magnetic nature of the present system. Another advantage of the new material is the large possibility for doping and perovskite-type structure. Since the perovskite-type Sr$_{4}$Sc$_{2}$O$_{6}$ layer is structurally and chemically flexible, control of the carrier concentration by doping, for all sites, with various elements will be possible. In addition, complete substitution at Sr$^{2+}$ and Sc$^{3+}$ sites and a change of the perovskite structure to control the thickness of the blocking layer and $a$-axis length hold promise as regards finding new superconductors having higher $T_c$. In other words, the feasibility of doping or structural optimization in the perovskite layer containing compounds has more options than in the 1111 system.

4. Conclusions

A new layered iron pnictide oxide Sc-22426: (Fe$_{2}$P$_{2}$)(Sr$_{4}$Sc$_{2}$O$_{6}$), with the space group of $P4/\bar{n}mm$ was successfully synthesized. This material has a layer stacking of anti-fluorite Fe$_{2}$P$_{2}$ and perovskite Sr$_{4}$Sc$_{2}$O$_{6}$ layers and its interlayer Fe–Fe distance of 15.5 Å is the longest reported among the iron pnictide oxides. In both magnetization and resistivity measurements, a superconducting transition was observed with a $T_c$ (onset) of $\sim$17 K. This high $T_c$ is partly due to the higher tetrahedral symmetry at the FeP layer than in other iron phosphide oxides. Our results strongly indicate that pnictide oxides having a perovskite oxide layer could be a ‘new family’ of iron-based superconductors and that the large variety of perovskite-type structures and constituent elements will open new windows in the search for pnictide oxide superconductors.

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