Journal of Solid State Chemistry 221 (2015) 191–195

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

High-pressure densified solid solutions of alkaline earth hexaborides (Ca/Sr, Ca/Ba, Sr/Ba) and their high-temperature thermoelectric properties

M. Gürsoy [a], M. Takeda [b], B. Albert [a,*]

[a] Technische Universität Darmstadt, Eduard-Zintl-Institute of Inorganic and Physical Chemistry, Alarich-Weiss-Str. 12, 64287 Darmstadt, Germany
[b] Nagaoka University of Technology, Department of Mechanical Engineering, 1603-1 Kamitomioka, 940-2188 Nagaoka, Niigata, Japan

ARTICLE INFO

Article history:
Received 1 August 2014
Received in revised form
29 September 2014
Accepted 5 October 2014
Available online 15 October 2014

Keywords:
Boride
Thermoelectric
Solid solution
Alkaline earth metal

ABSTRACT

Solid solutions of alkaline earth hexaborides were synthesized and densified by spark plasma sintering at 100 MPa. The high-temperature thermoelectric properties (Seebeck coefficients, electrical and thermal diffusivities, heat capacities) were measured between room temperature and 1073 K. CaB_6, SrB_6, BaB_6 and the ternary hexaborides $Ca_xSr_{1-x}B_6$, $Ca_xBa_{1-x}B_6$, $Sr_xBa_{1-x}B_6$ ($x = 0.25$, 0.5, 0.75) are *n*-type conducting compounds over the whole compositional and thermal ranges. The values of the figure of merit ZT for CaB_6 (*ca.* 0.3 at 1073 K) were found to be significantly increased compared to earlier investigations which is attributed to the densification process.

1. Introduction

Thermoelectric materials are amongst the most discussed class of inorganic solids regarding the use of waste heat and energy recovery. By now, there are only few substances with promising thermoelectric properties at high temperatures. Notable candidates are $Si_{1-x}Ge_x$ with a maximum ZT value of *ca.* 0.6 at about 1150 K or $Yb_{14}MnSb_{11}$ with *ca.* 1.0 at about 1250 K, respectively [1,2]. In this context boron-rich materials are very interesting for high-temperature thermoelectric generators because of their refractory properties. Mori et al. described excellent *p*–*n* control in high-temperature thermoelectric borides [3,4]. Boron carbonitrides have been proposed as *n*-type counterparts to boron carbide [5–7]. Semiconducting boron-rich compounds such as *p*-type boron-carbide were discussed for thermoelectric applications since the 1960s [8–14]. Alkaline earth metal borides appear to be possible *n*-type equivalents with good Seebeck coefficients. The discussion of their electric properties has been controversial, SrB_6, for example, being described either as semimetallic [15–17] or semi-conducting [18]. Thermoelectric properties of the binary alkaline earth hexaborides were analyzed by Takeda et al. who found high negative Seebeck coefficients for CaB_6, SrB_6 and BaB_6 [19–23]. Hexaborides show a cubic structure of three-dimensionally connected B_6 octahedra that formally carry a negative charge, with metal ions in the holes and 24-foldly coordinated by boron atoms (cubic crystal system, *s.g.* $Pm\bar{3}m$) [18]. We found that alkaline earth metal (Ca, Sr, Ba) hexaborides are fully miscible and form ternary solid solutions [24,25]. We will now report on their synthesis as phase-pure, crystalline powders, their characterization and the full investigation of their high temperature-thermoelectric properties after compacting by spark plasma sintering.

2. Experimental

Calcium metal (99.9% purity, Smart Elements), strontium metal (99.5%, AlfaAeser, re-distilled), barium metal (99.3%, Chempur, re-distilled) and amorphous boron (99.9% purity, particle size: 1 μm, Chempur) were used as starting materials for the synthesis of binary and ternary alkaline earth hexaborides.

All of the preparations were performed in a glove box under argon atmosphere, due to air- and moisture-sensitivity of the alkaline earth metals. The alkaline earth metals (M^1 and M^2 = Ca, Sr or Ba) and amorphous boron powder were mixed in a ratio of 1:6 to form hexaborides of the composition $(M^1)_x(M^2)_{1-x}B_6$ with $x = 0$, 0.25, 0.5, 0.75 and 1. A slight excess of alkaline earth metal (5–10%) was used and the amount of the samples augmented to approx. 350–500 mg. The mixture was filled in a pre-boronated tantalum crucible. The crucible was sealed by melting in an electric arc. Samples were placed in a high-frequency induction furnace at an argon pressure of 300 mbar and heated for one hour

* Corresponding author. Tel.: +49 6151 162392.
E-mail address: albert@ac.chemie.tu-darmstadt.de (B. Albert).

http://dx.doi.org/10.1016/j.jssc.2014.10.001
0022-4596/

to the melting temperature of the highest (referring to the respective mixture of metals) melting alkaline earth metal (for example: 840 °C) and then for two hours to the boiling point of the highest boiling alkaline earth metal (for example 1630 °C) to ensure products that were as homogeneous as possible. The products obtained were ground, treated with water and hydrochloric acid to remove unreacted alkaline earth metal and then dried in vacuum overnight. The hexaborides were densified for more than one hour at temperatures between 1673 K and 2173 K at a pressure of 100 MPa (equivalent to 7.8 kN force). The compaction of the crystalline hexaboride powders was performed with a Dr. Sinter LAB Spark Plasma Sintering model SPS-211Lx (Fuji Electronic Industrial Co., Ltd.).

X-ray diffraction patterns were collected on a powder-diffraction system STOE STADI P. For measurements at room temperature monochromatized copper radiation was used (λ=154.060 pm, Ge (111) monochromator, transmission geometry). Rietveld refinements were performed using the program TOPAS [26].

Seebeck coefficients and electrical resistivities were measured up to 1073 K at 100 mbar helium atmosphere with a ZEM-3M8 system (Ulvac Technologies, Inc.).

Thermal diffusivities, heat capacities and thermal conductivities were measured up to 1073 K under purging argon atmosphere with a LFA 457 Microflash system (Netzsch Gerätebau GmbH).

3. Results and discussion

For the first time, the full series of solid solutions of calcium, strontium, and barium hexaborides was synthesized and structurally characterized by Rietveld refinements based on the structure model from literature (Table 1) [27].

X-ray diffraction data (examples in Fig. 1) showed that the samples were mono-phasic and exhibited the expected crystal structure. The lattice parameters and the positional parameters z of the boron atoms were refined freely. In a separate refinement cycle the occupancies of B and (M^1+M^2) were also refined freely and shown not to deviate from full occupancy. The expected M^1/M^2 ratios were confirmed in another separate refinement cycle, too, and then set to the theoretical values (values according to the ratios chosen for synthesis). Displacement parameters were refined isotropically and are given in Supplementary material.

The composition of the binary and ternary alkaline earth hexaborides $Ca_xSr_{1-x}B_6$, $Ca_xBa_{1-x}B_6$, and $Sr_xBa_{1-x}B_6$ (x = 0.25, 0.5, 0.75) was analyzed by investigating the variation of the lattice parameters with composition. As can be seen in Figs. 2–4 all of the compounds follow Vegard's law when the lattice parameter a is plotted *vs.* the amount x of the second metal. The theoretical values of x (values according to synthesis) are in perfect agreement with the values experimentally determined by refinements of the lattice parameters. The shift of the reflections is visualized in Fig. 5 for one reflection in one of the systems, $Sr_xBa_{1-x}B_6$ (x = 0, 0.25, 0.5, 0.75, 1.0). The samples were densified by spark plasma sintering and the densities obtained were higher than 95% of the theoretical densities.

Electrical conductivities and Seebeck coefficients of the binary and ternary alkaline earth hexaborides are shown in Figs. 6 and 7. Compared to earlier literature on CaB_6, SrB_6, and BaB_6 [23], an influence of densification at high pressures

Table 1
Structure refinement data for alkaline earth hexaborides $(M^1)_x(M^2)_{1-x}B_6$ (M^1/M^2=Ca, Sr, Ba).

$(M^1)_x(M^2)_{1-x}B_6$	a/pm	z/c	R_p	R_{wp}	R_{exp}	GOF
CaB_6	415.37 (5)	0.201 (1)	7.77	11.13	8.60	1.43
SrB_6	420.05 (3)	0.193 (5)	5.90	7.29	5.87	1.24
BaB_6	427.22 (2)	0.201 (9)	9.39	12.04	9.13	1.28
$Ca_{0.25}Sr_{0.75}B_6$	418.57 (3)	0.196 (5)	6.11	9.73	7.58	1.59
$Ca_{0.5}Sr_{0.5}B_6$	417.73 (5)	0.197 (6)	9.77	9.48	7.18	0.97
$Ca_{0.75}Sr_{0.25}B_6$	416.89 (3)	0.199 (4)	6.52	8.58	6.43	1.32
$Ca_{0.25}Ba_{0.75}B_6$	424.70 (2)	0.199 (9)	6.88	7.02	5.36	1.02
$Ca_{0.5}Ba_{0.5}B_6$	421.30 (4)	0.202 (1)	6.76	6.59	4.99	0.98
$Ca_{0.75}Ba_{0.25}B_6$	418.07 (4)	0.201 (9)	6.76	8.58	5.90	1.27
$Sr_{0.25}Ba_{0.75}B_6$	425.56 (6)	0.205 (2)	8.92	15.26	11.75	1.71
$Sr_{0.5}Ba_{0.5}B_6$	423.81 (5)	0.202 (7)	8.13	10.03	7.92	1.23
$Sr_{0.75}Ba_{0.25}B_6$	422.05 (3)	0.195 (6)	7.55	9.87	7.69	1.31

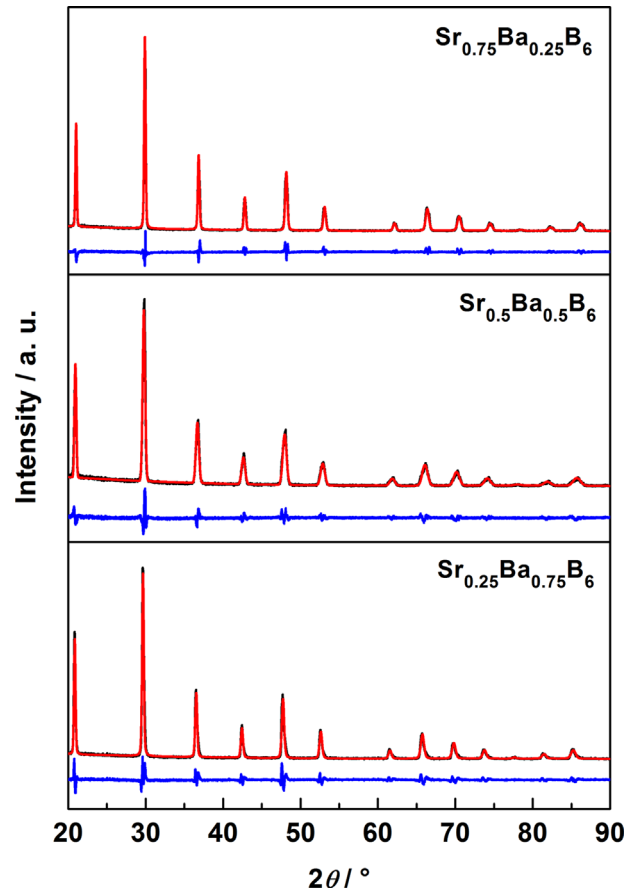

Fig. 1. X-ray diffraction patterns of $Sr_xBa_{1-x}B_6$ (black: observed, red: calculated, blue: difference curve).

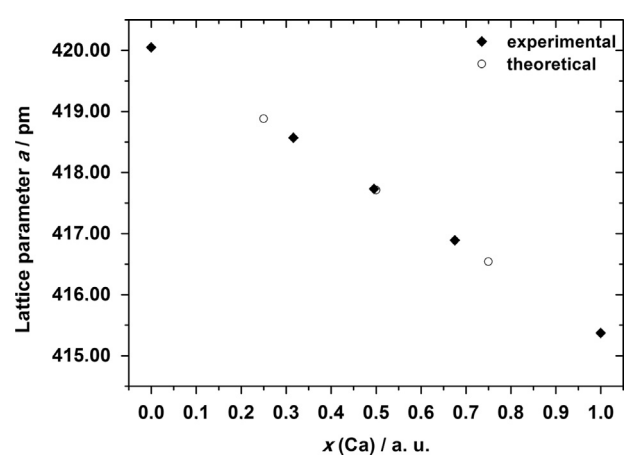

Fig. 2. Lattice parameters *vs.* the amount of x in the solid solutions $Ca_xSr_{1-x}B_6$.

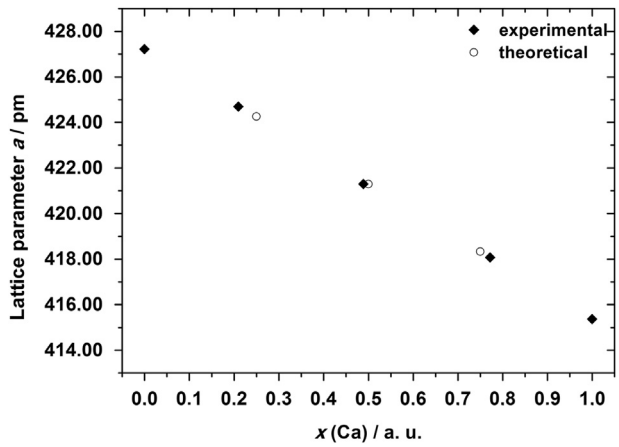

Fig. 3. Lattice parameters *vs.* the amount of x in the solid solutions $Ca_xBa_{1-x}B_6$.

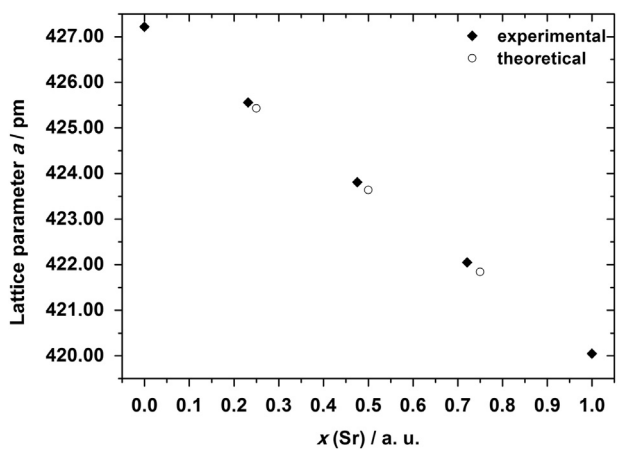

Fig. 4. Lattice parameters *vs.* the amount of x in the solid solutions $Sr_xBa_{1-x}B_6$.

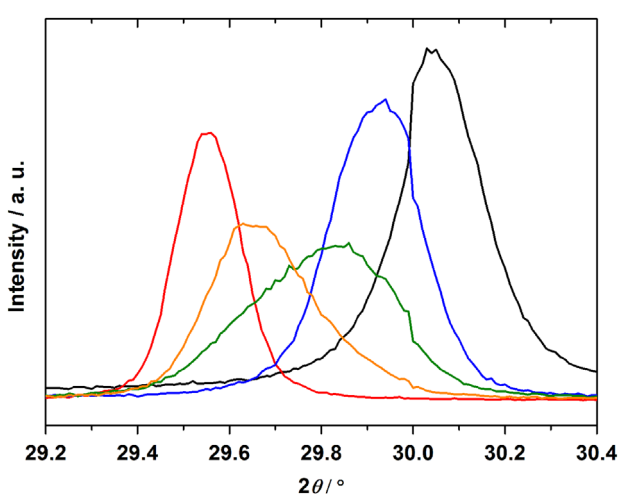

Fig. 5. Shift of the (111) reflection of the alkaline earth hexaborides $Sr_xBa_{1-x}B_6$ with $x = 0$ (red), 0.25 (orange), 0.5 (green), 0.75 (blue) and 1.0 (black).

(100 MPa *vs.* 50 MPa) is clearly seen although the resulting densities of the samples cannot be compared directly. Especially for compounds in the $Ca_xBa_{1-x}B_6$ system, higher electrical conductivities are observed. The absolute values of the electrical conductivity of calcium hexaboride densified at 100 MPa are found

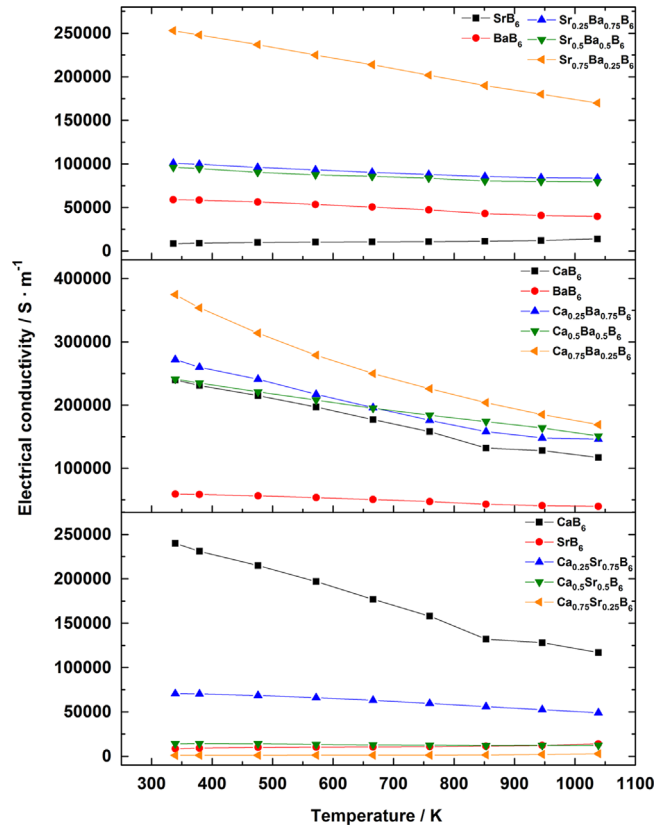

Fig. 6. Electrical conductivities of alkaline earth hexaborides.

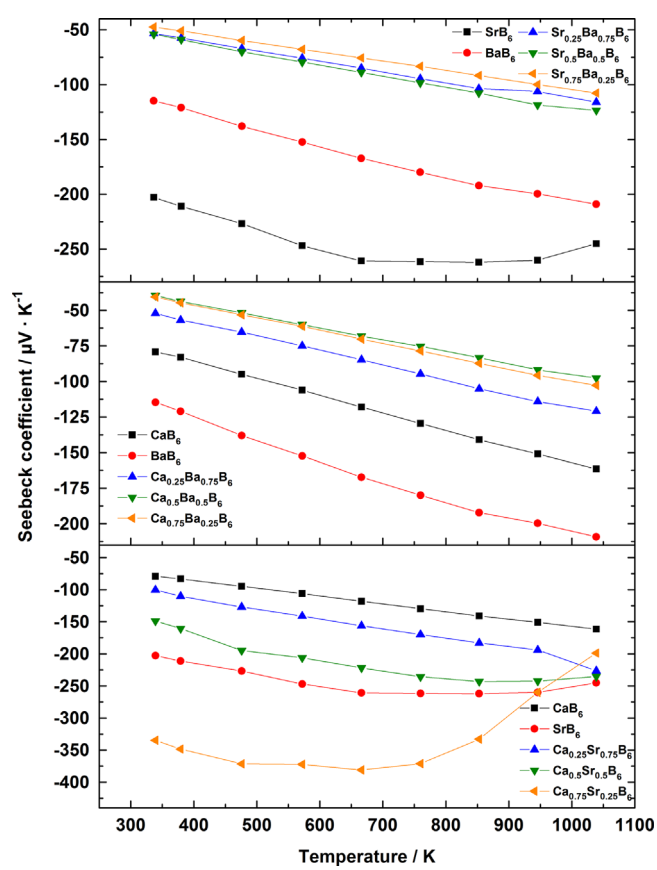

Fig. 7. Seebeck coefficients of alkaline earth hexaborides.

to be one magnitude higher than those of samples that were described earlier to be densified at 50 MPa [19,23]. This may result from the high densification pressures, but could also be due to defects or vacancies in the hexaboride structure, which were not observed in this study. At the same time the Seebeck coefficients are slightly lower than expected, but still rise to highly negative values at 1073 K, where the maximum does not seem to be reached yet. Based on the synthesis conditions, carbon impurities which could affect the electrical conductivities can be excluded. The densification process might have led to the introduction of carbon impurities into the surface, but this was not observed.

Fig. 8 shows the Jonker plot for the alkaline earth hexaborides under investigation. Seebeck coefficients are plotted *vs.* the natural logarithm of the electrical conductivities [28]. The analysis, originally developed for semi-conducting ceramics, is used to estimate additional information on the electrical properties of materials, for example, their electrical mobilities. Fig. 8 illustrates the dependency between Seebeck coefficients and electrical conductivities (which are measured simultaneously) at 323 K. To understand the electrical degeneration the binary alkaline earth hexaborides ($x = 0$ and 1) have to be compared to the solid solutions. A perfect Jonker plot exhibits an imaginary line between the binary compounds of a substitution series. All of the mixed ternary compounds should be adjudged along this line to be described as non-degenerated. In this work it is clearly seen that most of the mixed ternary alkaline earth hexaborides are located below this line in the so-called degenerated regime. The only exception is $Ca_{0.75}Sr_{0.25}B_6$, which is located above the line (Fig. 6). The analysis of the Jonker plot suggests that almost all of the hexaborides exhibit similar basic transport properties. Due to their common cubic crystal structure which only differs in the unit cell volume and the positional parameter z of the boron atoms, the scattering mechanisms for electrons can be assumed to be similar for all of the hexaborides. Small amount of defects and vacancies might influence the carrier concentration in the system and explain the different trends. The strongest effects seen for $Ca_xBa_{1-x}B_6$ might be attributed to lattice strain caused by the huge difference in the sizes of the cations. A future measurement of the carrier concentrations in mixed hexaborides will be essential to further elucidate the transport properties and to make sure that a possible influence of potential impurities will be identified if present.

The values of the specific heat (Fig. 9), thermal diffusivities (Fig. 10) and thermal conductivities (Fig. 11) were determined up to 1073 K. The values of the thermal conductivities are comparable to data that were earlier reported for binary hexaborides [23]. The high thermal conductivity and specific heat of calcium

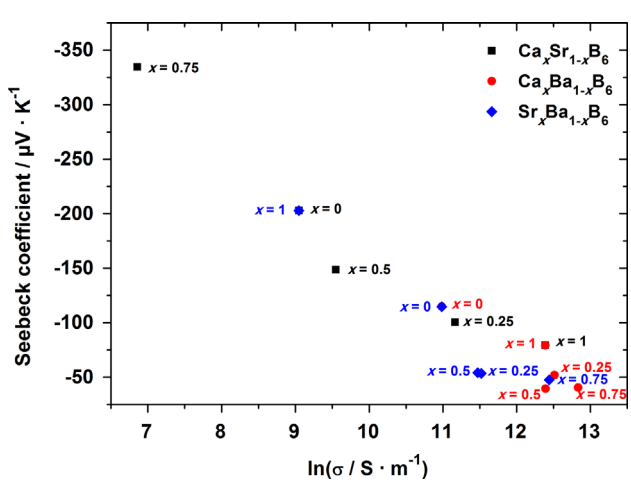

Fig. 8. Jonker plots for alkaline earth hexaboride solid solution series.

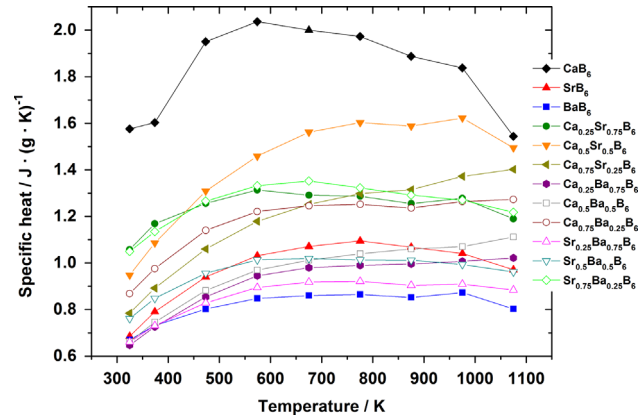

Fig. 9. Specific heats of alkaline earth hexaborides.

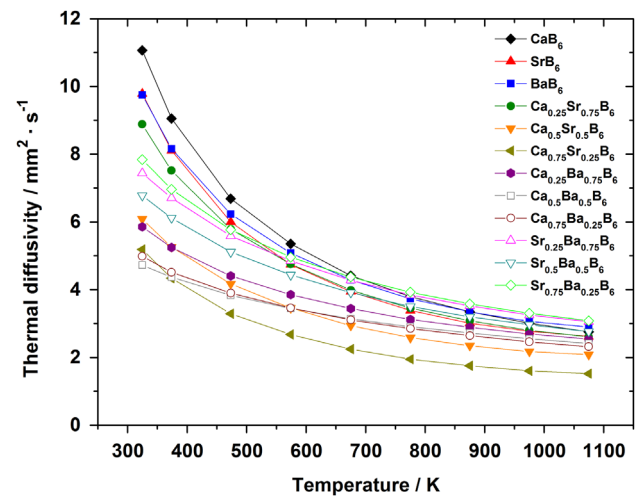

Fig. 10. Thermal diffusivities of alkaline earth hexaborides.

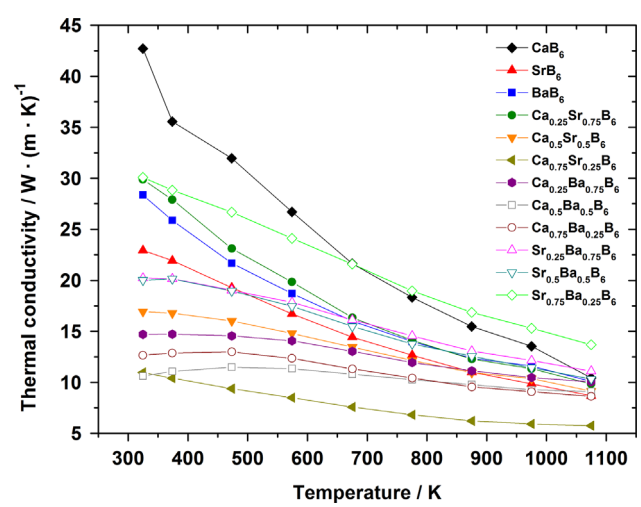

Fig. 11. Thermal conductivities of alkaline earth hexaborides.

hexaboride at temperatures between 323 K and 573 K are attributed to the high crystallinity of this compound. All of the hexaborides show thermal conductivities between 10 and 15 W m^{-1} K^{-1} except for $Ca_{0.75}Sr_{0.25}B_6$. This compound has a much lower thermal conductivity in accordance with its very low electrical conductivity, which suggests a very low carrier concentration. The reduction of the thermal conductivity by introducing a second, bigger cation into a hexaboride is due to a

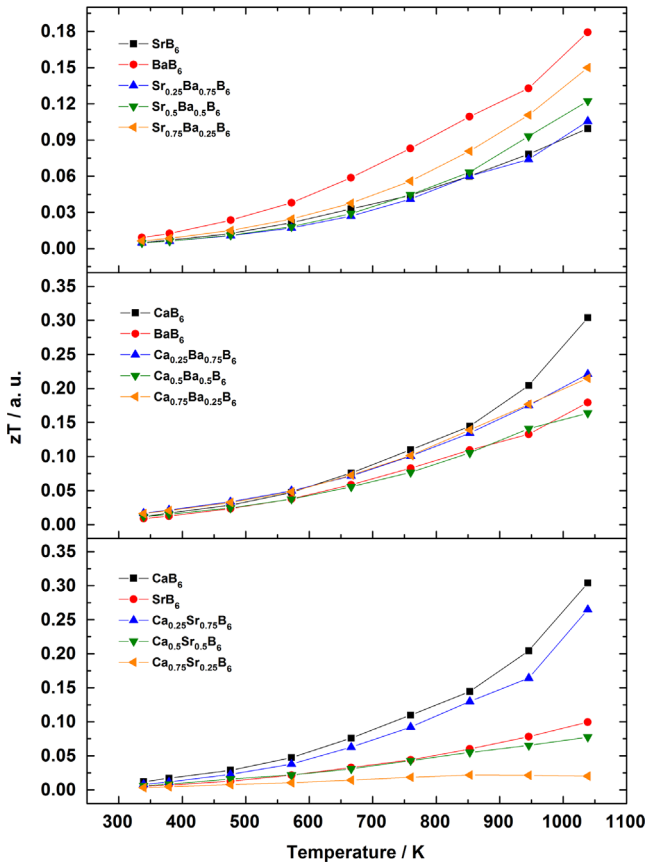

Fig. 12. Values of the figure of merit of alkaline earth hexaborides.

changed electronic situation and different scattering mechanisms. As a consequence, the thermal conductivities of the solid solutions $Ca_xBa_{1-x}B_6$ are decreased noticeably compared to pure CaB_6 and BaB_6.

ZT values are shown in Fig. 12. The high electrical conductivities of CaB_6 result in ZT values above 0.3 at high temperatures, equivalent to an enhancement of nearly 50% compared to earlier investigations on samples that were densified differently [23]. High ZT values are also reached for the solid solutions $Ca_{0.25}Sr_{0.75}B_6$, $Ca_{0.25}Ba_{0.75}B_6$, and $Ca_{0.75}Ba_{0.25}B_6$.

4. Conclusions

High-purity binary alkaline earth hexaborides and their solid solutions were synthesized and characterized via X-ray characterization. For the first time, structural data on the ternary compounds is given. All of the hexaborides proved to be exceptionally stable at high temperatures during synthesis, densification, and several measurement cycles, and they showed *n*-type conducting behavior. The thermoelectric performance of the compounds was investigated after high-pressure densification at 100 MPa. The figure of merit of calcium hexaboride was enhanced by about 50% compared to earlier work and resulted in $ZT > 0.3$. Mixed hexaborides like $Ca_{0.25}Sr_{0.75}B_6$ and $Ca_{0.25}Ba_{0.75}B_6$ were investigated for the first time and showed ZT values at 1073 K of 0.25 and 0.2, respectively. The ZT maximum of hexaborides is expected to be reached at even higher temperatures. The rigidity of the three-dimensional framework structure implies thermal expansion that is very small for huge temperature ranges. Thus, hexaborides are promising thermoelectric solids for applications at very high temperatures: being very stable and refractory, exhibiting low weight, and representing non-toxic as well as low-cost materials. Further reduction of the thermal conductivities of the hexaborides by nanostructurization is the focus of our current research.

Acknowledgment

Financial support of the project IN-TEG (03X3555G) within the framework of ThermoPower of the Bundesministerium of Bildung und Forschung is gratefully acknowledged.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jssc.2014.10.001.

References

[1] C. Wood, Rep. Prog. Phys. 51 (1988) 459–539.
[2] S.R. Brown, S.M. Kauzlarich, F. Gascoin, G.J. Snyder, Chem. Mater. 18 (2006) 1873–1877.
[3] S. Maruyama, Y. Miyazaki, K. Hayashi, T. Kajitani, T. Mori, Appl. Phys. Lett. 101 (2012) 152101.
[4] S. Maruyama, A. Prytuliak, Y. Miyazaki, K. Hayashi, T. Kajitani, T. Mori, J. Appl. Phys. 115 (2014) 123702.
[5] T. Mori, T. Nishimura, J. Solid State Chem. 179 (2006) 2908–2915.
[6] T. Mori, T. Nishimura, K. Yamaura, E. Takayama-Muromachi, J. Appl. Phys. 101 (2007) 093714.
[7] T. Mori, T. Nishimura, W. Schnelle, U. Burkhardt, Y. Grin, Dalton Trans. 43 (2014) 15048–15054.
[8] T.L. Aselage, D. Emin, S.S. McCready, R.V. Duncan, Phys. Rev. Lett. 81 (1998) 2316–2319.
[9] T.L. Aselage, D. Emin, S.S. McCready, Phys. Rev. B 64 (2001) 054302.
[10] M. Bouchacourt, F. Thevenot, J. Mater. Sci. 20 (1985) 1237–1247.
[11] I. Gunjishima, T. Akashi, T. Goto, Mater. Trans. 42 (2001) 1445–1450.
[12] S. Sasaki, M. Takeda, K. Yokoyama, T. Miura, T. Suzuki, H. Suematsu, W. Jiang, K. Yatsui, Sci. Technol. Adv. Mater. 6 (2005) 181–184.
[13] H. Suematsu, K. Kitajima, I. Ruiz, K. Kobayashi, M. Takeda, D. Shimbo, T. Suzuki, W. Jiang, K. Yatsui, Thin Solid Films 407 (2002) 132–135.
[14] C. Wood, D. Emin, Phys. Rev. B 29 (1984) 4582–4587.
[15] H.-R. Ott, M. Chernikov, E. Felder, L. Degiorgi, E.G. Moshopoulou, J.L. Sarrao, Z. Fisk, Z. Phys. B 102 (1997) 337–345.
[16] D.P. Young, D. Hall, M.E. Torelli, Z. Fisk, J.L. Sarrao, J.D. Thompson, H.-R. Ott, S.B. Oseroff, R.G. Goodrich, R. Zysler, Nature 397 (1999) 412–414.
[17] S. Massidda, A. Continenza, T.M. De Pascale, R. Monnier, Z. Phys. B 102 (1997) 83–89.
[18] K. Schmitt, C. Stückl, H. Ripplinger, B. Albert, Solid State Sci. 3 (2001) 321–327.
[19] M. Takeda, T. Fukuda, F. Domingo, T. Miura, J. Solid State Chem. 177 (2004) 471–475.
[20] M. Takeda, T. Fukuda, Y. Kurita, in: Proceedings of the 22nd International Conference on Thermoelectrics, 2003, pp. 259–262.
[21] M. Takeda, T. Fukuda, T. Miura, in: Proceeedings of the 21st International Conference on Thermoelectrics, 2002, pp. 173–176.
[22] M. Takeda, Y. Kurita, K. Yokoyama, T. Miura, T. Suzuki, H. Suematsu, W. Jiang, K. Yatsui, Mater. Res. Soc. Symp. Proc. 793 (2004) 219–224.
[23] M. Takeda, M. Terui, N. Takahashi, N. Ueda, J. Solid State Chem. 179 (2006) 2823–2826.
[24] M. Frotscher, Ph.D. thesis, Technische Universität Darmstadt, 2008.
[25] F. Stober, Ph.D. thesis, Technische Universität Darmstadt, 2012.
[26] Programme Topas 4.2, Bruker AXS, Karlsruhe, Germany, 2009.
[27] P. Blum, F. Bertaut, Acta Crystallogr. 7 (1954) 81–86.
[28] G. Jonker, Philips Res. Rep. 23 (1968) 131–138.