Multi-temperature structure of thermoelectric Mg_2Si and Mg_2Sn

Hidetaka Kasai,^{a,b} Lirong Song,^b Henrik Lyder Andersen,^b Hao Yin^c and Bo Brummerstedt Iversen^{b*}

Received 13 March 2017
Accepted 28 September 2017

Edited by T. N. Guru Row, Indian Institute of Science, India

Keywords: synchrotron X-ray powder diffraction; magnesium silicide; magnesium stannide; Debye temperature; thermoelectric materials.

CCDC references: 1577026; 1577027; 1577028; 1577029; 1577030; 1577031; 1577032; 1577033; 1577034; 1577035; 1577036; 1577037; 1577038; 1577039; 1577040; 1577041; 1577042; 1577043; 1577044; 1577045; 1577046; 1577047; 1577048; 1577049; 1577050; 1577051; 1577052; 1577053; 1577054; 1577055; 1577056; 1577057; 1577058; 1577059; 1577060; 1577061; 1577062; 1577063; 1577064; 1577065; 1577066; 1577067

Supporting information: this article has supporting information at journals.iucr.org/b

^aFaculty of Pure and Applied Sciences, Tsukuba Research Center for Energy Materials Science, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan, ^bCenter for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark, and ^cTEGnology ApS, Lundagervej 102, Hedensted, DK-8722, Denmark. *Correspondence e-mail: bo@chem.au.dk

A multi-temperature structural study of Mg_2Si and Mg_2Sn was carried out from 100 to 700 K using synchrotron X-ray powder diffraction. The temperature dependence of the lattice parameters can be expressed as $a = 6.3272(4) + 6.5(2) \times 10^{-5}T + 4.0(3) \times 10^{-8}T^2$ Å and $a = 6.7323(7) + 8.5(4) \times 10^{-5}T + 3.8(5) \times 10^{-8}T^2$ Å for Mg_2Si and Mg_2Sn , respectively. The atomic displacement parameters (ADPs) are reported and analysed using a Debye model for the averaged U_{iso} giving Debye temperatures of 425(2) K for Mg_2Si and 243(2) K for Mg_2Sn . The ADPs are considerably smaller for Mg_2Si than for Mg_2Sn reflecting the weaker chemical bonding in the Mg_2Sn structure. Following the heating, an annealing effect is observed on the lattice parameters and peak widths in both structures, presumably due to changes in the crystal defects, but the lattice thermal expansion is almost unchanged by the annealing. This work provides accurate structural parameters which are of importance for studies of Mg_2Si , Mg_2Sn and their solid solutions.

1. Introduction

Mg_2Si and Mg_2Sn are the two end members of $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ solid solutions which have attracted much attention as promising thermoelectric materials to be applied in power generation from waste heat recovery. The thermoelectric $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ compounds are especially attractive due to the earth-abundant, low-cost and non-toxic constituent elements as well as high thermoelectric figure-of-merit, zT , which can reach values larger than unity in n -type $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ solid solutions (Zaitsev *et al.*, 2006; Søndergaard *et al.*, 2012; Liu *et al.*, 2012, 2013). In addition, narrow-gap semiconducting Mg_2Si and Mg_2Sn are candidates for infrared optoelectronic devices (Udono *et al.*, 2015).

Detailed structural information of the end members Mg_2Si and Mg_2Sn is important in structural studies of the more complicated $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ solid solution compounds (Andersen *et al.*, 2017) as well as for understanding their properties and applications. For applications in thermoelectric modules, structural information such as thermal expansion and structural stability is essential (Søndergaard *et al.*, 2013b; Imai *et al.*, 2015; Andersen *et al.*, 2017). Recently, Imai *et al.* (2015) reported precise thermal expansion coefficients for Mg_2Si from 293 to 873 K. However, there is still a lack of precise experimental information on thermal expansion for Mg_2Sn as well as the dynamic behavior (thermal motion) for both Mg_2Si and Mg_2Sn . Here, we present a multi-temperature structural study of Mg_2Si and Mg_2Sn from 100 to 700 K using

© 2017 International Union of Crystallography

high-resolution synchrotron X-ray powder diffraction yielding precise structural information on lattice parameters and atomic displacement parameters (ADPs) as a function of temperature.

2. Experimental and methods

2.1. Sample preparation

Mg₂Si and Mg₂Sn were synthesized by the direct reaction of the pure elements (Mg 99.98%; Si 99.9+%; Sn 99.97%). The pure elements were weighed according to the stoichiometry of Mg_{2.2}Si and Mg_{2.2}Sn. An excess amount of Mg was added to compensate for evaporation. The elements were mixed in Al₂O₃ crucibles with lids and reacted at ~1673 K for less than 15 min in an induction furnace under a helium pressure of 0.7 MPa. The ingots produced were then crushed and ground to powders. After ball milling, the powders were densified by spark plasma sintering. Details about the sample preparation are given by Søndergaard *et al.* (2013a).

2.2. Synchrotron X-ray powder diffraction measurement

High-resolution synchrotron powder X-ray diffraction (PXRD) data were measured using a large Debye–Scherrer camera with an image plate (IP) detector at the BL44B2 beamline of SPring-8 (Kato *et al.*, 2010; Kato & Tanaka, 2016). The incident X-ray wavelengths were calibrated using PXRD data of a NIST CeO₂ standard sample [$a = 5.411651(6)$ Å]. The calibrated wavelengths were 0.49935 and 0.49961 Å for measurements at low temperatures and high temperatures, respectively. All data were collected from $2\theta = 2.5$ – 77° with a step of 0.01° . The collimator sizes were 0.5 mm $\times$ 3.0 mm and 0.5 mm $\times$ 1.0 mm for low temperature (LT) and high temperature (HT), respectively. The powder samples were packed in 0.2 mm glass and quartz capillaries for LT and HT,

respectively, after size selection using a powder floating technique. The LT data were collected from 100 to 300 K with 50 K intervals using a nitrogen flow cooler. The HT data were collected from 300 to 700 K with 50 K intervals for the first cycle, at 300 and 700 K for the second cycle, and finally at 300 K on an IP using a nitrogen flow heater. PXRD data of Cu, which previously had been used for temperature calibration (Wahlberg *et al.*, 2016), were also measured to confirm sample temperatures.

2.3. Data analysis

The PXRD data were analyzed by Rietveld refinements using program *Synchrotron Powder* (Nishibori *et al.*, 2007). Fig. 1 shows the structure of Mg₂Si and Mg₂Sn with $Fm\bar{3}m$ space group, where Mg is at the $8c$ ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) site and Si/Sn is at the $4a$ (0, 0, 0) site, illustrated using *CrystalMaker* (Palmer, 2014). The site symmetries of Mg and Si/Sn are $\bar{4}3m$ and $m\bar{3}m$, respectively, and therefore their ADPs are isotropic in the harmonic approximation. The refinements were carried out with full site occupancy using a pseudo-Voigt peak profile (two parameters) with three half-width parameters, a peak shift within 0.01° (one parameter) and peak asymmetry (two parameters). The background was treated by a 12th-order polynomial with extra Pearson VII distributions. Anomalous scattering factors were taken from the Sasaki table (Sasaki, 1989).

The ADPs were fitted to a Debye model (Willis & Pryor, 1975; Bientien *et al.*, 2005)

$$U_{\text{iso}}(T) = \frac{3\hbar^2 T}{mk_B \Theta_D^2} \left[\frac{T}{\Theta_D} \int_0^{\Theta_D/T} \frac{x}{\exp(x) - 1} dx + \frac{\Theta_D}{4T} \right] + d^2,$$

where T is the temperature, Θ_D is the Debye temperature, m is the mass of the atom, k_B is the Boltzmann constant, $\hbar$ is the reduced Planck constant and d^2 is a disorder parameter. Although the Debye expression is given for a monoatomic cubic crystal, it has been applied to more complicated materials to obtain useful information (Bientien *et al.*, 2005; Blichfeld & Iversen, 2015; Sist *et al.*, 2016). The fits to the integral Debye expression were performed using a program written by Blichfeld (2016).

3. Results and discussion

3.1. Confirmation of sample temperatures using copper

Fig. 2(a) shows the temperature dependence of the lattice parameters of Cu obtained from Rietveld refinement. The obtained lattice parameters were compared with those calculated using the thermal expansion from 20 to 800 K reported by Hahn (1970). The reported equation for the thermal expansion from 243 to 800 K was extended above 800 K for comparison in Fig. 2(a). In the calculation, the experimental lattice parameters of 3.614116 (5) and 3.615305 (6) Å at 300 K were used for LT and HT, respectively. There is 0.001 Å difference at 300 K between the lattice parameters for LT and HT. Such minor systematic differences between the LT and HT experimental procedure have been noted before for the

Figure 1

The crystal structure of Mg₂Si and Mg₂Sn. Yellow and blue spheres represent Mg and Si/Sn atoms, respectively.

present diffractometer setup (Skovsen *et al.*, 2010; Kastbjerg *et al.*, 2013). The obtained lattice parameters agree with those calculated using the reported thermal expansion.

Fig. 2(b) shows the U_{iso} values of Cu obtained from Rietveld refinement using LT data from 100 to 300 K and HT data from 300 to 750 K, which cover the temperature range for measurements of Mg_2Si and Mg_2Sn . A Debye temperature of $\Theta_D = 310$ (3) K is obtained from a fit to the Debye model. This Debye temperature is in good agreement with the reported values, *e.g.* $\Theta_D = 313$ (3) K (Butt *et al.*, 1988). The lattice parameters and ADPs of Cu confirm that the estimated sample temperatures are accurate.

3.2. Structural refinement of Mg_2Si and Mg_2Sn

Fig. 3 shows the PXRD patterns of Mg_2Si and Mg_2Sn measured at 100 and 700 K. In the Mg_2Si sample for LT measurements, tiny amounts of Al (space group: $Fm\bar{3}m$) and Si (space group: $Fd\bar{3}m$) were found as impurities. The weight fractions of Mg_2Si , Al and Si are estimated as 99.2%, 0.3% and 0.5%, respectively, using the equation proposed by Hill &

Figure 2

(a) Temperature dependence of the lattice parameter and U_{iso} of Cu. The parameters obtained from both the LT data (black circles) and the HT data (blue squares) are plotted. The experimental lattice parameters are compared with those calculated using the reported thermal expansion (Hahn, 1970). (b) Refined U_{iso} values fitted to a Debye model. Error bars (not shown) are smaller than the symbols.

Howard (1987). It may be noted that such minute amounts of impurities are only detected due to the high intensity of the synchrotron beam and the excellent signal-to-noise ratio of the data. In the Mg_2Si HT sample, only Al was found as an impurity with a weight fraction of 0.3%. In the case of Mg_2Sn , an Sn impurity (space group: $I4_1/amd$) with the weight fraction of 3% was refined which, however, completely disappeared between 500 and 550 K data because of the melting point at 505 K. The impurities were treated as second and

Figure 3

Results of Rietveld refinements of Mg_2Si and Mg_2Sn PXRD data. The results are shown for: (a) Mg_2Si at 100 K, (b) Mg_2Sn at 100 K, (c) Mg_2Si at 700 K and (d) Mg_2Sn at 700 K. Observed (black circles), calculated (red line) and difference intensities (green line) are represented together with calculated positions of Bragg peaks (black markers). Reliability factors based on weighted profile R_{wp} and Bragg intensity R_1 are (a) $R_{\text{wp}} = 3.51\%$, $R_1 = 4.06\%$, (b) $R_{\text{wp}} = 5.04\%$, $R_1 = 1.85\%$, (c) $R_{\text{wp}} = 1.75\%$, $R_1 = 4.00\%$, (d) $R_{\text{wp}} = 3.08\%$, $R_1 = 3.16\%$.

Figure 4

Temperature dependence of lattice parameters of Mg_2Si and Mg_2Sn . Error bars (not shown) are smaller than the symbols. The dashed and full red lines are the first and second degree polynomial fits, respectively.

Table 1

Lattice parameters, a , as a function of temperature, and thermal expansion coefficients, α_a , of Mg_2Si and Mg_2Sn .

	a (Å)	α_a ($\times 10^{-5} \text{ K}^{-1}$) at RT
Mg_2Si		
Present work	(First degree) $a = 6.3224(7) + 9.72(17) \times 10^{-5}T$	1.53(3)
	(Second degree) $a = 6.3272(4) + 6.5(2) \times 10^{-5}T + 4.0(3) \times 10^{-8}T^2$	1.40(6)
Imai <i>et al.</i> (2015)	(First degree) $a = 6.321(1) + 9.8(2) \times 10^{-5}T$	1.55(3)
	(Second degree) $a = 6.328(2) + 7.3(7) \times 10^{-5}T + 2.2(6) \times 10^{-9}T^2$	1.3(1)
Mg_2Sn		
Present work	(First degree) $a = 6.7278(7) + 1.152(17) \times 10^{-4}T$	1.70(3)
	(Second degree) $a = 6.7323(7) + 8.5(4) \times 10^{-5}T + 3.8(5) \times 10^{-8}T^2$	1.59(10)
References	6.762†, 6.761‡, 6.760§ at RT	1.9¶, 0.99††

† Anastassakis & Hawranek (1972). ‡ Clark *et al.* (1997). § Janot *et al.* (2006). ¶ Ganeshan *et al.* (2010). †† Jelinek *et al.* (1967).

third phases in the Rietveld refinements. In addition, broad diffraction peaks of MgO (space group: $Fm\bar{3}m$) grow gradually as the temperature increases. The broad MgO peaks were treated as background in the refinements. The details of the refined structural parameters are given in the CIF and the supporting information files.

Fig. 4 shows the refined lattice parameters of Mg_2Si and Mg_2Sn as a function of temperature. The lattice parameters increase almost linearly in the whole temperature range. Table 1 shows first- and second-degree polynomial fitting results. The lattice parameter of Mg_2Si is in good agreement with that reported using PXRD by Imai *et al.* (2015) with the exception of the coefficient of T^2 . It

is known that the thermal expansion coefficient changes a lot in the low-temperature range (Ganeshan *et al.*, 2010). Therefore, the difference of one order of magnitude in the coefficient of T^2 is attributed to the temperature ranges, which are from 100 to 700 K in this study, and from 293 to 873 K in the study by Imai *et al.* (2015). The obtained lattice parameter of Mg_2Sn agrees with the reported experimental values (Anastassakis & Hawranek, 1972; Clark *et al.*, 1997; Janot *et al.*, 2006).

The thermal expansion coefficients of the lattice parameters at 300 K are estimated as $\alpha = 1.53(3) \times 10^{-5}$ and $1.70(3) \times 10^{-5} \text{ K}^{-1}$ for Mg_2Si and Mg_2Sn , respectively. In Table 1, the obtained thermal expansion coefficients are compared with previously reported values. The thermal expansion coefficient of Mg_2Si agrees well with that reported recently by Imai *et al.* (2015), which is larger than $\alpha = 1.09 \text{ K}^{-1}$ reported by Gerstein *et al.* (1967). The thermal expansion coefficient of Mg_2Sn is close to that obtained theoretically by Ganeshan *et al.* (2010), which is larger than $\alpha = 0.99 \text{ K}^{-1}$ reported by Jelinek *et al.* (1967). The observed $\alpha(\text{Mg}_2\text{Sn}) > \alpha(\text{Mg}_2\text{Si})$ is consistent with

Figure 5
 U_{iso} of Mg, Si, and Sn in Mg_2Si and Mg_2Sn as a function of temperature. The red solid lines are the fits of the Debye expression.

Figure 6
Heating cycle dependence of lattice parameters and FWHM for Mg_2Si and Mg_2Sn . Lattice parameters at 300 and 700 K for (a) Mg_2Si and (b) Mg_2Sn . Error bars (not shown) are smaller than the symbols. (c) FWHM of the strongest diffraction peak at 300 and 700 K for Mg_2Si (squares) and Mg_2Sn (triangles).

the fact that Sn-rich samples have larger thermal expansion coefficients than Si-rich samples in $\text{Mg}_2\text{Si}_x\text{Sn}_{1-x}$ solid solutions (Søndergaard *et al.*, 2013a, 2013b).

3.3. Atomic displacement parameters of Mg_2Si and Mg_2Sn

Fig. 5 shows refined U_{iso} of Mg_2Si and Mg_2Sn as a function of temperature. $U_{\text{iso}}(\text{Mg}) > U_{\text{iso}}(\text{Si/Sn})$ can be understood by considering that U is inversely proportional to atomic mass (Willis & Pryor, 1975). On the other hand, the fact that $U_{\text{iso}}(\text{Mg in Mg}_2\text{Sn}) > U_{\text{iso}}(\text{Mg in Mg}_2\text{Si})$ cannot be explained by atomic mass but must relate to differences in the chemical bonding in the two structures. The larger vibration in Mg_2Sn indicates weaker bonding than in Mg_2Si . This is further supported by $U_{\text{iso}}(\text{Sn}) > U_{\text{iso}}(\text{Si})$ even though Sn is much more heavy than Si. The ADPs thus indicate that Mg_2Si is harder than Mg_2Sn , which is consistent with the Vickers hardness (Kevorkijian & Škapin, 2011). A complete analysis of the chemical bonding of Mg_2Si and Mg_2Sn is clearly of interest.

Table 2 shows the Debye temperatures obtained by fitting the Debye expression to the experimental ADPs. The obtained averaged Debye temperatures agree with those estimated from heat capacity measurements (Gerstein *et al.*, 1967; Jelinek *et al.*, 1967). The disorder parameters d^2 are almost zero within three sigma except for $d^2 = 0.0011$ (1) for Si. The disorder parameter for Si may indicate the presence of slight static disorder, but it is difficult to firmly establish minute disorder only using the fitted disorder parameter (Bentien *et al.*, 2005).

3.4. Heating cycle

Figs. 6(a) and 6(b) shows the lattice parameters at 300 and 700 K for each heating cycle. After the first heating cycle, the lattice parameters at 300 K become larger than those before heating for both of Mg_2Si and Mg_2Sn . On the other hand, the changes in the lattice parameters are relatively small at 700 K. The lattice expansion at 300 K after the first heating may be attributed to a decrease in vacancy concentration by heating. Fig. 6(c) shows the full widths at half-maximum (FWHM) of the 220 and 111 peaks for Mg_2Si and Mg_2Sn , respectively. The peak widths at 300 K become sharper after the first heating cycle, indicating that strain is reduced in Mg_2Si and Mg_2Sn . These structural changes can be understood as an annealing effect. In spite of the lattice expansion at 300 K after annealing, the linear thermal expansion coefficients after annealing are estimated to be almost the same values as for the first heating cycle. Therefore, the observed annealing effect presumably is not of consequence in the development of thermoelectric modules.

4. Conclusion

The thermal expansion and ADPs of Mg_2Si and Mg_2Sn have been investigated in the temperature range from 100 to 700 K by means of high-resolution synchrotron powder X-ray diffraction. The sample temperatures, which are important for a multi-temperature structural study, were confirmed using

Table 2

Debye temperatures of Mg_2Si and Mg_2Sn obtained from fitting of U_{iso} to the Debye expression.

The averaged values were estimated from fitting of averaged $U_{\text{iso}} = \frac{2}{3}U_{\text{iso}}(\text{Mg}) + \frac{1}{3}U_{\text{iso}}(\text{Si, Sn})$.

		Debye temperature Θ_D (K)	
		Present	1
Mg_2Si	Mg	405 (3)	
	Si	488 (2)	
	Average	425 (2)	417 at 300 K†
Mg_2Sn	Mg	345 (2)	
	Sn	193 (1)	
	Average	243 (2)	240 at 300 K‡

† Gerstein *et al.* (1967). ‡ Jelinek *et al.* (1967).

synchrotron PXRD data of copper. Precise lattice parameters were obtained and fitted to second-order polynomials in the temperature range of 100 to 700 K yielding $a = 6.3272$ (4) + 6.5 (2) $\times 10^{-5}T + 4.0$ (3) $\times 10^{-8}T^2$ Å and $a = 6.7323$ (7) + 8.5 (4) $\times 10^{-5}T + 3.8$ (5) $\times 10^{-8}T^2$ Å for Mg_2Si and Mg_2Sn , respectively. The linear thermal expansion coefficients at 300 K were estimated to be 1.53 (3) $\times 10^{-5}$ and 1.70 (3) $\times 10^{-5}$ K⁻¹ for Mg_2Si and Mg_2Sn , respectively. These values are consistent with the previously reported values, but more accurate in the temperature range of 100 to 700 K. The obtained ADPs were fitted to the Debye model and Debye temperatures for the averaged ADPs are 425 (2) and 243 (2) K for Mg_2Si and Mg_2Sn , respectively. These values are in agreement with those determined from modelling heat capacity data. The fact that the ADPs for Mg_2Sn are larger than those for Mg_2Si reflect differences in chemical bonding with weaker Mg–Sn interaction compared with Mg–Si. An annealing effect was observed on the lattice parameters and the diffraction peak widths of Mg_2Si and Mg_2Sn , which presumably originates from changes in defects.

Acknowledgements

We thank Anders B. Blichfeld for the program for the fit of the Debye expression. The synchrotron radiation experiments were performed at BL44B2 in SPring-8 with the approval of RIKEN (Proposal No. 20110030).

Funding information

This work was supported by the Danish National Research Foundation (Center for Materials Crystallography, DNRF93), the Danish Council for Nature and Universe (DanScatt) and the JSPS Bilateral Open Partnership Joint Research Projects.

References

Anastassakis, E. & Hawranek, J. P. (1972). *Phys. Rev. B*, **5**, 4003–4007.
Andersen, H. L., Zhang, J., Yin, H. & Iversen, B. B. (2017). *Inorg. Chem. Front.* **4**, 456–467.
Bentien, A., Nishibori, E., Paschen, S. & Iversen, B. B. (2005). *Phys. Rev. B*, **71**, 144107.
Blichfeld, A. B. (2016). PhD thesis, Aarhus University, Denmark.

- Blichfeld, A. B. & Iversen, B. B. (2015). *J. Mater. Chem. C*, **3**, 10543–10553.
- Butt, N. M., Bashir, J., Willis, B. T. M. & Heger, G. (1988). *Acta Cryst. A* **44**, 396–399.
- Clark, C. R., Wright, C., Suryanarayana, C., Baburaj, E. G. & Froes, F. H. (1997). *Mater. Lett.* **33**, 71–75.
- Ganeshan, S., Shang, S. L., Wang, Y. & Liu, Z.-K. (2010). *J. Alloys Compd.* **498**, 191–198.
- Gerstein, B. C., Jelinek, F. J., Habenschuss, M., Shickell, W. D., Mullaly, J. R. & Chung, P. L. (1967). *J. Chem. Phys.* **47**, 2109–2115.
- Hahn, T. A. (1970). *J. Appl. Phys.* **41**, 5096–5101.
- Hill, R. J. & Howard, C. J. (1987). *J. Appl. Cryst.* **20**, 467–474.
- Imai, M., Isoda, Y. & Udono, H. (2015). *Intermetallics*, **67**, 75–80.
- Janot, R., Cuevas, F., Latroche, M. & Percheron-Guégan, A. (2006). *Intermetallics*, **14**, 163–169.
- Jelinek, F. J., Shickell, W. D. & Gerstein, B. C. (1967). *J. Phys. Chem. Solids*, **28**, 267–270.
- Kastbjerg, S., Bindzus, N., Søndergaard, M., Johnsen, S., Lock, N., Christensen, M., Takata, M., Spackman, M. A. & Iversen, B. B. (2013). *Adv. Funct. Mater.* **23**, 5477–5483.
- Kato, K., Hirose, R., Takemoto, M., Ha, S., Kim, J., Higuchi, M., Matsuda, R., Kitagawa, S. & Takata, M. (2010). *AIP Conf. Proc.* pp. 875–878.
- Kato, K. & Tanaka, H. (2016). *Adv. Phys. X*, **1**, 55–80.
- Kevorkijan, V. & Škapin, S. (2011). *Mater. Manuf. Processes*, **26**, 623–631.
- Liu, W., Tan, X., Yin, K., Liu, H., Tang, X., Shi, J., Zhang, Q. & Uher, C. (2012). *Phys. Rev. Lett.* **108**, 166601.
- Liu, W., Zhang, Q., Yin, K., Chi, H., Zhou, X., Tang, X. & Uher, C. (2013). *J. Solid State Chem.* **203**, 333–339.
- Nishibori, E., Sunaoshi, E., Yoshida, A., Aoyagi, S., Kato, K., Takata, M. & Sakata, M. (2007). *Acta Cryst. A* **63**, 43–52.
- Palmer, D. C. (2014). *CrystalMaker*. CrystalMaker Software Ltd, Begbroke, Oxfordshire, England.
- Sasaki, S. (1989). *KEK Report 88-14*, pp. 1–136. National Laboratory for High Energy Physics, Tsukuba, Japan.
- Sist, M., Zhang, J. & Iversen, B. B. (2016). *Acta Cryst. B* **72**, 310–316.
- Skovsen, I., Christensen, M., Clausen, H. F., Overgaard, J., Stiewe, C., Desgupta, T., Mueller, E., Spackman, M. A. & Iversen, B. B. (2010). *Inorg. Chem.* **49**, 9343–9349.
- Søndergaard, M., Christensen, M., Borup, K. A., Yin, H. & Iversen, B. B. (2012). *Acta Mater.* **60**, 5745–5751.
- Søndergaard, M., Christensen, M., Borup, K. A., Yin, H. & Iversen, B. B. (2013a). *J. Elec. Mater.* **42**, 1417–1421.
- Søndergaard, M., Christensen, M., Borup, K. A., Yin, H. & Iversen, B. B. (2013b). *J. Mater. Sci.* **48**, 2002–2008.
- Udono, H., Tajima, H., Uchikoshi, M. & Itakura, M. (2015). *Jpn. J. Appl. Phys.* **54**, 07JB06.
- Wahlberg, N., Bindzus, N., Christensen, S., Becker, J., Dippel, A.-C., Jørgensen, M. R. V. & Iversen, B. B. (2016). *J. Appl. Cryst.* **49**, 110–119.
- Willis, B. T. & Pryor, A. W. (1975). *Thermal Vibrations in Crystallography*. Cambridge University Press.
- Zaitsev, V. K., Fedorov, M. I., Gurieva, E. A., Eremin, I. S., Konstantinov, P. P., Samunin, A. Y. & Vedernikov, M. V. (2006). *Phys. Rev. B*, **74**, 045207.