Growth and Characterization of ROBiS₂ High-Entropy Superconducting Single Crystals

Yuma Fujita, Koki Kinami, Yuji Hanada, Masanori Nagao,*, Akira Miura, Shigeto Hirai, Yuki Maruyama, Satoshi Watauchi, Yoshihiko Takano, and Isao Tanaka

ABSTRACT: A series of high-entropy superconductors, ROBiS₂ (R = La + Ce + Pr + Nd + Sm), have been successfully grown in the form of single crystals using CsCl flux. The obtained single crystals have a platelike shape with a size of 0.5−2.0 mm and a thickness of 70−450 μm, and they are cleavable along the c-plane. The c-axis lattice constants of the obtained ROBiS₂ single crystals have similar values of 13.47−13.57 Å. The Ce in the obtained ROBiS₂ single crystals was in a mixed-valence state, comprising both Ce³⁺ and Ce⁴⁺. On the other hand, Pr and Sm showed only the trivalent state. The superconducting transition temperatures of ROBiS₂ single crystals were approximately 2−4 K. The superconducting transition temperature and superconducting anisotropies of R-site mixed high-entropy samples increased with a decrease in the mean ionic radius of the R-site. Moreover, a deviation in the tendency to exhibit superconducting properties was observed based on the difference in the R-site mixed entropy. R-site mixed entropy in ROBiS₂ superconductors may affect their superconducting properties.

1. INTRODUCTION

Layered superconductors often exhibit high superconducting transition temperatures, such as cuprate superconductors,¹−³ iron-based superconductors,⁴,⁵ and nitride-based layered superconductors.⁶ ROBiS₂ (R: rare earth elements) is a BiS₂-based layered superconductor⁷ that is composed of alternating stacking sequences of BiS₂ and RO layers. A schematic image of the crystal structure of ROBiS₂ is shown in Figure 1. Similar structural features and superconducting properties have been attracted for exploring new superconductors and their origin. Superconductivity of BiS₂-based compounds can be induced by carrier doping and/or in-plane chemical pressure.⁸,⁹ Their superconducting transition temperatures are approximately 2−5 K. Carrier doping can be achieved by doping of the O²⁻ sites with F⁻ or by valence fluctuation of the R-site, such as that with Ce³⁺ and Ce⁴⁺.¹⁰,¹¹ Moreover, the R-site can be substituted by various rare earth elements.¹²−¹⁶ High-entropy alloys (HEAs) are defined as alloys containing at least five elements with concentrations between 5 and 35 atom %.¹⁷,¹⁸ In recent years, HEAs have been extensively studied in various fields of structural materials. This concept has been applied as various functional materials including solid electrolytes,¹⁹ electrodes,²⁰ and capacitors.²¹,²² The HEA concept can be useful for developing new superconducting materials containing an HEA site and/or HEA-type layers. To start with, the HEA superconductor Ta−Nb−Hf−Zr−Ti, with a transition temperature of 7.3 K, was discovered.²³ In addition, this high-entropy alloy superconductor exhibits extraordinarily robust zero-resistance superconductivity under pressures up to 190 GPa.²⁴ Later, the relationship between superconductivity and...
the high-entropy effect was investigated. RBa₂Cu₃O₇−δ (R-
123) high-Tc cuprate superconducting polycrystalline samples
with the HEA concept in the R-site were investigated. In an
analogous way, previous reports showed the synthesis and
superconducting properties of ROₓF₀.₅BiS₂ polycrystalline
samples with the HEA concept in the R-site for the
improvement of superconducting properties. However, in
polycrystalline samples, the intrinsic properties were masked
by the impurities and grain boundaries. Especially, the
anisotropic properties cannot be measured using polycrystal-
line samples. In this paper, we report the growth and
characterization of HEA superconducting single crystals of
ROBiS₂ (R = La + Ce + Pr + Nd + Sm). The composition, the
mean ionic radius of the R-site, and the superconducting
properties of the obtained ROBiS₂ single crystals indicated
the presence of the HEA effect with mixed entropies (∆Smix) at the
R-site.

2. RESULTS

Figure 2 shows the typical scanning electron microscopy
(SEM) image and the corresponding energy-dispersive X-ray
spectrometry (EDS) mapping of ROBiS₂ single crystals. The
different compositions. We assumed that they were maintained
at a similar value due to the Ce valence fluctuation.

It is well known that Ce is trivalent and tetravalent in
ROBiS₂. To know the effect of carrier concentration, it is
important to determine the valence of rare earth elements. We
examined the valences of Ce, Pr, and Sm, which can adopt a
mixed-valence state by X-ray absorption spectroscopy (XAS)
analysis. Figure 4 shows the (a) Ce L₃-edge, (b) Pr L₃-edge,
and (c) Sm L₃-edge absorption spectra of the ROBiS₂ single
crystals at room temperature by XAS analysis. The Ce L₃-edge
of the ROBiS₂ single crystals showed a peak at approximately
5726 eV that was assigned as Ce³⁺, which is consistent with the
other XAS result for the trivalent electronic configuration
(Ce³⁺). The peaks at approximately 5730 and 5737 eV were
assigned to a tetravalent electronic configuration (Ce⁴⁺). Cerium
in the obtained ROBiS₂ single crystals was in a mixed-
valence state that comprised trivalent (Ce³⁺) and tetravalent
(Ce⁴⁺) states. The ratios of Ce³⁺ and Ce⁴⁺ in the Ce-site and
the R-site in the obtained ROBiS₂ single crystals are shown in
Table 2. In contrast, the Pr L₃-edge showed a peak at 5966 eV,
which can be assigned to a tetravalent electronic configuration
(Pr⁴⁺). This is consistent with the other XAS results for
Pr⁴⁺. The tetravalent electronic configuration (Pr⁴⁺) shows
a signature peak at 5978 eV, which was undetectable. On the
other hand, the Sm L₃-edge showed a peak at 6719 eV,
which can be assigned to a tetravalent electronic configuration
(Sm⁴⁺). This is consistent with the other XAS results for
Sm⁴⁺. The peak at approximately 6724 eV appeared in the
Sm L₃-edge absorption spectra, which was consistent with the
Nd L₃-edge absorption. Table 2 shows a summary of the XAS
measurement. While the ratio of Ce³⁺ in sample C is lower
than that in other samples, the ratio of Ce⁴⁺ is almost constant.
Considering the ion radii of all of the rare earth elements, the
average ion radii of the R-site decrease from A (1.112 Å) to D
(1.096 Å).

Figure 5 shows the ρ−T characteristics for all samples (A, B,
C, and D) in the temperature range of 1.8−10 K. Various
superconducting transition temperatures (Tc) and resistivity
behaviors were observed despite the similar c-axis lattice
constants. The resistivity basically showed semiconducting
behavior. The slope of sample C in the normal state is sharp,
indicating lower carrier concentration. The Tc values of samples A (Tc: 2.1−3.4 K) and C (Tc: 2.2−3.3 K) are lower
than those of samples B (Tc: 3.8−4.3 K) and D (Tc: 4.3−4.6 K).
This result suggests a complex relationship between the
superconducting properties and the structural property of the

The mixed entropies (∆Smix) of the R-site in the analyzed
compositions are calculated using

\[
\Delta S_{\text{mix}} = -R(C_{La} \ln C_{La} + C_{Ce} \ln C_{Ce} + C_{Pr} \ln C_{Pr} + C_{Nd} \ln C_{Nd} + C_{Sm} \ln C_{Sm})
\]

where R and ln are the gas constant and the natural logarithmic
operator, respectively. The estimated mixed entropies had
similar values except for those for sample C.

Figure 3 shows the X-ray diffraction (XRD) patterns of a
well-developed plane in the obtained ROBiS₂ single crystals.

| Composition | Tc (K) | ρ (μΩ cm) |
|-------------|--------|-----------|
| A           | 3.8    | 1000      |
| B           | 2.1    | 500       |
| C           | 4.3    | 1500      |
| D           | 2.2    | 200       |

Figure 2. Typical SEM image and La, Ce, Pr, Nd, Sm, Bi, and S
elemental mapping of ROBiS₂ single crystals.

Table 1. Mean ionic radius of the R-site, the superconducting
properties and the structural property of the

| Composition | Tc (K) | ρ (μΩ cm) |
|-------------|--------|-----------|
| A           | 3.8    | 1000      |
| B           | 2.1    | 500       |
| C           | 4.3    | 1500      |
| D           | 2.2    | 200       |
ROBiS₂ system. Typical superconducting properties of ROBiS₂ single crystals were detected in sample D, which has the highest $T_c$ of these samples. Figure 6 shows the temperature dependence of the resistivity for sample D under the magnetic field ($H$) parallel to the (a) $c$-plane ($H//c$-plane, $H = 0.01−9.0$ T) and to the (b) $c$-axis ($H//c$-axis, $H = 0.01−9.0$ T). The superconducting transition was drastically suppressed by an increase in the magnetic field parallel to the $c$-axis compared to those of the $c$-plane. Similar behaviors were observed for other samples (samples A, B, and C). Therefore, we predict that ROBiS₂ single crystals would exhibit highly superconducting anisotropy. The magnetic field dependence of the $T_c$ onset under the magnetic field ($H$) parallel to the $c$-plane ($H//c$-plane) and to the $c$-axis ($H//c$-axis) for sample D is plotted in Figure 7. The linear extrapolation of the $T_c$ onset values for the $H//c$-plane and the $H//c$-axis approached 23 and 0.6 T, respectively.

The upper critical field for the $c$-plane ($H_{c2}^{c//c}$-plane) and the $c$-axis ($H_{c2}^{c//c}$-axis) at zero temperature are estimated to be 16 and 0.42 T, as determined by the Werthamer–Helfand–Hohenberg (WHH) theory using eq 2

$$H_{c2}^{c//c}(0) = -0.693T_c(dH_{c2}^{c//c}/dT)_{T_c}$$

where $\xi$ is the coherence length.

We determined the superconducting anisotropy ($\gamma$) to be approximately 38 from the ratio of the upper critical field using eq 3

$$\gamma = H^{c//c}_{c2}/H^{c//c}_{c-axis} = \xi_{c//c-parallel}/\xi_{c//c-axis}$$

where $\xi$ is the coherence length.

In a conventional (BCS-like) superconductor at the weak-coupling limit, the Pauli limit ($H_p$) was calculated to be 8.46 T, since $H_p = 1.84T_c$ ($T_c$ onset = 4.6 K). Thus, the upper critical field in the $c$-plane ($H_{c2}^{c//c}$-plane = 16 T) is significantly higher than the Pauli limit ($H_p = 8.46$ T), indicating the possibility of an unconventional superconductor. For only sample C, the $H_{c2}^{c//c}$-plane value (4.9 T) was less than $H_p$ (6.07 T from $T_c$ onset = 3.3 K).

In contrast, the $\gamma$ values of ROBiS₂ single crystals were estimated by another approach using the effective mass model. The angular ($\theta$) dependence of resistivity ($\rho$) was measured under different magnetic fields ($H$) in the liquid state flux to estimate the $\gamma$. The reduced field ($H_{red}$) was

$$H_{red} = H / (H_p / \rho(\theta))$$

Table 1. $T_{max}$, $\Delta S_{mix}$, and Nominal and Analytical Compositions of ROBiS₂ Single Crystals

| sample | $T_{max}$ (°C) | $\Delta S_{mix}$ (estimated from analytical composition) |
|--------|----------------|--------------------------------------------------------|
| A      | 950            | 1.496R                                                  |
| B      | 950            | 1.487R                                                  |
| C      | 950            | 1.598R                                                  |
| D      | 850            | 1.517R                                                  |

Figure 3. XRD patterns of the well-developed plane of ROBiS₂ single crystals.

Figure 4. XAS spectra at room temperature for the ROBiS₂ single crystals and some standard valence samples at the (a) Ce L₃-edge, (b) Pr L₃-edge, and (c) Sm L₃-edge.
calculated using the following equation for an effective mass model (eq 4)

\[ H_{\text{red}} = H(\sin^2 \theta + \gamma_s^{-2} \cos^2 \theta)^{1/2} \]  

where \( \theta \) is the angle between the c-plane and the magnetic field.\(^{38,39}\) \( H_{\text{red}} \) is calculated from \( H \) and \( \theta \). The \( \gamma_s \) value was estimated from the best scaling of the \( \rho - H_{\text{red}} \) relationship. Figure 8 shows the \( \theta \) dependence of \( \rho \) at various magnetic fields (\( H = 0.01-9.0 \) T) in the liquid state flux for sample D. The \( \rho - \theta \) curve was represented by a 2-fold symmetry. The \( \rho - H_{\text{red}} \) scaling obtained from the \( \rho - \theta \) curves in Figure 8 using eq 4 is shown in Figure 9. The scaling was determined for \( \gamma_s = 33 \), as shown in Figure 9. The superconducting anisotropy (\( \gamma_s \)) values of sample D were estimated to be 38 and 33 using eqs 3 and eq 1, respectively. These values are comparable, which indicates that both approaches to determine the superconducting anisotropies are consistent for the ROBiS\(_2\) system.

### 3. DISCUSSION

R-sites can affect the carrier concentration, chemical pressure, and high-entropy effect of the ROBiS\(_2\) single crystals, that is, superconducting properties are affected by several parameters. Figure 10 shows the mixed entropy (\( \Delta S_{\text{mix}} \)) values, the mean R-site ionic radius, dependencies of superconducting transition temperature (\( T_c \)), upper critical field (\( H_{\text{C2}} \)), and superconducting anisotropy (\( \gamma_s \)) values for all samples (samples A, B, C, and D) are shown in Table 3.

### Table 2. Ce\(^{3+}\) and Ce\(^{4+}\) Contents and the Mean R-site Ionic Radii for the Obtained ROBiS\(_2\) Single Crystals

| Sample | Ce\(^{3+}\) | Ce\(^{4+}\) | Mean R-site ionic radius (Å) (calculated from the ratio of Ce\(^{3+}\) and Ce\(^{4+}\)) |
|--------|----------|----------|--------------------------------------------------|
| A      | 0.19     | 0.13     | 1.112                                            |
| B      | 0.18     | 0.11     | 1.108                                            |
| C      | 0.12     | 0.095    | 1.104                                            |
| D      | 0.19     | 0.096    | 1.096                                            |
can be dominated by either the chemical pressure or the high-entropy effect. While the mixed entropy ($\Delta S_{\text{mix}}$) value does not correlate with the superconducting transition temperature ($T_c$) and superconducting anisotropy ($\gamma_c$), a decrease in mean R-site ionic radius leads to an increase in the chemical pressure, which also increases $T_c$ and $\gamma_c$. This trend is similar to that in the Ce$_{1-x}$Nd$_x$OBiS$_2$, in which the $\Delta S_{\text{mix}}$ values are less than half (0.486$R$–0.619$R$). Therefore, chemical pressure can affect the superconducting properties and has no significant effect on the high-entropy effect.

Sample C, whose $\Delta S_{\text{mix}}$ value is higher than that of samples A, B, and D, does not follow this trend; both its $T_c$ and $\gamma_c$ are low. This characteristic can be explained by either the carrier concentration or the high-entropy effect. Even though the content of Ce$^{4+}$ in the case of sample C is similar to that of the other samples, its slope of resistivity in the normal state region indicates that it has the lowest carrier concentration (Figure 5). The carrier concentration may have been reduced by the reduced carrier transfer from the RO layer to the BiS$_2$ layer. A low carrier concentration can lower the transition temperature.

The other possibility is that a high $\Delta S_{\text{mix}}$ value can reduce $T_c$ and decrease $\gamma_c$. Also, a substantial high-entropy effect can reduce superconducting anisotropy by inducing different local structures near the RO layer. The value of the upper critical field ($H_{c2}$) for sample C is the only one less than the Pauli limit ($H_p$), which is one of the deciding criteria for conventional or unconventional superconductors. This result cannot be explained by carrier concentration only; therefore, we expect that the high $\Delta S_{\text{mix}}$ value is a possible explanation for this phenomenon. Further investigation, including the growth of other ROBiS$_2$ (R: rare earth elements) single crystals with different $\Delta S_{\text{mix}}$ values, is required to systematically reveal the relationship between the superconductivity and the high-entropy effect.

**4. CONCLUSIONS**

ROBiS$_2$ (R = La + Ce + Pr + Nd + Sm) HEA superconducting single crystals were grown using CsCl flux. The c-axis lattice constants of the obtained ROBiS$_2$ single crystals were approximately constant (13.47–13.57 Å) regardless of the composition of the R-site. However, there was no relationship between the c-axis lattice constant and $T_c$. $T_c$ and $\gamma_c$ exhibited similar tendencies as the mean R-site ionic radius in both ROBiS$_2$ (HEA-type) and Ce$_{1-x}$Nd$_x$OBiS$_2$ (conventional-type). In ROBiS$_2$ (HEA-type), the $T_c$ and $\gamma_c$ in higher $\Delta S_{\text{mix}}$ single crystals (sample C) deviated from the trend of other samples (samples A, B, and D). The mixed entropy values ($\Delta S_{\text{mix}}$) may introduce a high-entropy effect that alters the superconducting properties. Furthermore, we believe that the flexible compositions and various local structures of the R-site can expand the variety of superconducting materials, which can reveal new phenomena and applications of layered superconductors.

**5. EXPERIMENTAL SECTION**

ROBiS$_2$ (R = La + Ce + Pr + Nd + Sm) single crystals were grown using CsCl flux. Nominal compositions of the R-site were chosen for implementation in the high-entropy alloys.
(HEA) composed of five elements with concentrations between S and 35 atom %. Table 1 shows the nominal compositions and growth temperatures ($T_{max}$) of all samples. We note that the ionic radius of the R-site can be systematically changed for these samples. The starting materials for the growth of ROBiS$_2$ single crystals were La$_2$S$_3$, Ce$_2$S$_3$, Pr$_2$S$_3$, Nd$_2$S$_3$, Sm$_2$S$_3$, Bi$_2$S$_3$, Bi$_2$O$_3$, and CsCl flux. The raw materials were weighed to obtain a nominal composition, La$_2$Ce$_2$Pr$_2$Nd$_2$Sm$_2$Bi$_2$O$_3$. A mixture of raw materials (0.8 g) and the CsCl flux (5.0 g) was ground using a mortar and pestle and then sealed in an evacuated (~10 Pa) quartz tube. The quartz tube was heated at $T_{max}$ for 10 h, followed by cooling to 650 °C at a rate of 1 °C/h. Then, the quartz tube was cooled to room temperature in the furnace. The heated quartz tube was opened in air, and the obtained materials were washed and filtered with distilled water to remove the CsCl flux.

Scanning electron microscopy (SEM) was conducted using a TM3030 system from Hitachi High-Technologies. The compositional ratio of the grown ROBiS$_2$ single crystals was evaluated using energy-dispersive X-ray spectrometry (EDS, Quantax 70, Bruker). The atomic content of each element was evaluated using energy-dispersive X-ray spectrometry (EDS, Andor, Odyssey) using Cu Kα radiation. We would like to thank ACS Authoring Services and Editage (www.editage.com) for English language editing.

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The XAS experiments were conducted at the BL05S1 of Aichi Synchrotron Radiation Center, Aichi Science & Technology Foundation, Aichi, Japan (Experimental No. 201905108). This research was partially supported by Grants-in-Aid for Scientific Research (C) (JSPS KAKENHI Grant Number JP19K05248). We would like to thank ACS Authoring Services and Editage (www.editage.com) for English language editing.

## REFERENCES

1. Bednorz, J. G.; Müller, K. A. Possible high $T_c$ superconductivity in the Ba-La-Cu-O system. Z. Phys. B: Condens. Matter 1986, 64, 189–193.
2. Wu, M. K.; Ashburn, J. R.; Thorg. C. J.; Hor, P. H.; Meng, R. L.; Gao, L.; Huang, Z. J.; Wang, Y. Q.; Chu, C. W. Superconductivity at 93 K in a new mixed-phase Y-Ba-Cu-O compound system at ambient pressure. Phys. Rev. Lett. 1987, 58, No. 908.
3. Maeda, H.; Tanaka, Y.; Fukutomi, M.; Asano, T. A New High-$T_c$ Oxide Superconductor without a Rare Earth Element. Jpn. J. Appl. Phys. 1988, 27, No. L209.
4. Kamihara, Y.; Watanabe, T.; Hirano, M.; Hosono, H. Iron-Based Layered Superconductor La[O1-xFx]FeAs ($x = 0.05 – 0.12$) with $T_c$ = 26 K. J. Am. Chem. Soc. 2008, 130, 3296–3297.
5. Chen, X. H.; Wu, T.; Wu, G.; Liu, B. H.; Chen, H.; Fang, D. F. Superconductivity at 43 K in SmFeAsO1-xF$_x$. Nature 2008, 453, 761–762.
6. Yamanaka, S.; Hotohama, K.; Kawai, H. Superconductivity at 25.5 K in electron-doped layered hafnium nitride. Nature 1998, 392, 580–582.

## AUTHOR INFORMATION

### Corresponding Author

Masanori Nagao — University of Yamanashi, Kofu, Yamanashi 400-8511, Japan; orcid.org/0000-0002-1139-7838; Phone: (+81)55-220-8610; Email: mnagao@yamanashi.ac.jp; Fax: (+81)55-220-8270

### Authors

Yuma Fujita — University of Yamanashi, Kofu, Yamanashi 400-8511, Japan
Koki Kinami — University of Yamanashi, Kofu, Yamanashi 400-8511, Japan
Yuji Hanada — University of Yamanashi, Kofu, Yamanashi 400-8511, Japan
Akira Miura — Faculty of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan; orcid.org/0000-0003-0388-9696
Shigeto Hirai — School of Earth, Energy and Environmental Engineering, Kitami Institute of Technology, Kitami, Hokkaido 090-8507, Japan; orcid.org/0000-0001-8420-8711
Yuki Maruyama — University of Yamanashi, Kofu, Yamanashi 400-8511, Japan; orcid.org/0000-0001-6904-4191
Satoshi Watauchi — University of Yamanashi, Kofu, Yamanashi 400-8511, Japan
Yoshihiko Takano — MANA, National Institute for Materials Science, Tsukuba, Ibaraki 305-0047, Japan
Isao Tanaka — University of Yamanashi, Kofu, Yamanashi 400-8511, Japan; orcid.org/0000-0002-2736-7107

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.0c01969
(7) Mizuguchi, Y.; Demura, S.; Deguchi, K.; Takano, Y.; Fujihisa, H.; Gotoh, Y.; Izawa, H.; Miura, O. Superconductivity in Novel BiS2-Based Layered Superconductor LaO$_x$F$_{1-x}$BiS$_2$. J. Phys. Soc. Jpn. 2012, 81, No. 114725.

(8) Mizuguchi, Y. Review of superconductivity in BiS$_2$-based layered materials. J. Phys. Chem. Solids 2015, 84, 34–48.

(9) Mizuguchi, Y.; Miura, A.; Kajitani, J.; Hiroi, T.; Miura, O.; Tadanaga, K.; Konuma, N.; Magome, E.; Moriyoshi, C.; Kuroiwa, Y. In-plane chemical pressure essential for superconductivity in BiS$_2$-based (Ch: S, Se) layered structure. Sci. Rep. 2015, 5, No. 14968.

(10) Tanaka, M.; Miura, A.; Ueta, I.; Watauchi, S.; Tanaka, I. Superconductivity in CeOBiS$_2$ with cerium valence fluctuation. Solid State Commun. 2016, 245, 11–14.

(11) Tanaka, M.; Nagao, M.; Matsumoto, R.; Kataoka, N.; Ueta, I.; Tanaka, H.; Watauchi, S.; Tanaka, I.; Takano, Y. Growth and characterization of (La,Ce)OBiS$_2$ hybrid single crystals. J. Alloys Compd. 2017, 722, 467–473.

(12) Hanada, Y.; Nagao, M.; Miura, A.; Maruyama, Y.; Watauchi, S.; Takano, Y.; Tanaka, I. Growth and characterization of (La,Ce)OBiS$_2$ single crystals. Jpn. J. Appl. Phys. 2019, 58, No. 063001.

(13) Mizuguchi, Y.; Miura, A.; Uruishiha, D.; Maruyama, Y.; Gotoh, Y.; Demura, S.; Misumi, Y.; Moriyoshi, C.; Watauchi, Y.; Watauchi, S.; Asaka, T.; Takano, Y.; Tadanaga, K.; Tanaka, I. Superconducting Properties of (Ce,Pr)OBiS$_2$ Single Crystals. Front. Chem. 2020, 8, No. 44.

(14) Demura, S.; Mizuguchi, Y.; Deguchi, K.; Okazaki, H.; Hara, H.; Watanabe, T.; Denholme, S. J.; Fujikawa, M.; Ozaki, T.; Fujihisa, H.; Gotoh, Y.; Miura, O.; Yamaguchi, T.; Takeya, H.; Takano, Y. New Member of BiS$_2$-Based Superconductor NdO$_{1.6}$F$_{0.4}$BiS$_2$. J. Phys. Soc. Jpn. 2013, 82, No. 033708.

(15) Kinami, K.; Hanada, Y.; Nagao, M.; Miura, A.; Gotoh, Y.; Maruyama, Y.; Watauchi, S.; Takano, Y.; Tanaka, I. Growth of Superconducting Sm(O,F)BiS$_2$ Single Crystals. Cryst. Growth Des. 2019, 19, 6136–6140.

(16) Yazici, D.; Huang, K.; White, B. D.; Chang, A. H.; Friedman, A. J.; Maple, M. B. Superconductivity of F-substituted LnOBiS$_2$ (Ln = La, Ce, Pr, Nd, Yb) compounds. Philos. Mag. 2013, 93, 673–680.

(17) George, E. P.; Raabe, D.; Ritchie, R. O. High-entropy alloys. Nat. Rev. Mater. 2019, 4, S15–S34.

(18) Yeh, J. W.; Chen, S. K.; Lin, S. J.; Gan, J. Y.; Chin, T. S.; Shun, T. T.; Tsau, C. H.; Chang, S. Y. Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Studies of Interatomic Distances in Halides and Chalcogenides. Acta Crystallogr., Sect. A: Found. Adv. 1976, A32, 751–767.

(19) Bérandard, D.; Franger, S.; Meena, A. K.; Dragoe, N. Room temperature lithium superionic conductivity in high entropy oxides. Mater. Chem. A 2016, 4, 9536–9541.

(20) Zhao, C.; Ding, F.; Lu, Y.; Chen, L.; Hu, Y.-S. High-Entropy Layered Oxide Cathodes for Sodium-Ion Batteries. Angew. Chem., Int. Ed. 2020, 59, 264–269.

(21) Bérandard, D.; Franger, S.; Dragoe, D.; Meena, A. K.; Dragoe, N. Colossal dielectric constant in high entropy oxides. Phys. Status Solidi RRL 2016, 10, 328–333.

(22) Jin, T.; Sang, X.; Unocic, R. R.; Kinch, R. T.; Liu, X.; Hu, J.; Liu, H.; Dai, S. Mechanochemical-Assisted Synthesis of High-Entropy Metal Nitride via a Soft Urea Strategy. Adv. Mater. 2018, 30, No. 1707512.

(23) Koželj, P.; Vrutnik, S.; Jelen, A.; Jazbec, S.; Jagličić, Z.; Maiti, S.; Feuerbacher, M.; Steurer, W.; Dolinšek, J. Discovery of a Superconducting High-Entropy Alloy. Phys. Rev. Lett. 2014, 113, No. 107001.

(24) Guo, J.; Wang, H.; von Rohr, F.; Wang, Z.; Cai, S.; Zhou, Y.; Yang, K.; Li, A.; Jiang, S.; Wu, Q.; Cava, R. J.; Sun, L. Robust zero resistance in a superconducting high-entropy alloy at pressures up to 190 GPa. Proc. Natl. Acad. Sci. U.S.A. 2017, 114, 13144–13147.

(25) Shukunami, Y.; Yamashita, A.; Goto, Y.; Mizuguchi, Y. Synthesis of R-123 high-T$_c$ superconductors with a high-entropy-alloy-type RE site. Phys. C 2020, 572, No. 1353623.