Superconductivity in Se-doped La$_2$O$_2$Bi$_2$Pb$_2$S$_6$–$x$Se$_x$ with a Bi$_2$Pb$_2$Ch$_4$-type thick conducting layer

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Abstract – La$_2$O$_2$Bi$_2$Pb$_2$S$_6$ is a layered Bi-based oxychalcogenide with a thick four-layer–type conducting layer. Although La$_2$O$_2$Bi$_2$Pb$_2$S$_6$ is a structural analogue of La$_2$O$_2$Bi$_3$Ag$_6$, which is a superconductor, insulating behavior has been observed in La$_2$O$_2$Bi$_2$Pb$_2$S$_6$ at low temperatures, and no superconductivity has been reported. Herein, we demonstrate superconductivity in La$_2$O$_2$Bi$_2$Pb$_2$(Se$_{0.5}$,S$_{0.5}$)$_6$ via partial substitution of Se in the S sites. Owing to the Se doping, the normal state electrical resistivity of La$_2$O$_2$Bi$_2$Pb$_2$(Se$_{0.5}$,S$_{0.5}$)$_6$ at low temperatures was dramatically suppressed, and superconductivity was observed at a transition temperature ($T_c$) of 1.2 K for $x = 0.5$. $T_c$ increased with increasing Se concentration: $T_c = 1.9$ K for $x = 1.0$. By applying high pressure for $x = 1.0$, bulk superconductivity was confirmed and the $T_c$ increased up to 3.6 K at 0.89 GPa.

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Introduction. – Layered compounds have been widely studied in the search for new superconductors since the discovery of (high-transition-temperature) high-$T_c$ cuprates [1]. After the cuprates, Fe-based and BiCh$_2$-based superconductors (Ch: S and Se) have been discovered, and many others have been synthesized [2–5]. In those layered superconductors, the important structure is a superconducting layer commonly contained in the layer stacking: a CuO$_2$ layer in cuprates and an FeAs or FeSe layer in Fe-based superconductors [6–8]. In BiCh$_2$-based superconductors, a BiCh$_2$ layer is the basic superconducting layer [3–5].

Since the discovery of BiS$_2$-based superconductors, namely, Bi$_4$O$_4$S$_3$ and La(O,F)BiS$_2$, in 2012 [3,4], many related superconductors with BiS$_2$ [9–18], BiSe$_2$ [19,20], or Bi(S,Se)$_2$ superconducting layers [21–24] have been synthesized. The crystal structure of BiCh$_2$-based compounds has an interesting feature, that is, the presence of a van der Waals gap between two BiCh$_2$ layers. The space in this gap could be used to create new BiCh$_2$-type compounds with a thick conducting layer [25–27].

As studied in cuprates, stacking many conducting planes along the c-axis could be a promising way to achieve a higher $T_c$ in a layered system [6,28,29]. Hence, layered oxychalcogenides, such as La$_2$O$_2$M$_4$I$_6$ (M: metals like Bi, Pb, Sn, and Ag), with a thicker four-layer–type conducting layer of M$_4$S$_6$ have been synthesized with the expectation of demonstrating a higher $T_c$ than that observed in two-layer–type BiCh$_2$-based superconductors [25–27]. The four-layer–type La$_2$O$_2$M$_4$I$_6$ compounds typically have a tetragonal structure with a space group of P4/nmm. The structure can be regarded as a stacking of La$_2$O$_2$, BiS$_2$, M$_2$S$_2$, and BiS$_2$ layers in sequence [26]; a crystal structure image for M = Pb is displayed in fig. 1(d). A rock-salt–type M$_2$S$_2$ layer is inserted between two BiS$_2$ layers where a van der Waals gap would exist in a two-layer–type LaOBI$_2$S$_2$ (described as La$_2$O$_2$Bi$_2$S$_4$ for one unit cell). In fact, the outer layers are basically BiS$_2$ layers, and the inner rock-salt layer is occupied by M and S ions. From a structural viewpoint, the composition can be described as La$_2$O$_2$Bi$_2$M$_2$S$_6$.

Recently, we observed superconductivity with a $T_c$ of 0.5 K in La$_2$O$_2$Bi$_3$AgS$_6$ (M = Bi, Ag) [30]. Furthermore, we have studied the effects of doping on the superconductivity of the La$_2$O$_2$Bi$_3$AgS$_6$ system. Partial substitution of Ag by Sn increased $T_c$ up to 2.5 K in La$_2$O$_2$Bi$_3$Ag$_{0.5}$Sn$_{0.5}$S$_6$ [31]. Additionally, partial Se substitution for S resulted in bulk superconductivity at 3.5 K in La$_2$O$_2$Bi$_3$Ag$_{0.5}$Sn$_{0.5}$S$_{5.7}$Se$_{0.3}$ [31]. $T_c$ further increased up to 4.0 K with RE-site substitution in

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La$_{2-x}$RE$_x$O$_2$Bi$_3$As$_{0.6}$S$_{0.4}$S$_6$ (RE = Eu, Nd, and Pr) compounds [32,33]. Based on these recent developments with regard to new four-layer–type Bi-based superconductors, we found that the chemical pressure effect was useful for inducing bulk superconductivity in La$_2$O$_2$Bi$_2$M$_2$S$_6$ systems. The chemical pressure effect has been proposed as one of the essential parameters for the emergence of bulk superconductivity in typical BiCh$_2$-based compounds [14,21–24,34]. In the RE(O,F)BiCh$_2$ system, in-plane chemical pressure, which was tuned by RE-site and/or Ch-site substitutions, suppresses in-plane local disorder, which is unfavorable for the emergence of bulk superconductivity [35–39]. As mentioned previously, four-layer–type La$_2$O$_2$Bi$_2$M$_2$S$_6$ compounds are also sensitive to chemical pressure effects. Therefore, the chemical pressure could be useful for further exploration of new four-layer–type superconductors.

In this study, we have investigated the effects of substituting Se in the S sites in La$_2$O$_2$Bi$_2$Pb$_2$S$_6$, which was the first four-layer–type compound synthesized by Sun et al. and proposed as a promising thermoelectric material [25]. Although theoretical calculations suggested that La$_2$O$_2$Bi$_2$Pb$_2$S$_6$ is a metal [26], the obtained samples showed insulating behavior at low temperatures [25]. We have investigated the effects of partial substitutions of the Pb sites by Ag, Cd, In, Sn, and Sb, but all of the examined samples showed insulating characteristics at low temperatures. Therefore, in this study, we have investigated the effects of substituting Se in the S sites in La$_2$O$_2$Bi$_2$Pb$_2$S$_6$–xSe$_x$. Owing to the Se substitution, the insulating behavior was suppressed, and electrical resistivity that was apparently lower than that of pure La$_2$O$_2$Bi$_2$Pb$_2$S$_6$ was observed even at the lowest temperature of our system (T = 0.4 K). We observed superconductivity at $T_c = 1.2$ K for $x = 0.5$ and $T_c = 1.9$ K for $x = 1.0$.

**Experimental details.** – Polycrystalline samples of La$_2$O$_2$Bi$_2$Pb$_2$(S$_{6-x}$Se$_x$) ($x = 0$, 0.5, and 1.0) were prepared by a solid-state reaction method. Powders of La$_2$S$_3$ (99.99%), Bi$_2$O$_3$ (99.9%), Pb (99.99%), and Bi$_2$Se$_3$ (99.99%, pre-synthesized from Bi and Se) with a nominal composition of La$_2$O$_2$Bi$_2$Pb$_2$(S$_{6-x}$Se$_x$) ($x = 0$, 0.5, and 1.0) were mixed using a pestle and mortar, pelletized, sealed in an evacuated quartz tube, and heated at 690°C for 15 h. The heated samples were reground, pelletized, and heated at 740°C for 35 h. The optimal annealing conditions and the phase purity of the prepared samples were examined using laboratory X-ray diffraction (XRD) with a Cu-K$_\alpha$ radiation by a conventional $\theta$–$2\theta$ method. To discuss the lattice structure, Rietveld analyses were performed with RIETAN-FP [40]. We assumed perfect site selectivity of Bi and Pb based on the previous structural analyses for La$_2$O$_2$Bi$_2$Pb$_2$S$_6$ [26]. As the obtained XRD intensity and profile were not sufficient for the determination of displacement parameters, we have performed refinements with fixed isotropic displacement parameters. A schematic image of the crystal structure was drawn using VESTA [41]. The actual composition of the synthesized samples was investigated by energy dispersive X-ray spectroscopy (EDX) on a scanning electron microscope SEM (TM-3030 (Hitachi)). The electrical resistivity down to $T = 0.5$ K was measured by a four-probe method using a $^3$He probe platform on the Physical Property measurement system (PPMS: Quantum Design). The Seebeck coefficient was measured by a four-probe method at room temperature on ZEM-3 (advance RIKO). The temperature dependence of the Hall coefficient was measured with a standard five-prove configuration on PPMS. The temperature dependence of magnetic susceptibility was measured by a SQUID (superconducting interference devise) magnetometer (MPMS3: Quantum Design) with an applied magnetic field of 1 mT. For high-pressure measurements, a piston-cylinder–type pressure cell was used. Applied pressure was estimated using a $T_c$ of Pb.

**Results and discussion.** – Figure 1(a) shows room temperature powder XRD patterns for La$_2$O$_2$Bi$_2$Pb$_2$(S$_{6-x}$Se$_x$) ($x = 0$, 0.5, and 1.0) compounds. The obtained samples are crystallized in a tetragonal crystal structure with a space group of P4/nmm. For all the samples, the main phase was La$_2$O$_2$Bi$_2$Pb$_2$S$_6$–xSe$_x$. As indicated by the symbol, a La$_2$O$_2$S impurity phase was observed. The refined lattice constant for the La$_2$O$_2$S phase was $a = 4.047(2)$ Å and $c = 6.944(3)$ Å for $x = 0$ and $a = 6.0498(6)$ Å and $c = 6.9502(9)$ Å, which is consistent with the known value for La$_2$O$_2$S with a space group of P-3m1). In addition, very small impurity peaks due to PbO, Pb$_2$Bi$_2$Ch$_5$, and/or PbBi$_2$Ch$_4$ were observed. The impurity phase did not disappear when heat treatment conditions were changed. Therefore, we have investigated crystal structure and physical properties of the system with multi-phase samples. We performed two-phase Rietveld analyses to determine lattice constants for all the obtained samples. For convenience in the superconducting property part, we mention the characteristics of the impurity phases incorporated in the examined samples. La$_2$O$_2$S and PbO is insulators. Pb$_2$Bi$_2$Ch$_5$, and PbBi$_2$Ch$_4$ are semiconductors with Pb$^{2+}$ and Bi$^{3+}$. Although a band gap of these phases could be modified by the Se concentration of the Ch site, these systems should be basically semiconducting. Using a database (SuperCon, NIMS database: https://supercon.nims.go.jp/), we have checked that those compositions are not superconducting.

The results of the Rietveld refinement are summarized in table 1. The lattice constants $a$ and $c$ increase with Se substitution for $x = 0.5$, but the lattice constants for $x = 1.0$ were comparable to those for $x = 0.5$. Those shifts in lattice constants are consistent with the observed peak shifts, as shown in fig. 1(b), (c). Based on such facts, we consider the solubility limit of Se in S to be less than $x = 1.0$. We have analyzed the actual compositions of
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Fig. 1: (a) Powder XRD patterns for all the samples of La$_2$O$_2$Bi$_2$Pb$_2$S$_{6-x}$Se$_x$. The peak of the La$_2$O$_2$S impurity phase was indicated by an asterisk symbol. The numbers in the figures are Miller indices of typical peaks. (b) Zoomed profiles of 006 peaks. (c) Zoomed profiles of 110 peaks. (d) Schematic image of La$_2$O$_2$Bi$_2$Pb$_2$S$_{6}$Se$_{0.5}$ crystal structure drawn with parameters obtained from the Rietveld analysis. (e) Powder XRD pattern and the Rietveld fitting for the La$_2$O$_2$Bi$_2$Pb$_2$S$_{6}$Se$_{0.5}$ sample. The Rietveld analysis was performed by two-phase refinement with a La$_2$O$_2$S impurity phase as a second phase.

Elements at the conducting layer in La$_2$O$_2$Bi$_2$Pb$_2$S$_{6-x}$Se$_x$ ($x = 0, 0.5$ and $1.0$) by EDX analysis at five analysis points (table 1). The obtained compositions for the sample are almost the same as the initial nominal compositions, but the Se concentration for $x = 1.0$ is slightly lower than the nominal value. However, the Se concentrations were different for the samples with $x = 0.5$ and $1.0$, and the superconducting property was also different. Therefore, for clarity to the readers, we labelled the samples according to the initial nominal compositions in this paper.

Figure 1(c) shows the result of Rietveld refinement for $x = 0.5$. To refine the XRD pattern for an Se-doped sample, we needed to determine the S site where Se is doped. The inset of fig. 1(e) shows the reliability factor ($R_{wp}$) obtained for the cases with no Se and those with Se-doped S1, S2, and S3 sites (see fig. 1(d) for the label of S sites). $R_{wp}$ decreases with incorporation of Se at the S sites and becomes the lowest when Se substitution at the in-plane S1 site was assumed. Although we need further detailed structural parameters to draw firm conclusions regarding the Se-doping site, herein, we consider that Se was selectively substituted at the S1 site. This assumption is consistent with the emergence of metallic conductivity and superconductivity in Se-doped samples, which can be explained by the concept of in-plane chemical pressure via Se substitution at the S1 sites of BiS$_2$ layers [21–24,34].

Figure 2 shows the temperature dependence of the electrical resistivity ($\rho(T)$) from 300 to 2 K for La$_2$O$_2$Bi$_2$Pb$_2$S$_6$. The electrical resistivity largely increases with decreasing temperature, which is in agreement with the typical behavior of semiconductors. The result is consistent with a previous report by Sun et al. [25]. However, the band calculation has suggested a metallic band structure for La$_2$O$_2$Bi$_2$Pb$_2$S$_6$ [26]. The inconsistency may imply that the semiconducting-like behavior of electrical resistivity is caused by anomalous carrier localization, not from characteristics of a band insulator.

Figure 3(a) shows the temperature dependence of electrical resistivity ($\rho(T)$) from 300 to 0.5 K for the Se-doped La$_2$O$_2$Bi$_2$Pb$_2$S$_{6-x}$Se$_x$ ($x = 0.5$ and $1.0$) samples. At 300 K, the electrical resistivity is clearly lower than that of La$_2$O$_2$Bi$_2$Pb$_2$S$_6$. Furthermore, the semiconducting-like behavior was dramatically suppressed by Se substitution. The normal-state resistivity of Se-doped compounds still shows a slight increase with decreasing temperature, which may be due to weak carrier localization, which is typically observed in BiS$_2$-based systems. The weak carrier localization seems to be suppressed with increasing Se concentration from $x = 0.5$ to $x = 1.0$. The changes in resistivity caused by Se substitution can be understood by the effects of in-plane chemical pressure, which was introduced previously. For two-layer–type BiCh$_2$-based compounds, it has been extensively demonstrated that in-plane chemical pressure effects successfully suppressed the in-plane local disorder of the conducting layer [14,21–24,34]. Thus, we consider that the semiconducting-like behavior observed for $x = 0$ and the weak localization behavior observed for Se-doped samples are both related to the presence of local disorders in the BiS$_2$ layers in La$_2$O$_2$Bi$_2$Pb$_2$S$_{6-x}$Se$_x$. To investigate the local disorder, precise estimation of the displacement parameters using synchrotron X-ray diffraction or X-ray absorption spectroscopy, or single-crystal structural analysis. So far, we have not succeeded in the growth of single crystals or single-phase polycrystalline samples of La$_2$O$_2$Bi$_2$Pb$_2$S$_{6-x}$Se$_x$, which can be used for the investigation on the local disorder. Therefore, the scenario of the suppression of localized carriers is based on the analogy to the cases of BiS$_2$-based systems, in which huge displacements of in-plane atoms caused by the presence of Bi lone pairs were suppressed by Se substitution for the in-plane S site (in-plane chemical pressure effect).

We observed superconductivity in both the Se-doped samples, as shown in fig. 3(b), which is the zoomed view of fig. 3(a) near the superconducting transition region. $T_c$ increases with increasing Se concentration in La$_2$O$_2$Bi$_2$Pb$_2$S$_{6-x}$Se$_x$. The zero-resistivity $T_c$ ($T_c^{\text{zero}}$) is 1.2 K for $x = 0.5$ and 1.9 K for $x = 1.0$. Thus far, superconductivity in La$_2$O$_2$Bi$_2$M$_2$S$_6$ has been observed for La$_2$O$_2$Bi$_3$AgS$_6$-based compounds [30–33]. La$_2$O$_2$Bi$_3$AgS$_6$
Table 1: Rietveld analysis results, lattice constants, reliability factor $R_{wp}$, and mass fraction of the major phase to the impurity phase in La$_2$O$_2$Bi$_2$Pb$_x$S$_6$ ($x = 0, 0.5,$ and 1.0).

| Sample label | La$_2$O$_2$Bi$_2$Pb$_2$S$_6$ ($x = 0$) | La$_2$O$_2$Bi$_2$Pb$_2$S$_{5.5}$S$_{0.5}$ ($x = 0.5$) | La$_2$O$_2$Bi$_2$Pb$_2$S$_{5.0}$S$_{1.0}$ ($x = 1.0$) |
|-------------|---------------------------------|---------------------------------|---------------------------------|
| $a$ (Å)     | 4.0920(4)                       | 4.1039 (3)                      | 4.1038 (4)                      |
| $c$ (Å)     | 19.680(2)                       | 19.7682 (14)                   | 19.777 (2)                      |
| $R_{wp}$    | 12.8%                           | 10.5%                           | 11.7%                           |
| Mass fraction of the main phase to La$_2$O$_2$S | 95%                             | 95%                             | 82%                             |
| Actual composition (EDX) | Bi$_{1.98(3)}$Pb$_{2.09(5)}$S$_{6.04(9)}$ | Bi$_{2.01(1)}$Pb$_{1.89(5)}$S$_{5.52(8)}$S$_{0.46(3)}$ | Bi$_{2.04(1)}$Pb$_{1.95(2)}$S$_{5.18(5)}$S$_{0.81(10)}$ |

Fig. 2: Temperature ($T$) dependence of electrical resistivity ($\rho(T)$) from 300 K to 2 K for La$_2$O$_2$Bi$_2$Pb$_2$S$_6$.

La$_2$O$_2$Bi$_2$Pb$_2$S$_6$ ($x = 0$) exhibits metallic conductivity without Se substitution but shows a CDW-like (charge density wave-like) anomaly in $\rho(T)$. Although the origin of the anomaly has not been clarified, it could be related to the anomalous insulating behavior observed in La$_2$O$_2$Bi$_2$Pb$_2$S$_6$. The emergence of metallic conductivity and superconductivity via Se substitution in La$_2$O$_2$Bi$_2$Pb$_2$S$_{6-x}$Se$_x$ could provide us with important information for the further development of four-layer–type Bi-based superconductors.

Figures 4(a) and (b) show the temperature dependence of electrical resistivity under various magnetic fields ($\rho(T, B)$) for La$_2$O$_2$Bi$_2$Pb$_2$S$_{6-x}$Se$_x$ ($x = 0.5$ and 1.0). $T_c$ shifts towards a lower temperature with an increase in the magnetic field. We observed an onset drop in the resistivity due to the superconductivity even at $B = 2$ T for $x = 1.0$. The $T_c$ onset shifts gradually with an increasing magnetic field as opposed to the shift in $T_{c0}^\text{zero}$, which is the characteristic behavior of layered superconductivity against the magnetic field. The magnetic field-temperature phase diagrams are plotted in fig. 4(c). The upper critical fields are estimated based on the temperature where resistivity becomes 90% of the normal-state resistivity near $T_c$. The upper critical field $B_{c2}(T)$ at absolute zero temperature, $B_{c2}(0)$, is analyzed using the conventional one-band Werthamer-Helfand-Hohenberg (WHH) equation [42], which gives $B_{c2}(0) = -0.693T_c(dB_{c2}/dT)_{T=T_c}$. $B_{c2}(0)$ is 0.76 and 1.15 T for $x = 0.5$ and 1.0, respectively.

To investigate the changes in carrier concentration, Seebeck coefficient ($S$) and Hall coefficient ($R_{H}$) were measured for La$_2$O$_2$Bi$_2$Pb$_2$S$_{6-x}$Se$_x$. Although the samples contain a La$_2$O$_2$S impurity phase and tiny amount of PbO and Pb-Bi-Ch phases, we consider that we can qualitatively analyze the changes in carrier concentration.

Fig. 3: (a) Temperature dependence of electrical resistivity from 300 to 0.5 K for La$_2$O$_2$Bi$_2$Pb$_2$S$_{6-x}$Se$_x$ ($x = 0.5$ and 1.0). (b) $\rho(T)$ curve in the temperature range 3.0–0.5 K.
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or mobility by Se substitution. As shown in fig. 5, the Seebeck coefficient is negative, which indicates that the dominant carriers are electrons. The absolute value of $S$ decreases from $x = 0$ to $x = 0.5$. Seebeck coefficient for $x = 0.5$ and 1.0 is almost the same. From the results, we can roughly estimate that the carrier concentration slightly increased by Se substitution. Figure 6(a) shows the temperature dependence of Hall coefficient ($-R_H$) from 2K to 300K under the fixed magnetic field of 9T for La$_2$O$_2$Bi$_2$Pb$_2$S$_{6-x}$Se$_x$ ($x = 0$ and 0.5). Hall coefficients are all negative, which is consistent with the results of Seebeck coefficient, but $-R_H$ for $x = 0.5$ is largely suppressed as compared to that for $x = 0$. To investigate the carrier density we have used the simple single band model $n = |1/eR_H|$, where $n$ is the charge carrier density and $e$ is the electron charge, as demonstrated for other layered Bi-based compounds [25,43,44]. Figure 6(b) shows the temperature dependences of electron carrier density for La$_2$O$_2$Bi$_2$Pb$_2$S$_{6-x}$Se$_x$ ($x = 0$ and 0.5), which suggests that the carriers density increases by Se substitution. Having considered the valence state of S and Se, which
the local disorder in the BiS
be considered as resulting from carrier localization due to
With this assumption, low carrier density for
huge change in carrier concentration estimated here is re-
Se substitution. From those facts, we consider that the
pressure effects. As a fact, metalicity has been induced by
change in carrier concentration. Thus, the huge increase
is considered as $-2$ for both, we do not expect a huge
change in carrier concentration. Thus, the huge increase
in carrier density may be related to the in-plane chemical
pressure effects. As a fact, metallicity has been induced by
Se substitution. From those facts, we consider that the
huge change in carrier concentration estimated here is re-
lated to the increase in the concentration of mobile carrier.
With this assumption, low carrier density for $x = 0$ can
be considered as resulting from carrier localization due to
the local disorder in the BiS$_2$ layers.

To investigate the bulk nature of the superconductivity,
we have performed magnetic susceptibility measurements
for $x = 1.0$, but a large shielding signals could not be due
to the low $T_c$ of 1.9 K, which is close to the temperature
limit of our SQUID system, 1.8 K. Therefore, we have
performed susceptibility measurements under high pres-
ure. Figure 7(a) shows the temperature dependences of
normalized susceptibility $4\pi\chi$ under high pressure. (The
data was normalized at 6 K because superconducting
signals of Pb manometer is detected above 6 K.) $T_c$
increased with increasing pressure and reached 3.6 K at 0.89 GPa.
Large shielding signals are observed. $T_c$ estimated from the
susceptibility drop in fig. 7(a) is plotted in fig. 7(b)
as a function of pressure. The improvement of supercon-
ducting properties of $x = 1.0$ by external pressure effect is
basically consistent with the above in-plane chemical
pressure effect by Se substitution. In BiS$_2$-based systems,
both external pressure and chemical pressure improved
superconducting properties [4,5,34,45]. Both pressure ef-
ects modify an in-plane crystal structure. To further in-
vestigate the effect of external and/or chemical pressure
to the crystal structure and superconducting properties of
the La$_2$O$_2$Bi$_2$Pb$_2$S$_6$–xSe$_x$ system, local structure analyses
under high pressure are needed.

**Conclusion.** – La$_2$O$_2$Bi$_2$Pb$_2$S$_6$ is a four-layer–type Bi-
based compound that shows insulating transport prop-
eties at low temperatures. Hence, in this study, we
have investigated the effects of Se substitution on the
structural, transport, and superconducting properties of
La$_2$O$_2$Bi$_2$Pb$_2$S$_6$–xSe$_x$. Owing to Se doping, the normal
state electrical resistivity at low temperatures was dras-
tically suppressed, and superconductivity at a transition
temperature ($T_c$) of 1.2 K was observed for $x = 0.5$. $T_c$
increased with increasing Se concentration: $T_c = 1.9$ K for
$x = 1.0$. According to XRD analyses, we proposed that
Se was substituted for the in-plane S1 site in the BiS$_2$
layers. Both the Seebeck coefficient and the Hall coeffi-
cient suggested that electrons were the dominant carri-
ers. From the Hall coefficient, carrier concentration was
estimated. Owing to Se substitution, the concentration
of mobile carriers increased considerably; this could be
related to the suppression of carrier localization caused
by Se substitution. On the basis of the obtained results
and the discussion based on the analogy of two-layer–type
systems, the emergence of metallicity and superconduc-
tivity was explained by the in-plane chemical pressure
effects. The estimated $B_c2(0)$ was 0.76 and 1.15 T for
$x = 0.5$ and 1.0, respectively. By applying high pressure
for $x = 1.0$, bulk superconductivity was confirmed and the
$T_c$ increased up to 3.6 K at 0.89 GPa. The demonstration
of metallicity and superconductivity in La$_2$O$_2$Bi$_2$Pb$_2$S$_6$-
based compounds can be useful for further development
of four-layer–type Bi-based superconductors.

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