Preparation, thermoelectric properties, and crystal structure of boron-doped Mg$_2$Si single crystals

Kei Hayashi, Wataru Saito, Kazuya Sugimoto, Kenji Ohoyama, Kouichi Hayashi, Naohisa Hoppo, Masahide Harada, Kenichi Oikawa, Yasuhiro Inamura, and Yuzuru Miyazaki

Cite as: AIP Advances 10, 035115 (2020); https://doi.org/10.1063/1.5143839
Submitted: 06 January 2020 . Accepted: 25 February 2020 . Published Online: 12 March 2020

© 2020 Author(s).
Preparation, thermoelectric properties, and crystal structure of boron-doped Mg$_2$Si single crystals

Kei Hayashi, Wataru Saito, Kazuya Sugimoto, Kenji Ohoyama, Kouichi Hayashi, Naohisa Happo, Masahide Harada, Kenichi Oikawa, Yasuhiro Inamura, and Yuzuru Miyazaki

AFFILIATIONS
1 Department of Applied Physics, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan
2 Institute of Quantum Beam Science, Graduate School of Science and Engineering, Ibaraki University, Tokai 319-1106, Japan
3 Department of Physical Science and Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan
4 Frontier Research Institute for Materials Science, Nagoya Institute of Technology, Nagoya 466-8555, Japan
5 Department of Computer and Network Engineering, Graduate School of Information Sciences, Hiroshima City University, Hiroshima 731-3194, Japan
6 Materials and Life Science Division, J-PARC Center, Tokai 319-1195, Japan
7 Author to whom correspondence should be addressed: hayashik@crystal.apph.tohoku.ac.jp

ABSTRACT

Mg$_2$Si is a potential thermoelectric (TE) material that can directly convert waste energy into electricity. In expectation of improving its TE performance by increasing electron carrier concentration, the element boron (B) is doped in Mg$_2$Si single crystals (SCs). Their detailed crystal structures are definitely determined by using white neutron holography and single-crystal x-ray diffraction (SC-XRD) measurements. The white neutron holography measurement proves that the doped B atom successfully substitutes for the Mg site. The SC-XRD measurement confirms the B-doping site and also reveals the presence of the defect of Si vacancy (V$_{Si}$) in the B-doped Mg$_2$Si SCs. The fraction of V$_{Si}$ increases with increasing B-doping concentration. In the case of B-doped Mg$_2$Si polycrystals (PCs), V$_{Si}$ is absent; this difference between the SCs and PCs can be attributed to different preparation temperatures. Regarding TE properties, the electrical conductivity, $\sigma$, and the Seebeck coefficient, $S$, decreases and increases, respectively, due to the decrease in the electron carrier concentration, contrary to the expectation. The power factor of the B-doped Mg$_2$Si SCs evaluated from $\sigma$ and $S$ does not increase but rather decreases by the B-doping. The tendencies of these TE properties can be explained by considering that the donor effect of the B atom is canceled by the acceptor effect of V$_{Si}$ for the B-doped Mg$_2$Si SCs. This study demonstrates that the preparation condition of Mg$_2$Si should be optimized to prevent the emergence of an unexpected point defect.

© 2020 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5143839

I. INTRODUCTION

Thermoelectric (TE) materials have attracted attention in recent times because they can directly convert waste heat into electricity via the Seebeck effect. The performance of TEs is evaluated in terms of the dimensionless figure of merit, $zT (=S^2\sigma T/\kappa)$, and the power factor (PF) ($=S^2\sigma$), where $S$, $\sigma$, $T$, and $\kappa$ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively. Generally, $zT > 1$ or PF > $2 \times 10^{-3}$ W/K$^2$ m is required for practical use. Mg$_2$Si is one of the promising TE materials due to its preferred characteristics such as lightweight, low cost, and low toxicity. The crystal structure is cubic ($Fm\bar{3}m$), so-called the antifluorite structure (Fig. 1). Magnesium (Mg) and silicon (Si) atoms occupy 8c(1/4 1/4 1/4) and 4a(0 0 0) sites, respectively. In addition, a small fraction of Mg is present at the 4b(1/2 1/2 1/2) interstitial site with an occupancy of ~1%. This interstitial Mg...
(Mg) generates electrons,3,5 and hence, MgSi is an n-type semiconductor.

Because MgSi does not exhibit high $zT$ and PF [e.g., $zT = 0.05$ at 860 K and $PF = 4 \times 10^{-4}$ W/K$^2$ m at 300 K for a Mg$_2$Si polycrystal (PC)], partial substitution for MgSi has been extensively performed.21 Recently, our group prepared boron (B)-doped Mg$_2$Si PCs and successfully increased $\sigma$.22 Consequently, $zT$ and PF was about 0.68 at 850 K and $3.2 \times 10^{-3}$ W/K$^2$ m at 350 K, respectively, with a B-doping concentration of 0.75%. The increase in $\sigma$ is due to the increase in electron carrier concentration, i.e., the doped B atom acts as an electron donor. Although the doped B atom was predicted to substitute for the Si site and generate holes,22 another calculation assuming the presence of Mg suggested that it was located at the interstitial site or the Mg site generating electrons.19

In this study, we have prepared B-doped Mg$_2$Si single crystals (SCs), whose $\sigma$ is expected to further increase because the carrier mobility of a SC is generally higher than that of a PC. However, it should be noted that the preparation temperature of a SC is mostly higher than that of a PC. At a high preparation temperature, unexpected point defects would be generated. In the case of B-doped Mg$_2$Si SCs, we found a killer defect that canceled the effect of the B atom as the electron donor, which is discussed from the results of single-crystal x-ray diffraction (SC-XRD), TE properties, and the novel technique called white neutron holography.

Atomic resolution holography is a powerful probe to directly reveal a three-dimensional local structure in the region of approximately 20 Å from a dopant atom in materials without any proper structure models. X-ray fluorescence holography and photoelectron holography are actively used in novel materials science, for example, in the investigation of dilute magnetic semiconductors, relaxor ferroelectric materials, topological insulators, and so on.3,4,23-30 In particular, neutron holography is indispensable for novel materials science because of higher sensitivity to light elements, such as hydrogen (H), B, and oxygen (O), which play important roles in functional materials. For example, the local structures around a H atom in Al$_2$Ga$_2$O$_3$(OH)$_3$ and ZrO$_2$8,22 SCs and around a cadmium (Cd) atom in Pb$_{0.9974}$Cd$_{0.0026}$ and ScCd$_{0.0026}$ SCs have been observed by using neutron holography in reactor facilities. It should be emphasized that the accuracy of atomic images can be drastically enhanced by using white neutrons.7,9,23 By white neutron holography, local structures around a europium (Eu) atom in a 1 at. % Eu-doped CaF$_2$ SC11 and around a B atom in a 0.26 at. % B-doped Si SC28 have been accurately reconstructed. From the local structures, the position of the dopant atoms, the B atom in the Mg$_2$Si SC in this study, can be determined.

II. EXPERIMENTAL PROCEDURES

Before the preparation of B-doped Mg$_2$Si SCs, Mg$_2$Si powder was synthesized by the solid-state reaction. Mg powder (2N5, 180 μm, Kojundo Chemical Laboratory) and Si powder (4Nup, 300 μm, Kojundo Chemical Laboratory) were weighed in the nominal composition of Mg$_2$Si = 2:1 and was heated at 823 K for 6 h in an evacuated quartz tube. Subsequently, the synthesized Mg$_2$Si powder and B powder (2 N, 45 μm pass, Kojundo Chemical Laboratory) were mixed in the nominal composition of Mg$_2$Si:B = 100:x (x = 0, 0.25, 0.50, and 0.75). The mixed powder was melted at 1413 K in a quartz tube filled with an Ar gas at a pressure of 1.3 atm, followed by gradual cooling down to 1313 K for 24 h and finally to room temperature for 9 h to obtain a melted ingot. An x-ray Laue diffraction pattern, observed by using an x-ray Laue camera (RINT, Rigaku), clearly confirmed that the obtained ingot was the B-doped Mg$_2$Si SC (Fig. 2).

To elucidate the B-doping site in Mg$_2$Si, we adopted neutron holography measurement at the beam line 10 (BL10) of Materials and Life Science Experimental Facility (MLF) in the Japan Proton Accelerator Research Complex (J-PARC) in Tokai, Japan. The B-doped Mg$_2$Si SC with the B-doping concentration x = 0.75 was used for the measurement, whose size was $5 \times 8 \times 10$ mm$^3$. The atomic images of local atomic structures around the doped B were reconstructed using 66 holograms with different wavelengths in the range of 0.63–3.96 Å (the energy range was 5.22–206.0 meV). The details and principles of white neutron holography are also reported in Refs. 37 and 38. To characterize the crystal structure of all B-doped Mg$_2$Si SCs, we performed SC-XRD with Mo K$_\alpha$ radiation (D8 QUEST, Bruker AXS) using a small piece of SC (typically, $30 \times 10 \times 0.5$ μm$^3$) picked up from the SCs. Crystal structure refinement was carried out by using the least-squares calculation code JANA2006.25 The measurement temperature for neutron holography and SC-XRD was set at 300 K.

Regarding the TE properties, the Seebeck coefficient, $S$, and electrical conductivity, $\sigma$, were measured in vacuum from 300 K to 850 K using an automated Seebeck tester (RZ2001i, Ozawa Science Co.). To evaluate the electron carrier concentration, $n$, and carrier mobility, $\mu$, a Hall coefficient was measured under ~50 000 Oe to 50 000 Oe magnetic fields at 300 K using the physical property measurement system (PPMS, Quantum Design). The sample size for the
TE measurements and Hall measurements was $\sim 3 \times 3 \times 9 \text{ mm}^3$ and $\sim 2.5 \times 6 \times 0.8 \text{ mm}^3$, respectively.

III. RESULTS AND DISCUSSION

We investigated the B-doping site in the Mg$_2$Si SC using white neutron holography. Figure 3(a) shows an atomic image in the [100] plane which includes the doped B atom in the Mg$_2$Si SC at room temperature. Bright spots indicate the presence of some kind of atoms, not a ghost, which was periodically located around the B atom (the orange circle) set at the center of the atomic image. The distance between the B atom and the nearest neighbor atom was $\sim 3.18 \text{ Å}$, corresponding to that between the Mg sites or between the Si and interstitial sites. This means that the B atom substitutes for a specific site in the Mg$_2$Si SC. Assuming that the B atom is introduced to the Mg site, Mg atoms are expected to exist in the green circles, as shown in Fig. 3(b). The observed atoms coincided with the green circles, which directly demonstrate that the B atom substitutes for the Mg site. In Fig. 3(c), the expected location of Si atoms is indicated by the red circles in case the B atom is assumed to substitute for the Si site. In the same plane, there are also interstitial sites (the yellow circles). The observed atoms can be assigned to the red and yellow circles on halves. This means that the Si and interstitial sites are occupied at the same rate; however, it is not reasonable because the occupancy of the interstitial site (only $\sim$1% if a small fraction of Mg exists) and that of the Si site (approximately 100%) are different in the case of the Mg$_2$Si PC. The same discussion holds for the case where the B atom is assumed to substitute for the interstitial site [Fig. 3(d)]. The observed atoms are considered to be located at the interstitial site and at the Si site whose occupancy is the same, but it is not conceivable. Thus, a possibility that the B atom substitutes for the Si or interstitial site is denied. Figure 3(a) shows the first experimental evidence that doped B is located at the Mg site. From the white neutron holography measurement, electron carriers will increase because the B atom at the Mg site acts as an electron donor.

The B-doping site was further examined by the SC-XRD measurement using the B-doped Mg$_2$Si SC with $x = 0.75$. We considered three situations; the B atoms are introduced to the Mg, Si, or interstitial site. As listed in Table I, the reliability factor, $R$, and goodness-of-fitness, $gof$, for the case of the Mg site was the lowest among the three situations. Thus, it is concluded that the B atom substitutes for the Mg site, consistent with the result of the white neutron holography measurement. Table II lists the refined structural parameters for all B-doped Mg$_2$Si SCs. The lattice parameter decreased with increasing $x$, supporting the successful substitution of B in the Mg$_2$Si SCs. Importantly, it was found that the Si vacancy (V$_{\text{Si}}$) is formed in the B-doped Mg$_2$Si SCs. In contrast, V$_{\text{Si}}$ was not observed for the B-doped Mg$_2$Si PCs.$^{19}$ This difference is probably due to the higher preparation temperature of SCs (1413 K) than that of PCs (1123 K$^{19}$). As mentioned, the B atom at the Mg site introduces electrons, making the chemical potential near the conduction band minimum. In this case, V$_{\text{Si}}$ is an acceptor-type defect, according to a theoretical
calculation. Thus, $V_{Si}$ can act like a killer defect that compensates electrons generated from the B atom.

To investigate the B-doping effect on electron concentration, we measured temperature-dependent electrical conductivity, $\sigma$, of the B-doped Mg$_2$Si SCs (Fig. 4). The filled symbols are the data for the SCs. The data of B-doped Mg$_2$Si PCs are shown for comparison (the open symbols). In the case of PCs, $\sigma$ increases by B-doping; however, the B-doping for the Mg$_2$Si SC resulted in the decrease in $\sigma$. To reveal the reason for this difference, the electron carrier concentration, $n$, and carrier mobility, $\mu$, of the B-doped Mg$_2$Si SCs were measured at 300 K [Figs. 5(a) and 5(b)]. In the figures, the $n$ and evaluated $\mu$ of B-doped Mg$_2$Si PCs are also shown. The $n$ of the non-doped Mg$_2$Si SC was comparable with that of the non-doped Mg$_2$Si PC. On the other hand, the non-doped Mg$_2$Si SC exhibited ten times higher $\mu$ than the non-doped Mg$_2$Si PC. This is a reason for the higher $\sigma$ of the non-doped Mg$_2$Si SC than the non-doped Mg$_2$Si PC. With increasing $x$, the $n$ increased for the case of PCs, whereas it slightly decreased from $1.1 \times 10^{19}$ cm$^{-3}$ ($x = 0$) to $8.4 \times 10^{18}$ cm$^{-3}$ ($x = 0.75$) for the case of SCs. The decrease in $n$ from $x = 0$ to $x = 0.75$ amounts to ~24%, which is not considered to result from the change in the lattice constant induced by B-doping. The lattice constant decreased from $x = 0$ to $x = 0.75$ by ~0.12%, which may rather increase $n$ by +0.36%. Thus, an effect of the lattice constant on $n$ and also on the TE properties can be neglected. Instead, the decrease in $n$ can be explained by the competition between the donor-type B-dopant and the acceptor-type $V_{Si}$ defect in the B-doped Mg$_2$Si SCs. The $\mu$ of the non-doped Mg$_2$Si SC was 279 cm$^2$/V s, which is in the same order with literature values. The $\mu$ of the B-doped Mg$_2$Si SCs and PCs both decreased with increasing $x$, probably due to the B-dopant and/or the $V_{Si}$ defect acting as a scattering center of electron carriers. Although the $\mu$ of the SCs kept a higher level in the order of $10^7$ cm$^2$/V s, the decrease in $n$ resulted in the lower electrical conductivity of the B-doped Mg$_2$Si SCs than the non-doped Mg$_2$Si SC as well as the B-doped Mg$_2$Si PC with $x = 0.75$.

The decrease in $n$ for the B-doped Mg$_2$Si SC is further confirmed by the measured Seebeck coefficient, $S$, as shown in Fig. 6. Although there is not much difference in $S$ among the SCs and PCs, one can find that the absolute value of $S$ decreased by B-doping in the case of the PCs. In contrast, it increased with increasing $x$ in the case of the SCs, which is a typical behavior when $n$ decreases.

Finally, we calculated the PF of the B-doped Mg$_2$Si SCs, and plotted its temperature dependence as shown in Fig. 7 (the filled symbols). The open symbols indicate the PF of B-doped Mg$_2$Si SCs.

### Table I. Reliability factor ($wR$) and good-of-fitness (gof) for the structural refinement of the B-doped Mg$_2$Si single crystal with the B-doping concentration $x = 0.75$, assuming that the B-doping site is the Mg, Si, or interstitial site.

| B-doping site | $wR$ | gof |
|---------------|------|-----|
| Mg site       | 5.44 | 3.68 |
| Si site       | 5.50 | 3.70 |
| Interstitial site | 28.7 | 19.3 |

*The Mg/B occ. was fixed to 0.75% due to a difficulty in the determination of the small fraction of the light element boron.

### Table II. Reliability factor ($wR$), good-of-fitness (gof), lattice constant, occupancies, and isotropic atomic displacement parameters ($U_{iso}$) of the B-doped Mg$_2$Si single crystals.

| B-doping concentration $x$ (%) | $wR$ | gof | Lattice constant (Å) | Mg/B occ. (%) | Si occ. (%) |
|-------------------------------|------|-----|----------------------|---------------|-------------|
|                               |      |     | 6.3577(2)            | 100/0         | 99.2(8)     |
| 0                             | 3.14 | 2.19| 6.3577(2)            | 0.0090(2)     | 0.0057(2)   |
| 0.25                          | 2.66 | 1.58| 6.3558(6)            | 97.75/0.25    | 96.6(7)     |
| 0.50                          | 5.01 | 3.29| 6.3521(3)            | 99.50/0.50    | 98.7(12)    |
| 0.75                          | 5.44 | 3.68| 6.3501(7)            | 99.25/0.75    | 97.7(14)    |

*The Mg/B occ. was fixed to the nominal composition due to a difficulty in the determination of the small fraction of the light element boron.

![Graph showing temperature dependence of electrical conductivity, $\sigma$, of the B-doped Mg$_2$Si single crystals (SCs). The data of B-doped Mg$_2$Si polycrystals (PCs) are also shown.](image-url)
FIG. 5. (a) Electron carrier concentration, \(n\), and (b) carrier mobility, \(\mu\), of the B-doped MgSi single crystals (SCs) as a function of the B-doping concentration \(x\). The solid lines are only a guide for the eye. The \(n\) of B-doped MgSi polycrystals (PCs)\(^{19}\) is also shown in (a). The \(\mu\) of B-doped MgSi PCs plotted in (b) is evaluated from the electrical conductivity and \(n\) reported in Ref. 19.

Contrary to the case of the MgSi PC, B-doping deteriorated the PF of the MgSi SC, mainly reflecting the decrease in \(\sigma\). The maximum PF of the non-doped MgSi SC and the B-doped MgSi SC with \(x = 0.75\) was \(2.0 \times 10^{-3}\) W/K\(^2\) m at 348 K and \(1.7 \times 10^{-3}\) W/K\(^2\) m at 348 K, respectively, which was lower than that of the B-doped MgSi PC with \(x = 0.75\).

In this study, we attempted to enhance the TE performance of MgSi by preparing its SC in combination with B-doping. This attempt was partially successful; a higher \(\mu\) was achieved for the SCs relative to the PCs, but the \(V_{\text{Si}}\) defect was unexpectedly formed in the SCs and canceled the effect of the doped B atom as the electron donor. The concentration, \(N\), of doped B atoms or \(V_{\text{Si}}\) can be estimated by using the formula, \(N = \exp(-E_f/k_B T)\), where \(E_f\) and \(k_B\) are the formation energy and Boltzmann constant, respectively. In Ref. 22, the \(E_f\) of the B doping to the Mg site in MgSi, \(E_{\text{B-Mg}}\), is calculated to be \(\sim 0.4\) eV in the case that one Mg atom in a \(2 \times 2 \times 2\) MgSi supercell is replaced by B. The expected B concentration at 1123 K and 1413 K, where B-doped MgSi PCs\(^{19}\) and SCs were prepared, is 1.6% and 3.7%, respectively. Thus, the doped B atoms are considered to successfully substitute for the Mg site in both MgSi PCs\(^{19}\) and SCs because the B doping concentration is 0.75% at maximum. On the other hand, the concentration of \(V_{\text{Si}}\) can be affected by the preparation temperature, because the \(E_f\) of \(V_{\text{Si}}\), \(E_{\text{V-Si}}\), is \(\sim 1.6\) eV,\(^{40}\) which is higher than that of \(E_{\text{B-Mg}}\). It should be noted that this \(E_{\text{V-Si}}\) is calculated for MgSi, not for B-doped MgSi. However, we can speculate that \(E_{\text{V-Si}}\) is higher than \(E_{\text{B-Mg}}\) because of the fact that \(V_{\text{Si}}\) only appeared for the B-doped MgSi SCs prepared at 1413 K, not for the B-doped MgSi PCs prepared in 1123 K. To avoid the formation of \(V_{\text{Si}}\), the preparation temperature should be decreased in order to selectively eliminate \(V_{\text{Si}}\) but needs to be high enough to prepare a SC. The B-doped MgSi SC without \(V_{\text{Si}}\) is the most preferable because it should exhibit high electrical conductivity owing to high electron carrier concentration as well as high carrier mobility. The control of the preparation condition, in particular, the decrease in the preparation temperature, of the B-doped MgSi SC is underway.

IV. CONCLUSIONS

We have prepared B-doped MgSi single crystals (SCs) and investigated the effect of B-doping on their crystal structures and thermoelectric (TE) properties. White neutron holography and single-crystal x-ray diffraction (SC-XRD) measurements reveal that the doped B atom substitutes for the Mg site in MgSi SC together with the formation of Si vacancy (\(V_{\text{Si}}\)). It is expected that the B atom

FIG. 6. Temperature dependence of the Seebeck coefficient, \(S\), of the B-doped MgSi single crystals (SCs). The data of B-doped MgSi polycrystals (PCs)\(^{19}\) are also shown.

FIG. 7. Temperature dependence of the power factor, PF, of the B-doped MgSi single crystals (SCs). The data of B-doped MgSi polycrystals (PCs)\(^{19}\) are also shown.
at the Mg site can be an electron donor. The fraction of $V_{\text{Si}}$ increases as the B-doping concentration $x$ increases. The presence of $V_{\text{Si}}$ was not reported for the B-doped Mg$_x$Si polycrystals (PCs). This difference between the B-doped Mg$_x$Si SCs and PCs is probably due to the preparation temperature. With a higher preparation temperature of the SCs, the formation of $V_{\text{Si}}$ is evident.

Regarding the TE properties, the electrical conductivity, $\sigma$, of the non-doped Mg$_x$Si SC is higher than that of the non-doped Mg$_x$Si PC, and this can be seen as a result of their difference in carrier mobility. Opposite to the expectation that B-doping increases $\sigma$, electron carrier concentration, $n$, of the Mg$_x$Si SC decreases with increasing $x$, which can be explained by considering that the $V_{\text{Si}}$ defect acts as a killer defect against the doped B atom. In other words, electron carriers generated from the B atom are compensated by the acceptor-type $V_{\text{Si}}$ defect. Due to the decrease in $n$, the absolute value of the Seebeck coefficient of the Mg$_x$Si SC slightly increases by B-doping. Consequently, the power factor, PF, of the Mg$_x$Si SC is not enhanced by B-doping. The maximum PF among the SCs is $2.0 \times 10^{-3}$ W/K$^2$ at $348$ K for the non-doped Mg$_x$Si SC, which is higher than that of the non-doped Mg$_x$Si PC but is lower than that of the B-doped Mg$_x$Si PC with $x = 0.75$.

This study demonstrates that some kind of point defect is unintentionally formed in Mg$_x$Si depending on its preparation condition, in particular, on the preparation temperature. White neutron holography and SC-XRD measurements are useful in determining the detailed crystal structure such as dopant sites and point defects in Mg$_x$Si. An optimized preparation condition to control the dopant site and point defects can be revealed by using these measurements, and the enhancement of the TE performance of the B-doped Mg$_x$Si SC will be realized in the future.

ACKNOWLEDGMENTS

This work was partially financed by the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan (Grant Nos. 25289222, 17H03398, 17H05207, 26105006, 17K05116, and 19H06655). The white neutron holography experiments were performed under the user program of the MLF of the J-PARC (Proposal Nos. 2018F0100, 2018B0049, and 2019A0082).

DATA AVAILABILITY

The data that supports the findings of this study are available within this article.

REFERENCES

1. M. Kubouchi, K. Hayashi, and Y. Miyazaki, J. Alloys Compd. 617, 389 (2014).
2. M. Kubouchi, Y. Ogawa, K. Hayashi, T. Takamatsu, and Y. Miyazaki, J. Electron. Mater. 45, 1389 (2016).
3. A. Kato, T. Yagi, and N. Fukusako, J. Phys.: Condens. Matter 21, 205801 (2009).
4. N. Hirayama, T. Iida, K. Nishino, Y. Kogo, K. Takarabe, and N. Hamada, Jpn. J. Appl. Phys. 56, 05DD05 (2017).
5. Y. Imai, Y. Mori, S. Nakamura, and K. Takarabe, J. Alloys Compd. 664, 369 (2016).
6. J. Tani and H. Kido, J. Alloys Compd. 466, 335 (2008).
7. J. Tani and H. Kido, Physica B 364, 218 (2005).
8. J. Tani and H. Kido, Intermetallics 15, 1202 (2007).
9. M. Yang, W. Luo, Q. Shen, H. Jiang, and L. Zhang, Adv. Mater. Res. 66, 17 (2009).
10. T. Sakamoto, T. Iida, S. Kurosaki, K. Yano, H. Taguchi, K. Nishio, Y. Kogo, and Y. Takahashi, J. Electron. Mater. 39, 1708 (2010).
11. W. You, K.-H. Park, I.-H. Kim, S.-M. Choi, W.-S. Seo, and S.-U. Kim, J. Electron. Mater. 41, 1675 (2011).
12. Y. Hayatsu, T. Iida, T. Sakamoto, S. Kurosaki, K. Nishio, Y. Kogo, and Y. Takahashi, J. Solid State Chem. 193, 161 (2012).
13. S. Battiston, S. Fiameni, M. Saleemi, B. Holdgrin, A. Faneggi, M. Stingeri, M. Stoprak, M. Fabrizio, and S. Barison, J. Electron. Mater. 42, 1956 (2013).
14. T. Nemoto, T. Iida, J. Sato, T. Sakamoto, N. Hirayama, T. Nakajima, and Y. Takahashi, J. Electron. Mater. 42, 2192 (2013).
15. M. Ioannou, G. Polymeris, E. Hatzikraniotis, A. U. Khan, K. M. Paraskevopoulos, and T. Kyratsis, J. Electron. Mater. 42, 1827 (2013).
16. M. Kubouchi, K. Hayashi, and Y. Miyazaki, Sci. Mater. 123, 59 (2016).
17. W. You, J. Li, J. Li, H. Yang, G. Chen, and P. Zhai, J. Mater. Sci.: Mater. Electron. 29, 10904 (2018).
18. J. Li, X. Li, B. Cai, C. Chen, Q. Zhang, Z. Zhao, L. Zhang, F. Yu, D. Yu, Y. Tian, and B. Xu, J. Alloys Compd. 741, 1148 (2018).
19. N. Hirayama, T. Iida, S. Morioka, M. Sakamoto, K. Nishio, Y. Kogo, Y. Takahashi, and N. Hamada, J. Mater. Res. 30, 2564 (2015).
20. W. Hu, K. Hayashi, T. Fukumura, K. Akagi, M. Tsukada, N. Hanno, S. Hosokawa, K. Ohwada, M. Takahasi, M. Suzuki, and M. Kawasaki, Appl. Phys. Lett. 106, 224203 (2015).
21. W. Hu, K. Hayashi, K. Ohwada, J. Chen, N. Hanno, S. Hosokawa, M. Takahasi, A. A. Bokov, and Z. Ye, Phys. Rev. B 89, 140103 (2014).
22. K. Hayashi, N. Uchitomi, K. Yamagami, A. Suzuki, H. Yoshizawa, J. T. Asubar, N. Hanno, and S. Hosokawa, J. Appl. Phys. 119, 125703 (2016).
23. Y. Wakabayashi, D. Nakajima, Y. Ishiguro, K. Kimura, T. Kimura, S. Tsutsui, A. Q. R. Baron, K. Hayashi, N. Hanno, S. Hosokawa, K. Ohwada, and S. Nakatsuji, Phys. Rev. B 93, 245117 (2016).
24. A. Sato-Tomita, N. Shibayama, N. Hanno, K. Kimura, T. Okabe, T. Matsushita, S.-Y. Park, Y. C. Sasaki, and K. Hayashi, Rev. Sci. Instrum. 87, 063707 (2016).
25. Y. Yamamoto, K. Hayashi, N. Hanno, S. Hosokawa, and H. Tajiri, Acta Mater. 131, 534 (2017).
26. S. Hosokawa, J. R. Stellhorn, T. Matsushita, N. Hanno, K. Kimura, K. Hayashi, Y. Ebisu, T. Ozaki, H. Ikemoto, H. Setoyama, T. Okajima, Y. Yoda, H. Ishii, Y.-F. Liao, M. Kitaura, and M. Sasaki, Phys. Rev. B 96, 214207 (2017).
27. T. Hayatsu, T. Terao, T. Uchiyama, T. Ueno, K. Kobayashi, A. Sato-Tomita, N. Shibayama, N. Happo, K. Kimura, T. Okabe, T. Matsushita, S.-Y. Park, Y. C. Sasaki, and K. Hayashi, Rev. Sci. Instrum. 87, 063707 (2016).
28. B. Sur, R. R. Rogge, R. P. Hammond, V. N. P. Anghel, and J. Katsaras, Nature 414, 525 (2001).
29. L. Cser, G. Török, G. Krexzen, M. Prem, and I. Sharkov, Appl. Phys. Lett. 85, 1149 (2004).
30. K. Hayashi, K. Ohoyama, S. Orimo, Y. Nakamori, H. Takahashi, and K. Shibata, Jpn. J. Appl. Phys. 47, 2291 (2008).
31. K. Hayashi, K. Ohoyama, S. Orimo, H. Takahashi, and K. Shibata, Phys. Rev. B 91, 024102 (2015).
32. L. Cser, G. Török, G. Krexzen, I. Sharkov, and B. Faragó, Phys. Rev. Lett. 89, 175504 (2002).
33. A. Szakási, M. Markó, and L. Cser, Phys. Rev. B 93, 174115 (2016).
34. K. Hayashi, K. Ohoyama, N. Hanno, T. Matsushita, S. Hosokawa, M. Harada, Y. Inamura, H. Nitan, T. Shishido, and K. Yubuta, Sci. Adv. 3, e1700294 (2017).
K. Ohoyama and K. Hayashi, Phys. Status Solidi B 255, 1800143 (2018).

V. Petricek, M. Dusek, and L. Palatinus, JANA2006: The Crystallographic Computing System, Institute of Physics, Praha, 2006.

X. Liu, L. Xi, W. Qiu, J. Yang, T. Zhu, X. Zhao, and W. Zhang, Adv. Electron. Mater. 2, 1500284 (2016).

R. G. Morris, R. D. Redin, and G. C. Danielson, Phys. Rev. 109, 1909 (1958).

M. W. Heller and G. C. Danielson, J. Phys. Chem. Solids 23, 601 (1962).

D. Tamura, R. Nagai, K. Sugimoto, H. Udono, I. Kikuma, H. Tajima, and I. J. Ohsugi, Thin Solid Films 515, 8272 (2007).

K. Sekine, M. Midonoya, H. Udono, and Y. Yamada, Phys. Procedia 11, 171 (2011).

T. Tokairin, J. Ikeda, and H. Udono, J. Cryst. Growth 468, 761 (2017).