【Discovery of BiS_2-based superconductors】

The discoveries of high transition temperature (high T_c) superconductivity (SC) in cuprate [1], Fe-based [2], and MgB_2 [3] superconductors accelerated exploration of layered superconductors. In 2012, we discovered new layered superconductors with a BiS_2 layer [4,5]. As shown in the figure, the structure is composed of alternate stacks of a SC layer and a blocking layer. Since the electronic band structure near the Fermi level is composed of Bi-6p and S-3p, BiS_2 layer is a conducting layer. So far, many kinds of BiS_2-based superconductors have been discovered, and the highest record of T_c is 11 K in $LaO_{0.5}F_{0.5}BiS_2$. The BiS_2 family of superconductor shows notable characteristics as two dimensional (and possibly unconventional) SC states.

[1] J. G. Bednorz, K. A. Müller, Z. Phys. B-Condens. Matter 64, 189 (1986). [2] Y. Kamihara et al., J. Am. Chem. Soc. 130, 3296 (2008). [3] J. Nagamatsu et al., Nature 410, 63 (2001). [4] Y. Mizuguchi et al., Phys. Rev. B 86, 220510 (2012). [5] Y. Mizuguchi et al., J. Phys. Soc. Jpn. 81, 114725 (2012).

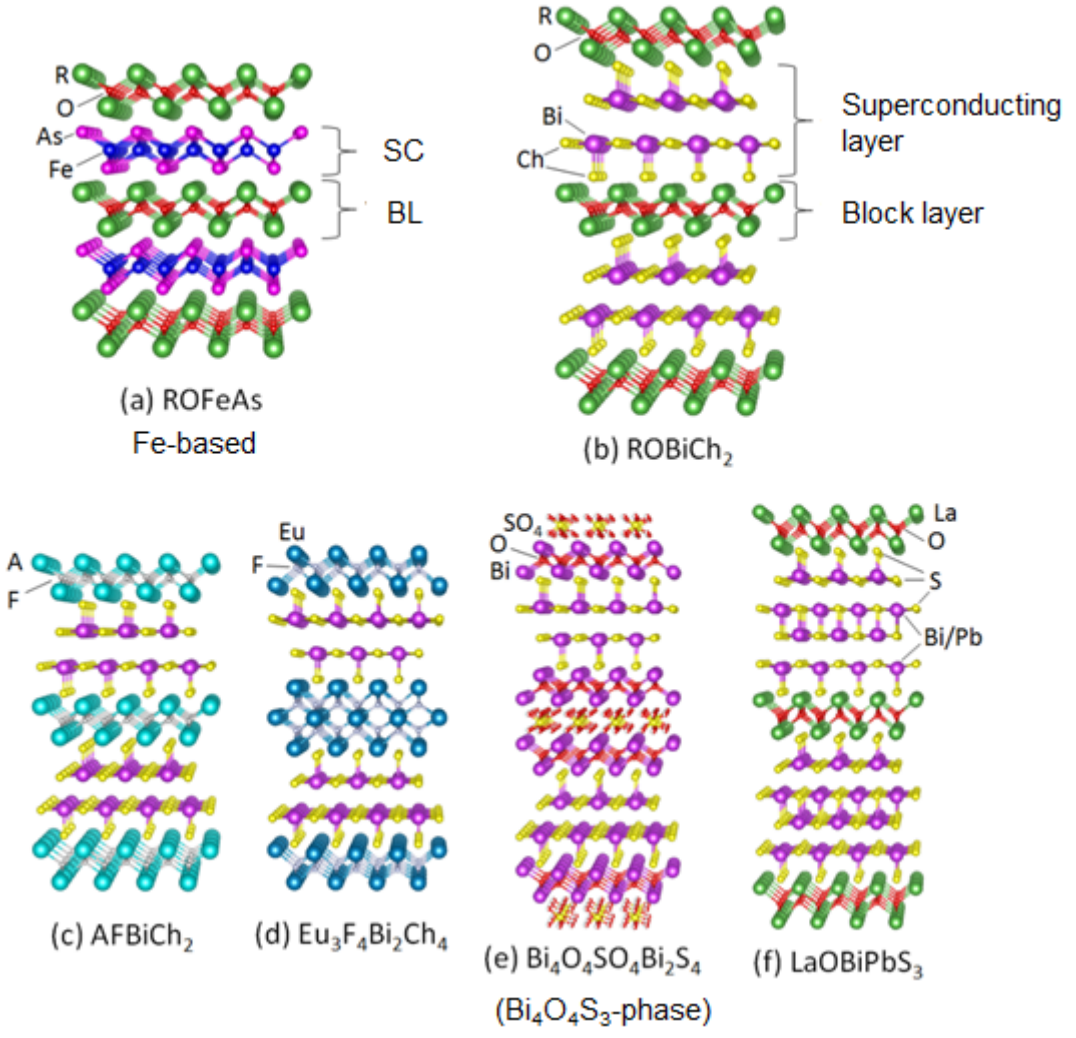


Fig. Crystal structure images of Fe-based and BiS_2-based SC.

【Clarification of the parameter essential for the emergence of BiS_2 superconductivity】

Superconductivity of BiS_2-based compounds can be induced by electron doping, but the bulk SC is absent for some cases. Due to this problem, Detailed investigation on the mechanisms of SC of this family was not fully successful. Therefore, we tried to clarify the parameter essential for the emergence of bulk superconductivity using chemical pressure effect in two systems. For $REO_{0.5}F_{0.5}BiS_2$, RE (rare earth) site can be substituted with RE ions with various ionic radius, and for $LaO_{0.5}F_{0.5}BiS_{2-x}Se_x$, Se substitution can expand lattice volume. We found that "in-plane chemical pressure" can be generated for both substitutions, and that was the structural parameter essential for the emergence of bulk superconductivity [1-3]. Furthermore, we revealed that the in-plane chemical pressure effect can suppress in-plane local static disorder, which is intrinsically existing in the BiS2-based compounds due to the presence of lone pair electrons [4,5].

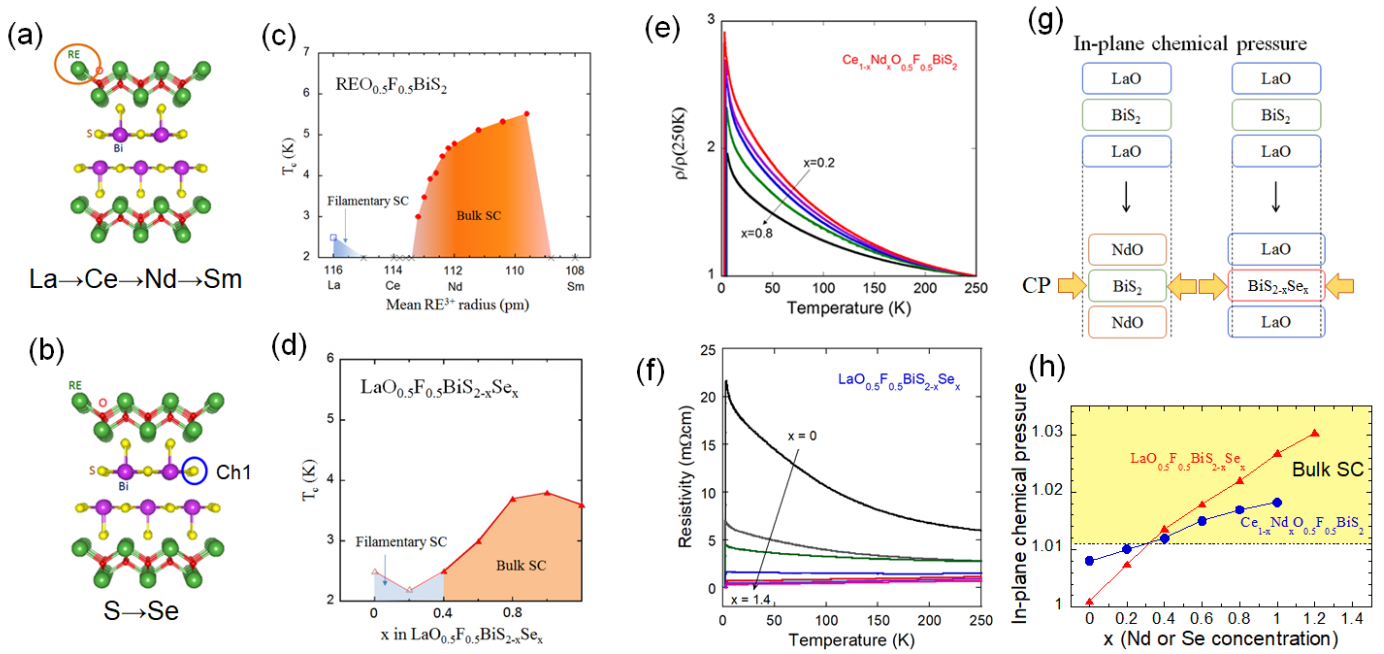


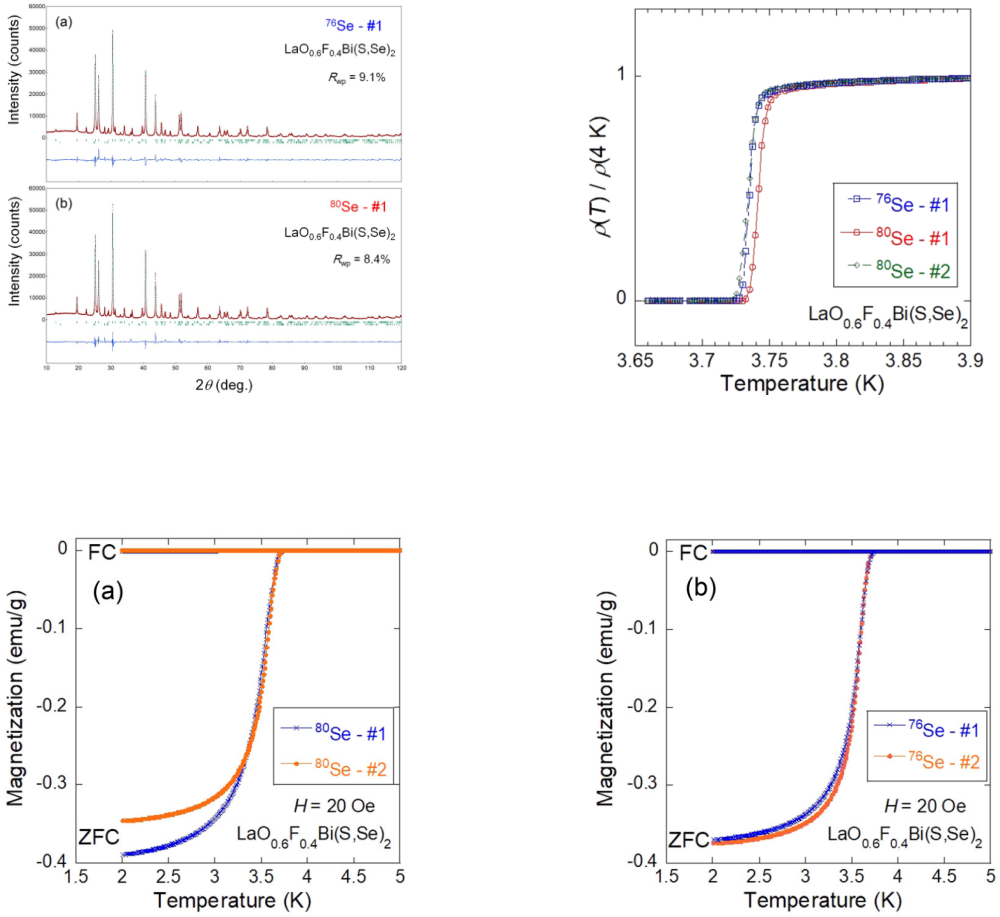
Fig. (a, c, e) Crystal structure image, superconductivity phase diagram, and the temperature dependence of resistivity for the $REO_{0.5}F_{0.5}BiS_2$ system. (b, d, f) Crystal structure image, superconductivity phase diagram, and the temperature dependence of resistivity for the $LaO_{0.5}F_{0.5}BiS_{2-x}Se_x$ system. (g) Schematic image for the in-plane chemical pressure effect. (h) In-plane chemical pressure parameter plotted as functions of doping level.

[1] Y. Mizuguchi et al., Sci. Rep. 5 (2015) 14968. [2] J. Kajitani et al., J. Phys. Soc. Jpn. 84, 044712 (2015). [3] T. Hiroi et al., J. Phys. Soc. Jpn 84, 024723 (2015). [4] K. Nagasaka et al., J. Phys. Soc. Jpn. 86, 074701 (2017). Y. Mizuguchi et al., J. Phys. Soc. Jpn. 87, 023704 (2018).

※ Kajitani-san, Hiroi-san, and Nagasaka-san were master course students of our group.

【Isotope effect in $BiCh_2$-based $LaO_{0.6}F_{0.4}BiSSe$】

To investigate the importance of phonon to the superconductivity mechanisms of BiS_2-based SC, we have investigated the Se isotope effect in $LaO_{0.6}F_{0.4}BiSSe$. In the case of conventional phonon-mediated SC, T_c and the mass of element M shows the relationship of $T_c \propto M^{\alpha}$, where α is an isotope effect exponent. α close to 0.5 was found in conventional SC [1,2]. In contrast, negative α or absence of correlation between T_c and M was found for unconventional SC such as cuprates [3] and Fe-based SC [4]. Since the new BiS_2-based layered SC has a structure similar to the cuprates and Fe-based SC [5], we expected unconventional SC. In addition, ARPES study and theoretical calculation of T_c revealed the possibility of unconventional SC in this family [6,7]. As shown in the figure, our Se isotope effect showed very small change in T_c in between ^{76}Se and ^{80}Se. This may be the evidence of non-phonon SC states in $LaO_{0.6}F_{0.4}Bi(S,Se)_2$ [8].



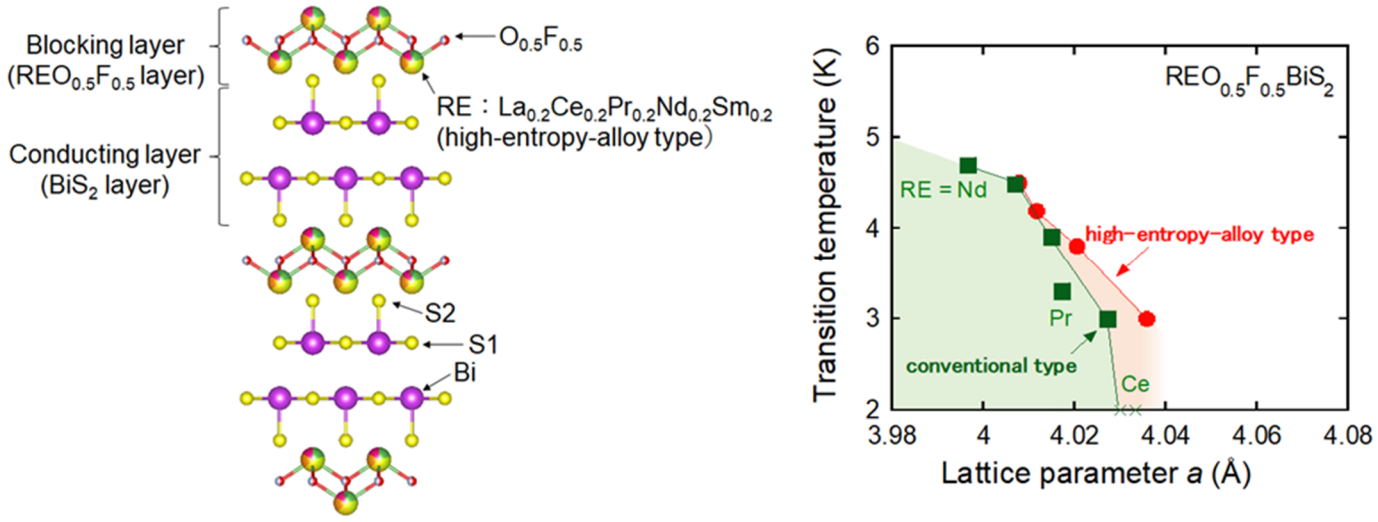
Figs. XRD patterns, the temperature dependences of resistivity, and the temperature dependences of magnetization for the ^{76}Se and ^{80}Se samples of $LaO^{0.6}F_{0.4}BiSSe$.

[1] S. L. Bud'ko et al., *Phys. Rev. Lett.* 86, 1877 (2001). [2] D. D. Lawrie, J. P. Franck, *Physica C* 245,159 (1995). [3] C. C. Tsuei et al., *Phys. Rev. Lett.* 65, 2724 (1990). [4] P. M. Shirage et al., *Phys. Rev. Lett.* 103, 257003 (2009). [5] Y. Mizuguchi wr al., *J. Phys. Soc. Jpn.* 81, 114725 (2012). [6] Y. Ota et al., *Phys. Rev. Lett.* 118, 167002 (2017). [7] C. Morice et al., *Phys. Rev. B* 95, 180505 (2017). [8] K. Hoshi, Y. Goto, Y. Mizuguchi, *Phys Rev B* 97, 094509 (2018). ※Hoshi-san is a master course student of our group.

【SC in $REO_{0.5}F_{0.5}BiS_2$ with high-entropy-alloy-type blocking layers】

High entropy alloy (HEA) is an alloy which contains five or more different elements at one crystallographic site. Particularly, in the field of structural and bio-functional materials, HEA has been actively studied due to its extremely high functionalities [1]. In 2014, SC with a T_c of 7.3 K was found in $Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$ [2], and robust zero resistivity states were observed even at 190 GPa [3].

We considered that the HEA effect can be applied to the layered structure. If one layer (for example, blocking layer of layered SC) was modified by the HEA effect, the other layer (for example, SC layer) can be affected. To test this assumption, we selected the $REO_{0.5}F_{0.5}BiS_2$ system because we have already revealed that the in-plane local structure disorder causes the suppression of bulk SC. Although the in-plane disorder can be suppressed by in-plane chemical pressure effect [4], we expected the similar effects by the introduction of HEA layers. We successfully synthesized $REO_{0.5}F_{0.5}BiS_2$ samples with HEA-type REO blocking layers (RE site is in HEA state) [5]. As shown in the figure, the SC dome was expanded, which should be the evidence for the suppression of the in-plane disorder by the HEA effects. The strategy of HEA-type layered structure will be useful for developing materials in the field of superconductivity, thermoelectric materials, and other functional materials.



Figs. Crystal structure image of HEA-type BiS_2-based $REO_{0.5}F_{0.5}BiS_2$. Superconductivity phase diagram: the comparison between non-HEA samples and HEA-type samples.

[1] J. W. Yeh et al., Adv. Eng. Mater. 6, 299 (2004). [2] P. Koželj, Set al., Phys, Rev. Lett. 113, 107001 (2014).

[3] J. Guo et al., Proc. Natl. Acad. Sci. 114, 13144 (2017). [4] Y. Mizuguchi et al., J. Phys. Soc. Jpn. 87, 023704 (2018). [5] R. Sogabe, Y. Goto, and Y. Mizuguchi, Appl. Phys. Express 11, 053102 (2018).

※Sogabe-san is a master course student of our group.

【$BiCh_2$-based thermoelectric materials】

By tuning the carrier concentration and local crystal structure of the BiS_2-based compound, we discovered new thermoelectric material LaOBiSSe [1]. Se substitution for the S site of $LaOBiS_2$ enhances carrier mobility and suppresses electrical resistivity (ρ). In addition, Se substitution does not suppress Seebeck coefficient (S) [2,3]. The power factor $PF = S^2/\rho$ increases by Se substitution. Furthermore, thermal conductivity (κ) decreases by Se substitution. Finally, the dimensionless figure-of-merit $ZT = S^2T/\rho\kappa$ reached 0.36 for x = 1 at $T \sim 650$ K [4].

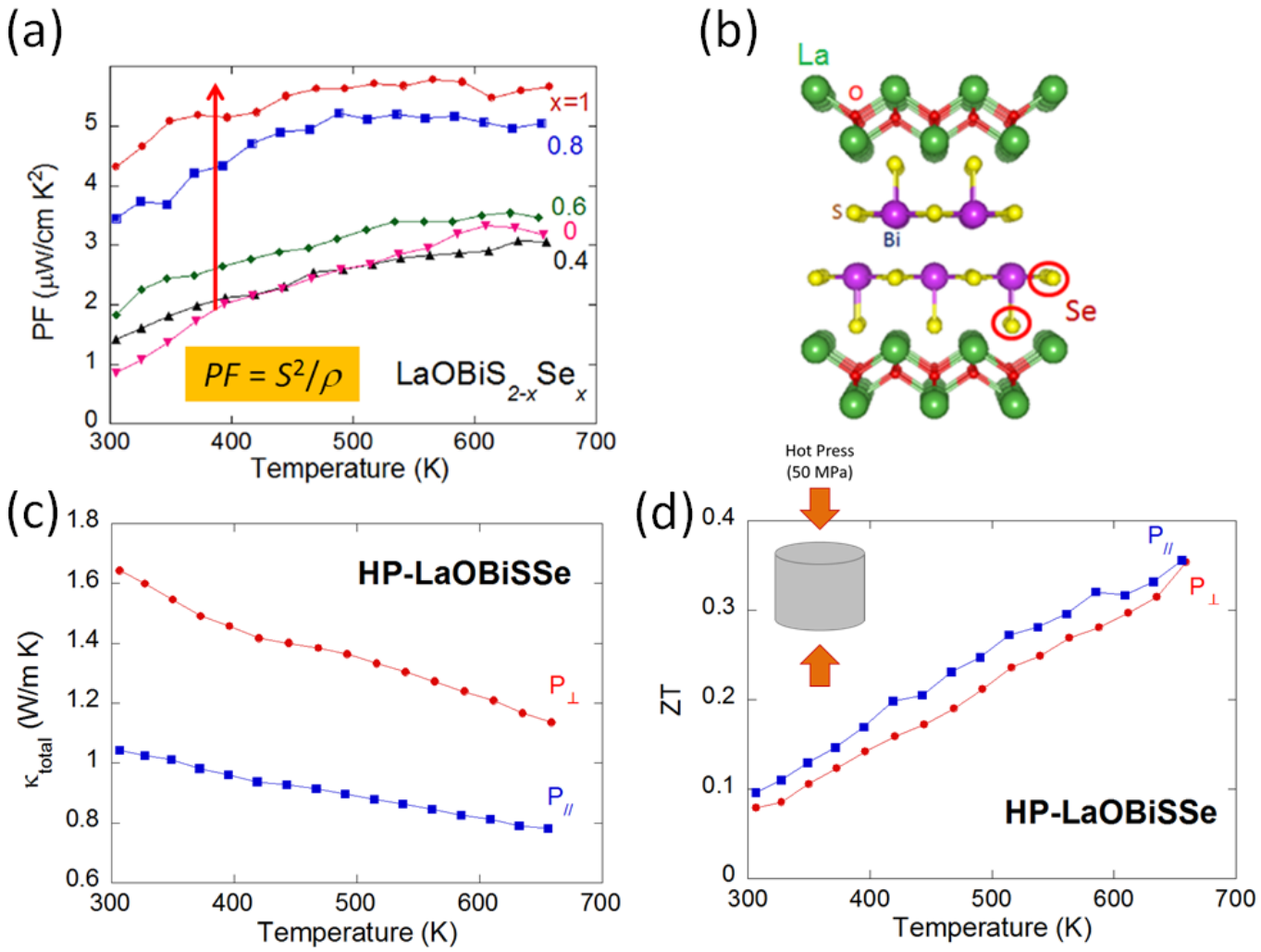


Fig. (a) Temperature dependence of power factor (PF) for $LaOBiS_{2-x}Se_x$. (b) Crystal structure image of LaOBiSSe（x = 1）. (c,d) Temperature dependences of thermal conductivity and dimensionless figure-of-merit (ZT) for LaOBiSSe.

[1] Y. Mizuguchi et al., J. Appl. Phys. 116, 163915 (2014). [2] A. Omachi et al., J. Appl. Phys. 115, 083909 (2014). [3] A. Nishida et al., J. Phys. Soc. Jpn. 85, 074702 (2016). [4] A. Nishida et al., Appl. Phys. Express 8, 111801 (2015).

※Omachi-san and Nishida-san were master course students of our group.

【High-pressure synthesis of $Sn_{0.8}Ag_{0.2}Te$ superconductor】

Recently, topological superconductivity is one of the hottest topics in the field of condensed matter physics. The candidate materials for the topological superconductor are $Cu_xBi_2Se_3$ [1] and $Sn_{1-x}In_xTe$ [2]. To extend the candidate material variation, we explored for new dopant for SnTe. We found that Ag can be substituted up to 50% for the Sn site of SnTe by high-pressure (HP) synthesis, and superconductivity was found for x = 0.15-0.33 [3]. Bulk SC was confirmed by specific heat measurements [4]. The discovery of new dopant for SnTe using HP synthesis will be useful for further material development of NaCl-type topological mateirals.

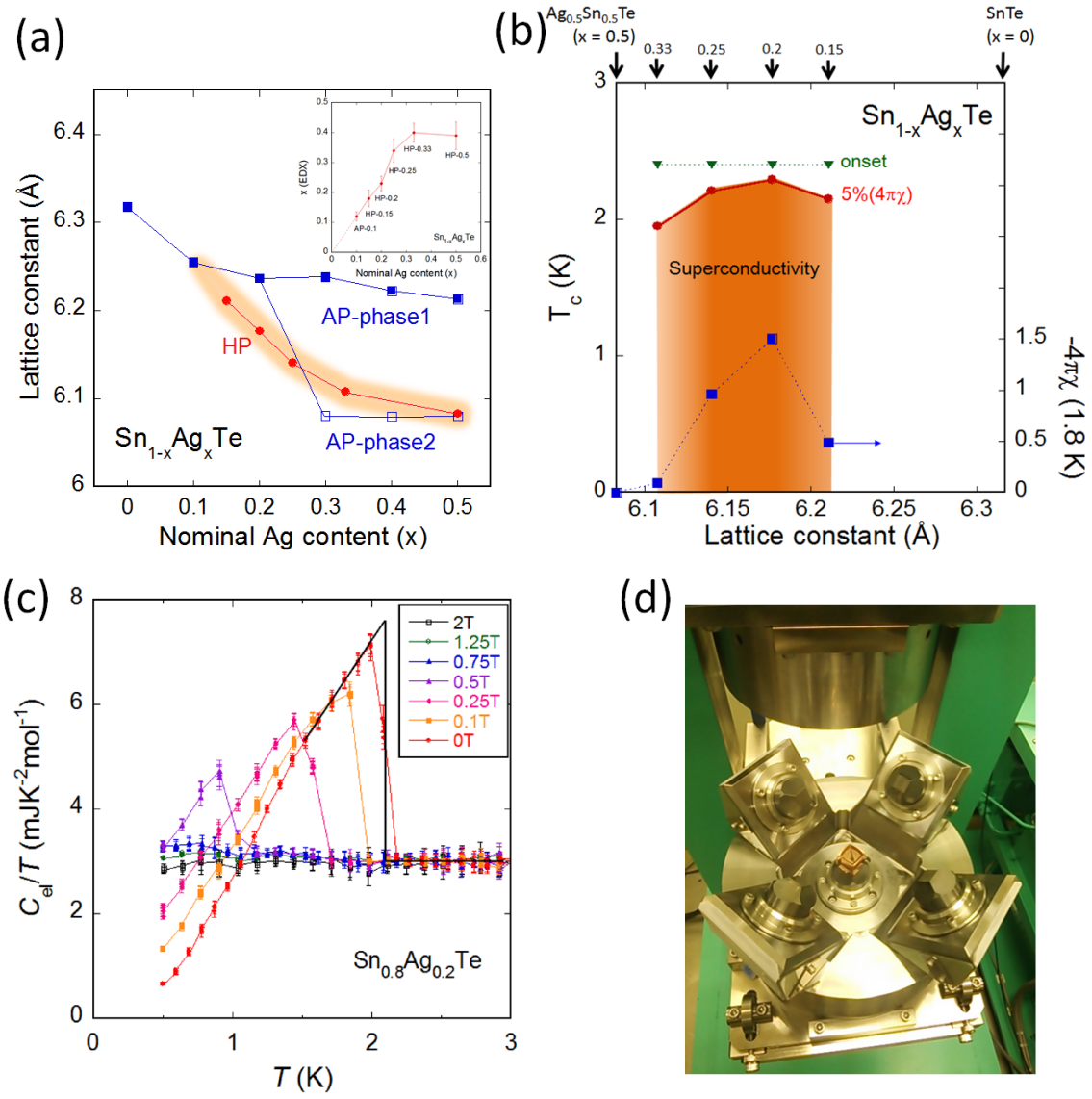


Fig. (a) Ag concentration dependences of lattice constant for the samples prepared at ambient pressure (AP) and high pressure (HP). (b) SC phase diagram. (c) T dependence of specific heat for x = 0.2. (d) Picture of our HP synthesis instrument (180 ton press).

[1] Y. S. Hor et al., Phys. Rev. Lett. 104, 057001 (2010). [2] A. S. Erickson et al., Phys. Rev. B 79, 024520 (2009). [3] Y. Mizuguchi, O. Miura, J. Phys. Soc. Jpn. 85, 053702 (2016). [4] Y. Mizuguchi et al., J. Phys. Soc. Jpn. 85, 103701 (2016).

【SnPn-based novel layered superconductors】　(Y. Goto)

In 2017, we discovered SnAs-based layered superconductor [1]. As shown in the figure, its crystal structure consists of two layers of a buckled honeycomb network of SnAs, bound by the van der Waals (vdW) forces and separated by Na ions. Such bonding due to vdW forces is readily exfoliated, as exemplified by graphene. Indeed, $NaSn_2As_2$ can be exfoliated down to several nanometers [2]. We demonstrated that $NaSn_2As_2$ exhibits superconductivity with a transition temperature (T_c) of 1.3 K [1]. The result suggests that SnPn-based (Pn: pnictogen) compounds are a novel family of layered superconductors with vdW structure. In 2018, we also discovered novel superconductor $Na_{1-x}Sn_2P_2$ (T_c = 2.0 K) [3]. Enhancement of T_c is envisioned in this family of compounds.

[1] Y. Goto et al. J. Phys. Soc. Jpn. **86**, 123701 (2017).

[2] M. Q. Arguilla et al. ACS Nano **10**, 9500 (2016).

[3] Y. Goto et al. Sci. Rep. **8**, 12852 (2018).

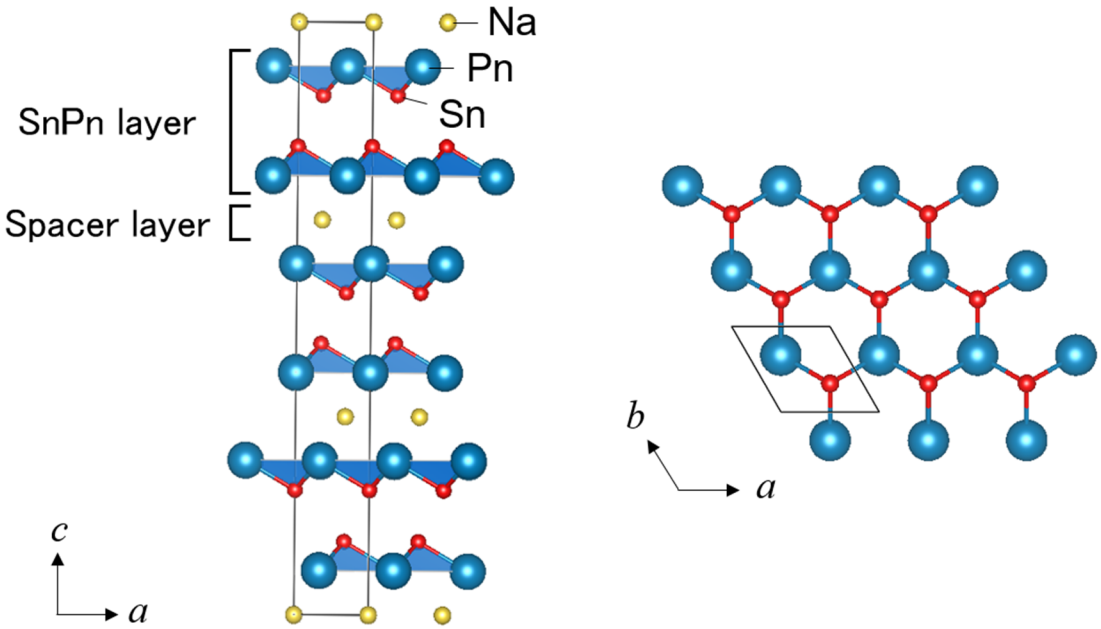


Fig.　Crystal structure of $NaSn_2Pn_2$.