Superconductivity at 28.3 K and 17.1 K in (Ca$_4$Al$_2$O$_{6-y}$)(Fe$_2$Pn$_2$) ($Pn =$ As and P)

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Abstract: Here we report on discovery of (Ca$_4$Al$_2$O$_{6-y}$)(Fe$_2$Pn$_2$) ($Pn =$ As and P) (Al-42622($Pn$)) superconductor using high-pressure synthesis technique. Al-42622($Pn$) exhibit superconductivity for both $Pn =$ As and P with the transition temperatures of 28.3 K and 17.1 K, respectively. The $a$-lattice parameters of Al-42622($Pn$) ($a =$ 3.713 Å and 3.692 Å for $Pn =$ As and P, respectively) are smallest among the iron-pnictide superconductors. Correspondingly, Al-42622(As) has the smallest As-Fe-As bond angle (102.1 °) and the largest As distance from the Fe planes (1.500 Å).

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One of the salient features of the recently-discovered iron (Fe)-based superconductors is their wide material variation. Their basic crystal structure is an alternative stacking of the FePn (Pn=P, As) layers sandwiched by the blocking layers. Variety of crystal structures can be realized by employing different blocking layers, such as LnO (Ln=rare earth)[1], Ae (Ae=Ba, Sr, Ca, Eu)[2], and A (A=Li, Na) [3]. Most recent achievement is the discovery of superconductors possessing perovskite-type blocking layers, (Sr₄Sc₂O₆)(Fe₂P₂)[4], (Sr₄M₂O₆₋₁₋ₓ)(Fe₂As₂) (M = V[5] and MgTi[6]), (Sr₄M₂O₆)(Fe₂As₂) (M = ScTi ), (Ba₄Sc₃O₇₊₅)(Fe₂As₂) [7], (Ca₄₋ₓ₋ₘ(M,Ti)ₓO₇₋₇₋ₘ)(Fe₂As₂) (M = Sc[8], Mg[9,10] and Al[11], n = 2, 3, 4 and 5, m = 1, 2 ), with \( T_c \) reaching as high as 47 K for (Ca₄(Mg,Ti)₃O₇)(Fe₂As₂). Another interesting feature is the strong correlation between their superconducting transition temperature (\( T_c \)) and the configuration of the FeAs₄ local structure, such as the \( Pn-Fe-Pn \) bond angle (\( \alpha \)) and/or the height of \( Pn \) atoms relative to the neighboring Fe layers (\( h_{Pn} \))[12, 13] and many theories have been proposed to account for the correlation [14, 15]. Considering these situations, synthesis of materials possessing either (1) new type of blocking layers or (2) unachieved FeAs₄ configurations, should be tremendously beneficial for understanding the high-\( T_c \) mechanism, and, eventually, for enhancing \( T_c \), of the Fe-based superconductors.

Based on the above background, in this study we have attempted to synthesize perovskite-type FePn superconductors using a high-pressure (HP) technique. HP technique is established as a versatile tool to explore new materials beyond the limitation of ambient synthesis conditions [16]. By enforcing the stacking between the FeAs layers and the blocking layers with smaller in-plane unit cell length (\( a \)-lattice parameters), this method allows us to synthesize materials with extremely smaller unit cell volumes. For example, we have succeeded in synthesizing a series of \( LnFeAsO_{1-y} \)
superconductors (\(Ln=\text{La, Ce, Pr, Nd, Sm, Gd, Tb, Dy}\)) that possess small \(Ln\) atoms, which yield small \(LnO\) blocking layers [17]. The unit cell volume largely shrinks from 141 Å\(^3\) (\(Ln=\text{La}\)) to as small as 124 Å\(^3\) (\(Ln=\text{Dy}\)). In this study, we have applied the HP technique in synthesizing materials containing perovskite-type blocking layers which are extremely small and therefore cannot be synthesized under ambient conditions. Along this line, we have discovered a series of \((\text{Ca}_4\text{Al}_2\text{O}_{6-y})\text{(Fe}_2\text{Pn}_2)\) (\(Pn=\text{As and P}\)) (abbreviated as Al-42622(\(Pn\))) superconductors with \(T_c = 28.3\) K and 17.1 K, respectively. As a consequence of HP synthesis, the synthesized compounds possess the unique structural characteristics never realized in the existing Fe-based superconductors, namely, shortest \(a\)-axis lattice parameters, smallest As-Fe-As bond angle, and longest As-Fe plane distance. Here we demonstrate the synthesis method and the characterization of Al-42622(\(Pn\)).

Polycrystalline samples of Al-42622(\(Pn\)) were synthesized by the solid-state reaction method using a cubic-anvil-type HP apparatus. It should be noted that one cannot synthesize Al-42622(\(Pn\)) by conventional ambient pressure synthesis [11]. Starting materials were powders of CaO, Al, As, P, Fe and \(\text{Fe}_2\text{O}_3\). The powders were mixed with a nominal composition of \((\text{Ca}_4\text{Al}_2\text{O}_{6-y})\text{(Fe}_2\text{Pn}_2)\). Here the oxygen content \(6-y\) was controlled by adjusting the ratio of Fe and \(\text{Fe}_2\text{O}_3\). We have found that the purity of the obtained samples strongly depends on the oxygen content in the starting composition. The suitable oxygen content turned out to be \(6 - y = 5.6 \sim 5.8\). The starting materials were ground using an agate mortar and pressed into a pellet in a glove box filled with \(\text{N}_2\) gas. The pellet was loaded in a high-pressure cell and heated at 1150 and 1300 °C for \(Pn=\text{As and P}\), respectively, under a pressure of 4.5 GPa for 1 h.

Powder X-ray diffraction (XRD) patterns were measured using CuK\(\alpha\) radiation.
Neutron scattering measurement was carried out using the high-resolution powder diffractometer HERMES of the Institute for Materials Research, Tohoku University, installed at the JRR-3 reactor of JAERI in Japan. Incident neutron wavelength was fixed at 1.8484 Å using a Ge monochromator. The data were analyzed by the Rietveld method using the Rietan program. The dc magnetic susceptibility was measured using a SQUID magnetometer (Quantum Design MPMS) under a magnetic field of 5 Oe. The resistivity was measured by a four-probe method.

Fig. 1 represents the XRD patterns of Al-42622(Pn) samples with nominal compositions of (a) Ca$_4$Al$_2$O$_{5.65}$Fe$_2$As$_2$ and (b) Ca$_4$Al$_2$O$_{5.80}$Fe$_2$P$_2$, respectively. Major peaks can be indexed based on the tetragonal crystal structure with $a = 3.713$ Å and $c = 15.407$ Å for Al-42622(As) while with $a = 3.692$ Å and $c = 14.934$ Å for Al-42622(P). Small impurity phases of CaO, and FeAs were detected in the Al-42622(As) samples. Note that the $a$-lattice parameter of Al-42622(As) is significantly smaller than those of Fe-As related compounds containing Ca-based perovskite-derived blocking layers, such as (Ca$_4$(Mg,Ti)$_3$O$_y$)(Fe$_2$As$_2$) ($a = 3.877$ Å, $T_c = 47$ K) [9] and (Ca$_5$(Mg,Ti)$_4$O$_y$)(Fe$_2$As$_2$) ($a = 3.864$ Å, $T_c = 43$ K) [10]. The contraction of the $a$-lattice parameter is reasonable, considering the smaller ionic radius size of Al$^{3+}$ ($R_{\text{Al}} = 0.535$ Å) compared to Mg$^{2+}$ ($R_{\text{Mg}} = 0.720$ Å) and Ti$^{4+}$ ($R_{\text{Ti}} = 0.605$ Å) [18]. Similarly, the $a$-lattice parameter of Al-42622(P) is much smaller compared to the iso-structure compound, (Sr$_4$Sc$_2$O$_6$)(Fe$_2$P$_2$) ($a = 4.016$ Å, $T_c = 17$ K), which contains larger Sc$^{3+}$ ($R_{\text{Sc}} = 0.745$ Å). It is worth stressing that the $a$-parameters of Al-42622(Pn) are smallest among ever-reported Fe-based superconductors. For example, typical materials having short $a$-lattice parameter are FeSe ($a = 3.769$ Å, $T_c = 8$ K)[19], LiFeAs ($a = 3.7914$ Å, $T_c = 18$ K) [3], (Ca,Na)Fe$_2$As$_2$ ($a = 3.880$ Å, $T_c = 26$ K)[20] or DyFeAsO$_{1-y}$ ($a = 3.820$ Å, $T_c = 43$ K)[17].
The c-lattice parameters of Al-42622(\(Pn\)) are also significantly smaller than those of iso-structural 42622(\(Pn\)), such as \((\text{Sr}_4\text{M}_2\text{O}_{6-y})(\text{Fe}_2\text{As}_2)\) (\(c = 15.809\) Å for \(M = \text{Sc}\), 15.683 Å for \(M = \text{Cr}\) and 15.673 Å for \(M = \text{V}\)), \([5, 21]\) due to the smaller ionic radii of \(\text{Ca}^{2+} (R_{\text{Ca}} = 1.00\) Å\) and \(\text{Al}^{3+}\) compared to those of \(\text{Sr}^{2+} (R_{\text{Sr}} = 1.180\) Å\), \(\text{Sc}^{3+} (R_{\text{Sc}} = 0.745\) Å\), \(\text{Cr}^{3+} (R_{\text{Cr}} = 0.615\) Å\) and \(\text{V}^{3+} (R_{\text{V}} = 0.640\) Å\). Small lattice parameters of Al-42622(\(Pn\)) naturally explain why these compounds are synthesized only by HP technique. It also demonstrates the usefulness of HP technique for synthesizing materials possessing extremely smaller unit cell volumes.

Fig. 2(a-b) shows the temperature \((T)\) dependence of the zero-field-cooled (ZFC) and the field-cooled (FC) magnetic susceptibility \((\chi)\) for the (a) Al-42622(As) and (b) Al-42622(P) samples. As shown in the inset Fig. 2, the sample shows superconducting transition with their onset temperature \((T_{\chi-\text{onset}})\) at 26.8 K and 17.0 K for Al-42622(As) and Al-42622(P), respectively. The superconducting volume fraction estimated from \(\chi\) (ZFC) at 5 K without demagnetizing field correction are 115 % for Al-42622(As) and 96 % for Al-42622(P), respectively, ensuring the bulk superconductivity. For Al-42622(As), the reversible region, where ZFC and FC magnetization curves overlap with each other, exisits from \(T_{\chi-\text{onset}}\) to 21.5 K, possibly due to the grain pinning mechanism. The reversible behavior is a unique feature of the FeAs-based superconductors which contain the thick perovskite-type blocking layers, suggesting high anisotropy of their superconducting properties. In contrast, the reversible region of Al-42622(P) is extremely limited. This contrast indicates the difference of the anisotropy between the two systems, possibly because the spacing between Fe layers is shorter for Al-42622(P) compared to Al-42622(As).

In Fig. 3 \(T\)-dependent resistivity \((\rho)\) of (a) Al-42622(As) and (b) Al-42622(P) are shown. Metallic behavior \((d\rho/dT > 0)\) can be seen in the all \(T\)-range. In particular, for
42622(As), no kink in the resistivity, a signature of antiferromagnetic/orthorhombic transition, is observed. Accordingly, we can conclude that the system is away from the parent phase which possesses long-range structural/magnetic order. As indicated in the inset of Fig. 3(a), a broadening of transition (or a two-step transition) is recognized. $T$-range where the resistive broadening occurs seems to coincide with the reversible region observed in the $\chi$-$T$ curve. It may suggest that the broadening results from the flux creep in the reversible region. In Al-42622(P), very high (one order higher than Al-42622(As)) normal state resistivity and broad superconducting transition were observed. This is partly due to the poor sintering of the samples. As indicated in the insets, $T_c^{\rho=\text{onset}}$, $T_c^{\rho=\text{mid}}$, and $T_c^{\rho=0}$ are 28.3, 27.0, 23.0 K for Al-42622(As) and 17.1, 15.6, 6.0 K for Al-42622(P), respectively.

Our data indicate that the Al-42622($Pn$) systems have the shortest $a$-lattice parameters among all the Fe-based superconductors. One would naively expect that the shrinkage of the $a$-lattice parameters causes the elongation of the Fe$Pn_4$ tetrahedra along the $c$-axis. It is indeed confirmed by the neutron powder diffraction on Al-42622(As). Table I show the atomic positions of Al-42622(As) determined by the Rietveld analysis of the neutron powder diffraction. The calculated Fe-As-Fe bond angle $\alpha$ is 102.1(1)$^\circ$. This value is much smaller than those of any other Fe-pnictide superconductors. For example, $\alpha$ of the $Ln$FeAsO-based materials ranges from 113$^\circ$ ($Ln = La, T_c = 27$ K) to 108$^\circ$ ($Ln = Dy, T_c = 52$ K). Similarly, $\alpha$ of (Ba,K)Fe$_2$As$_2$ ($T_c = 38$ K) is 109$^\circ$. $\alpha$ of LiFeAs ($T_c = 18$ K) is rather smaller, but still 104$^\circ$. As for those containing Ca-based perovskite-derived blocking layers, $\alpha$ ranges from 107 $^\circ$ for Ca$_5$(Mg,Ti)$_4$O$_{11}$Fe$_2$As$_2$ [10] to 109 $^\circ$ for Ca$_4$(Sc,Ti)$_3$O$_8$Fe$_2$As$_2$ [8], estimated from the relation between the $a$-lattice parameter and $h_{Pn}$ in ref.[22]. Empirically it is pointed out that the highest $T_c$ materials possess $\alpha$ close to 109.5 $^\circ$, an angle where the FeAs$_4$
tetrahedron forms the regular shape. The relatively lower $T_c$ of 28.3 K for Al-42622(As) compared to other Ca-based perovskite counterparts with $T_c$'s reaching 47 K is likely due to the elongation of the FeAs$_4$ tetrahedron. It should be also remarked that the height of As atoms relative to the Fe layers ($h_{Pn}$) is 1.500 Å, which is the highest value among the Fe-pnictide superconductors.

In contrast, $T_c$ of 17 K for Al-42622(P) is much higher than most of the existing FeP-based superconductors, such as LaFePO ($T_c = 4$ K)[23], LiFeP ($T_c = 6$ K)[24], etc. The only material which exhibits comparable $T_c$ is (Sr$_4$Sc$_2$O$_6$)(Fe$_2$As$_2$) (Sc-42622(P)), which shares the same crystal structure as Al-42622(P). Note that their $a$-lattice parameters are significantly different from each other, $a = 3.692$ Å for Al-42622(P) and $a = 4.016$ Å for Sc-42622(P), respectively. The fact that $T_c$ does not change between these two systems suggests that $T_c$ of the FeP-based superconductors is rather insensitive to the structural parameters, contrary to the FeAs-based counterpart. Another possibility is that $T_c$ of the 42622(P) system takes its maximum value when the $a$-lattice parameter falls between 3.692 Å and 4.016 Å. In this regard, it is intriguing to synthesize an alloy of Al-42622(P) and Sc-42622(P) and check whether one can enhance its $T_c$.

In summary, we have utilized HP technique to synthesize (Ca$_4$Al$_2$O$_{6-y}$)(Fe$_2$P$_{n_2}$) ($Pn$ = As and P), which exhibit superconductivity at 28.3 K and 17.1 K for $Pn$=As and P, respectively. These materials possess the shortest $a$-lattice parameters, correspondingly the smallest $\alpha$ and the highest $h_{Pn}$ among the Fe-pnictide superconductors.

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Figure captions

Figs. 1 X-ray diffraction patterns of (a) Ca$_4$Al$_2$O$_6$$_y$Fe$_2$As$_2$ and (b) Ca$_4$Al$_2$O$_6$$_y$Fe$_2$P$_2$ samples.

Figs. 2 Temperature ($T$) dependence of susceptibility ($\chi$) of (a) Ca$_4$Al$_2$O$_6$$_y$Fe$_2$As$_2$ and (b) Ca$_4$Al$_2$O$_6$$_y$Fe$_2$P$_2$ samples. Data near the superconducting transitions. $T_c^{\chi-,onset}$ is determined from the intersection of the two extrapolated lines; one is drawn through $\chi$ in the normal state just above $T_c$, and the other is drawn through the steepest part of $\chi$ in the superconducting state.

Figs. 3 $T$-dependence of resistivity ($\rho$) of (a) Ca$_4$Al$_2$O$_6$$_y$Fe$_2$As$_2$ and (b) Ca$_4$Al$_2$O$_6$$_y$Fe$_2$P$_2$ samples. Data near the superconducting transitions and a determination of $T_c$ are shown in the insets. $T_c^{\rho-,onset}$ is determined from the intersection of the two lines; one is drawn through $\rho$ in the normal state just above $T_c$, and the other is drawn through the steepest part of $\rho$ in the superconducting state. $T_c^{\rho-,mid}$ is 50 % drop of $T_c^{\rho-,onset}$ and $T_c^{\rho=0}$ is zero resistivity.
Table I. Atomic parameters of Al-42622(As) (space group $P4/nmm$) determined by a Rietveld refinement of neutron powder diffraction data at room temperature. $B$ is the isotropic atomic displacement parameter. The lattice parameters are $a = 3.7133(1)$ Å and $c = 15.4035(6)$ Å. The $R$-factor is $R_{wp} = 5.261$.

| Atom | site | $x$  | $y$  | $z$  | $B$ (Å) |
|------|------|------|------|------|---------|
| Fe   | 2a   | 3/4  | 1/4  | 0.0  | 0.47(5) |
| As   | 2c   | 1/4  | 1/4  | 0.0974(2) | 0.66(8) |
| Ca(1) | 2c | 1/4  | 1/4  | 0.7997(3) | 0.18(9) |
| Ca(2) | 2c | 1/4  | 1/4  | 0.5819(3) | 0.33(11) |
| Al   | 2c   | 1/4  | 1/4  | 0.3181(4) | 0.50(14) |
| O(1) | 4f   | 3/4  | 1/4  | 0.2969(2) | 0.50(6) |
| O(2) | 2c   | 1/4  | 1/4  | 0.4340(3) | 0.69(9) |
Intensity (arb. units)

(a) (Ca₄Al₂O₆₋ₓ)(Fe₂As₂)

(b) (Ca₄Al₂O₆₋ₓ)(Fe₂P₂)

Figure 1 (a-b)
Figure 2 (a-b)

(a) \((\text{Ca}_4\text{Al}_2\text{O}_{6-y}\text{)}(\text{Fe}_2\text{As}_2)\)

\(T_c^{\chi_{\text{onset}}} = 26.8\) K

\(T_c^{\chi_{\text{onset}}} = 21.5\) K

(b) \((\text{Ca}_4\text{Al}_2\text{O}_{6-y}\text{)}(\text{Fe}_2\text{P}_2)\)

\(T_c^{\chi_{\text{onset}}} = 17.0\) K
Figure 3 (a-b)