Effect of non-magnetic rare earth substitution for A site in mixed anion APX superconductors

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Abstract. We report the improvement of superconducting transition temperature ($T_c$) by non-magnetic rare earth atom substitution for A site in APX-based Zr(P, S), Hf(P, Se), and Hf(P, S) superconductors. The partial non-magnetic rare earth Lu atom substitution at Zr site of ZrPS, as opposed to the case of Zr(P, Se)$_2$, shows that lattice constants $a$ and $c$ decrease monotonically with increasing nominal substitution $y$. It is shown that the maximum $T_c$ for ZrPS was increased from 3.70 K to 5.36 K. In HfP$_{1.35}$Se$_{0.45}$, when Hf site is partially substituted with Lu atoms (or Y atoms), lattice constant $a$ shrinks and $c$ expands monotonically with increasing nominal rare earth substitution $y$. $T_c$ was also increased from 4.88 K to 5.89 K. In HfP$_{1.45}$Se$_{0.55}$, when Hf site is partially substituted with Lu atoms (or Y atoms), lattice constant $a$ shrinks slightly and $c$ expands monotonically with increasing $y$. $T_c$ was also increased from 3.16 K to 5.86 K. In this paper, the doping behaviour by partial substitution and the increase of $T_c$ is discussed.

1. Introduction

The mixed anion PbFCl-type intermetallic AP$_2$X$_i$ (A=Zr, Hf, X=S and Se) superconductors has a tetragonal layer-like structure consisting of alternately stacked A-(P, X) frame units and P square net layers along the c-axis (see Figure 1). This crystal structure is the same as the topological Dirac ZrSiS semiconductor [1].

Using polycrystalline sample study, many new superconductors such as Zr-P-Se, Zr-P-S, Hf-P-Se, and Hf-P-S and their superconducting properties were reported [2, 3]. In ZrP$_2$Se$_4$, superconducting transition temperature ($T_c$) increases with increasing nominal composition $x$ at first, and reaches its maximum $T_c$ value (6.31 K) at around nominal composition $x=0.75$, after which it decreases monotonically [2, 3]. In AP$_2$X$_i$ (A=Zr, Hf, X=S and Se), $T_c$ was controlled by the nominal substitution concentration $x$ of (P, X) site in A-(P, X) frame units. The resultant phase diagrams are thus dome-like substitution dependence, as seen in high- $T_c$ cuprates [4] or iron-based superconductors [5]. From these results, an enhancement of $T_c$ was revealed by increasing the bonding length between P-P and nominal substitution concentration $x$ of (P, X) site in A-(P, X) frame units.

By non-magnetic rare earth (Ln= La, Y and Lu) substitution of Zr site for Zr-(P, X) frame units in ZrP$_2$Se$_4$, $T_c$ of (Zr$_{1-x}$Ln$_x$)P$_2$Se$_4$ shows also dome-like $y$ dependence and implying $T_c$ was controlled
by nominal non-magnetic rare earth concentration \( y \) [6, 7]. From these results, \( T_c \) may rise further if \( Zr \) is substituted by trivalent ions, which dissolve well for \( Zr-(P, Se) \) frame units.

In this study, \((A_{1-y}Ln_y)P_{2-x}X_x (A=Zr, Hf, Ln = Lu and Y, X=S and Se)\) polycrystalline samples were synthesized by a high-pressure technique using a cubic anvil press.

![Figure 1](image)

**Figure 1.** The crystal structure for mixed anion intermetallic PbFCl-type \( AP_{2-x}X_x (A=Zr, Hf, X=S, Se)\) superconductors. This PbFCl-type superconductor has a tetragonal layer-like structure consisting of alternately stacked \( A-(P, X)\) frame units and \( P \) square net layers along the \( c\)-axis.

2. Experiment and results

2.1. Experiment

\((A_{1,y}Ln_y)P_{2-x}X_x (A=Zr, Hf, Ln = Lu and Y, X=S and Se)\) polycrystalline samples were synthesized by a high-pressure technique using a cubic anvil press. \( Zr \) (powder, 98 %), \( Hf \) (powder, 99.9 %), \( Lu \) (powder, 99.9 %), \( Y \) (powder, 99.9 %), \( P \) (grain, 99.999%) and \( Se \) (grain, 99.999%) were mixed and pelletized in a nitrogen-filled glove box. The pellets (total mass: \( \sim 0.35 \) g) were put into BN crucibles and heated at \( \sim 1,425 \) \( ^\circ\)C \( \sim 1,651 \) \( ^\circ\)C under a pressure of approximately \( \sim 2.0 \) GPa for 1.0 h and then rapidly quenched to room temperature. Starting nominal compositions were \((Zr_{1-y}Ln_y)PS (Ln = Lu, Y), (Hf_{1-y}Ln_y)P_{1.5}Se_{0.45} (Ln = Lu, Y), and (Hf_{1-y}Ln_y)P_{1.42}S_{0.55} (Ln = Lu, Y)\), respectively.

The crystal structure was examined using the powder X-ray diffraction (XRD) technique. The intensity data were measured with a Rigaku Ultima-IV diffractometer using Cu K\( \alpha \) radiation and were collected over a 2\( \theta \) range of \( 3 \sim 80^\circ \) with a step width of 0.02\( ^\circ \) at 40 kV and 40 mA and a counting rate of 8.0\( ^\circ \) / minutes. Lattice parameters are calculated by least squares fitting to the positions of the reflection peaks in the diffraction patterns between \( 3 \sim 80^\circ \).

The temperature (\( T \)-) dependence of the DC magnetic susceptibility \( \chi (T) \) was measured at 20 Oe using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS). The data were collected during warming after zero-field cooling (Z.F.C) and then during field cooling (F.C).
2.2.1 Results in \((Zr_{1-y}Ln_{y})PS (Ln = Lu, Y)\) system.

In \(Zr(P_2 Se_3)\), single phase range was \(0.4 \leq y \leq 0.8\) for nominal Se substitution [3]. In \(Zr(P_2 S_3)\), single phase was \(0.4 \leq y \leq 0.6\) for nominal S substitution. In this study, we synthesized pseudo-quaternary intermetallic \((Zr_{1-y}Ln_{y})P_{1.5}S_{0.5}\) \((Ln = Lu and Y)\) system in advance, but it was difficult to judge the improvement in \(T_c\). Then, we synthesized \((Zr_{1-y}Ln_{y})PS (Ln = Lu and Y)\) system.

Figure 2(a) and 2(b) shows powder X-ray diffraction for obtained pseudo-quaternary intermetallic \((Zr_{1-y}Ln_{y})PS (Ln = Lu and Y)\) polycrystalline samples taken at room temperature. The impurity phase tends to precipitate with the increasing \(Ln\) atom substitution amount.

Figure 3(a) show the dependence of lattice parameters on \(y\). Both the \(a\)-axis and \(c\)-axis tend to monotonically shrink with increasing \(y\). These lattice parameters for the \(a\)-axis and \(c\)-axis show a linear behaviour and fulfil Vegard’s law. The changes in \(a\)-axis and \(c\)-axis length due to partial substitution for \(Zr\) sites by \(Y\) atoms are larger than these for \(Zr\) sites by \(Lu\) atoms. The 9-coordinate \(Zr\) metal atom radius were 1.587 Å, \(Lu\) metal atom radius were 1.727 Å and \(Y\) metal atom radius were 1.785 Å, respectively [8]. It is considered that \(Y\) atom substitution for \(Zr\) site in \(ZrPS\) distorts the crystal structure more than \(Lu\) atom substitution.

![Figure 2(a)](image_url)
**Figure 2(a)** Powder X-ray diffraction pattern of obtained \((Zr_{1-y}Ln_{y})PS (Ln = Lu)\) polycrystalline samples taken at room temperature. **2(b)** Powder X-ray diffraction pattern of obtained \((Zr_{1-y}Ln_{y})PS (Ln = Y)\) polycrystalline samples taken at room temperature.
With increasing the Lu atom substitution, $T_c$ shows a maximum at $y \approx 0.40$ (see Figure 3(c)). $T_c$ reached 6.36 K for (Zr$_{0.60}$Lu$_{0.40}$)PS and 5.36 K for (Zr$_{0.50}$Y$_{0.50}$)PS. These $T_c$ values are clearly higher.
than $T_c$ value of Zr(P, S)e value (5.0 K) [2]. It was clarified that controlling $T_c$ by carrier doping associated with non-magnetic rare earth atom substitution for Zr site is more effective than controlling $T_c$ by increasing P-P distance.

2.2.2 Results in (Hf$_{1-y}$Ln$_y$)P$_{1.55}$Se$_{0.45}$ ($Ln = Lu, Y$) system

The Zr metal atom radius and the Hf metal atom radius are 1.587 Å and 1.575 Å, respectively, which are almost the same size [8]. In Hf(P$_z$Se$_z$), single phase range $x$ was very narrow around $\approx 0.4$ for nominal Se substitution.

Figure 4(a) show the dependence of lattice parameters on $y$. In HfP$_{1.55}$Se$_{0.45}$, when Hf site is partially substituted with Lu atoms, lattice constant $a$-axis shrinks and $c$-axis expands monotonically with increasing $y$.

$T_c$ shows a maximum at $y \sim 0.40$ for Lu atom substitution and at $y \sim 0.20$ for Y atom substitution (Figure 4(b)). The $T_c$ reached at 5.89 K for (Hf$_{0.60}$Lu$_{0.40}$)P$_{1.55}$Se$_{0.45}$ and 4.96 K for (Hf$_{0.80}$Y$_{0.20}$)P$_{1.55}$Se$_{0.45}$, respectively. Maximum $T_c$ value for (Hf$_{1-y}$Lu$_y$)P$_{1.55}$Se$_{0.45}$ was higher than $T_c$ value for Hf(P, Se)$_2$ (5.5 K) [2]. In (Hf$_{1-y}$Ln$_y$)(P$_{1.55}$Se$_{0.45}$), $T_c$ is improved by the effect of the carrier concentration control of Hf site in Hf-(P, Se) frame units accompanying non-magnetic rare earth atom substitution.

**Figure 4(a)** The $y$ dependence of lattice parameters in (Hf$_{1-y}$Ln$_y$)P$_{1.55}$Se$_{0.45}$ ($Ln = Lu$ and Y). **4(b)** The $y$ dependence of $T_c$ for (Hf$_{1-y}$Ln$_y$)P$_{1.55}$Se$_{0.45}$ ($Ln = Lu$ and Y).
2.2.3 Results in (Hf$_{1-y}$Ln$_{y}$)P$_{1.45}$S$_{0.55}$ (Ln = Lu, Y) system

In Hf(P$_{2-x}$S$_x$), single phase range $x$ was very narrow around $x=0.55$ for nominal S substitution. Figure 5(a) show the dependence of lattice parameters on $y$. In HfP$_{1.45}$S$_{0.55}$, when Hf site is partially substituted with Lu atoms, lattice constant $a$-axis shrinks slightly and $c$-axis expands monotonically with increasing $y$.

$T_c$ shows a maximum at $y \approx 0.50$ for Lu atom substitution and at $y \approx 0.40$ for the Y atom substitution (Figure 5(b)). $T_c$ reached at 5.89 K for (Hf$_{0.60}$Lu$_{0.40}$)P$_{1.45}$S$_{0.55}$ and 4.72 K for (Hf$_{0.60}$Y$_{0.40}$)P$_{1.45}$S$_{0.55}$. These $T_c$ values were clearly higher than $T_c$ value of Hf(P, S)$_2$ (3.16 K) [2]. In (Hf$_{1-y}$Ln$_y$)P$_{1.45}$S$_{0.55}$, $T_c$ is improved by the effect of the carrier concentration control of Hf site in Hf-(P, S) frame units accompanying non-magnetic rare earth atom substitution.

![Figure 5(a)](image1)

**Figure 5(a)** The $y$ dependence of lattice parameters in (Hf$_{1-y}$Ln$_y$)P$_{1.45}$S$_{0.55}$ (Ln = Lu and Y).

![Figure 5(b)](image2)

**Figure 5(b)** The $y$ dependence of $T_c$ for (Hf$_{1-y}$Ln$_y$)P$_{1.45}$S$_{0.55}$ (Ln = Lu and Y).

3. Summary

From this study, it has been clarified that $T_c$ is improved by the effect of the carrier concentration control of A site in A-(P, X) frame units of $AP_{2-x}X_x$ (A = Zr, X = Se) accompanying non-magnetic rare earth atom substitution.
The maximum $T_c$ was increased from 3.70 K to 6.36 K by Lu atom substitution for Zr site in ZrPS. In HfP$_{1.55}$Se$_{0.45}$, $T_c$ was also increased from 4.88 K to 5.89 K by Lu atom substitution for Hf site. In HfP$_{1.45}$S$_{0.55}$, $T_c$ was also increased from 3.16 K to 5.86 K by Lu atom substitution for Hf site.

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