# Improvement of thermoelectric properties of alkaline-earth hexaborides

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## Abstract

Thermoelectric (TE) and transport properties of alkaline-earth hexaborides were examined to investigate the possibility of improvement in their TE performance. As carrier concentration increased, electrical conductivity increased and the absolute value of the Seebeck coefficient decreased monotonically, while carrier mobility was almost unchanged. These results suggest that the electrical properties of the hexaboride depend largely on carrier concentration. Thermal conductivity of the hexaboride was higher than 10 W/m K even at 1073 K, which is relatively high among TE materials. Alloys of $CaB_6$ and $SrB_6$ were prepared in order to reduce lattice thermal conductivity. Whereas the Seebeck coefficient and electrical conductivity of the alloys were intermediate between those of $CaB_6$ and $SrB_6$ single phases, the thermal conductivities of the alloys were lower than those of both single phases. The highest TE performance was obtained in the vicinity of $Ca_{0.5}Sr_{0.5}B_6$, indicating that alloying is effective in improving the performance.
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## 1. Introduction

Thermoelectric (TE) effects have received renewed attention in recent years, because they are expected to be used for electric power generation from waste heat and also for cooling devices which operate without using any refrigeration medium. The efficiency of a TE device is fundamentally limited by material properties of the n- and p-type materials that compose the TE device. The inherent efficiency of any TE material is determined by a dimensionless parameter $ZT$ given by

$$ZT = \frac{\alpha^2 \sigma}{\kappa} T, \tag{1}$$

where $\alpha$, $\sigma$, $\kappa$, and $T$ are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. In order to enhance the $ZT$ value, i.e. to improve TE performance, a high Seebeck coefficient, increased electrical conductivity and decreased thermal

conductivity are needed, but it is usually difficult to control the parameters independently in the desired directions.

Some boron-rich semiconductors are candidate materials for high-temperature TE conversion, and their TE properties have been studied [1–10]. Most of them are p-type materials with fairly high $ZT$ values at high temperatures, and n-type boron-rich semiconductors have been found in a few cases, such as V, Cr, or Fe doped $\beta$-rhombohedral boron [6,7]. We have studied TE properties of metal hexaborides, and we found that the divalent hexaborides were promising new candidates as n-type TE materials with a large Seebeck coefficient and high electrical conductivity [11]. In particular, the $ZT$ of $SrB_6$ reached approximately 0.3 at 1073 K even though its thermal conductivity was rather high compared to conventional TE materials [12].

In the present study, we examined the TE and transport properties of alkaline-earth hexaborides, namely $CaB_6$, $SrB_6$ and $BaB_6$, to investigate the possibility of further improvement in their TE performance. We also synthesized alloys of $(Ca,Sr)B_6$ to reduce their thermal conductivity. It was expected that lattice contribution to the thermal conductivity would be reduced, because the phonon mean free path could be shortened by alloying.

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## 2. Experimental

We prepared powders of $CaB_6$ and $SrB_6$ via borothermal reduction of metal oxides, i.e. $CaO$ and $SrO$, expressed as

$$MO + 7B \rightarrow MB_6 + BO \uparrow . \tag{2}$$

As for preparing $BaB_6$ powder, we synthesized the powder according to the following reaction using $BaCO_3$ instead of $MO$:

$$BaCO_3 + 7B \rightarrow BaB_6 + BO \uparrow + CO_2 \uparrow . \tag{3}$$
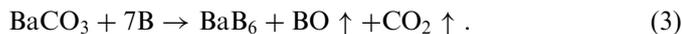
Mixtures of the oxide or carbonate and boron powders were pressed into pellets, and heated at 1743 K in a vacuum. The resultant pellets were ground into powder, and subsequently the powder was sintered at 2073–2273 K and 50 MPa for 20 min using the "Pulse Electric Current Sintering" system. We also synthesized $Ca_{1-x}Sr_xB_6$ alloys from the mixture of CaO, SrO and boron powders by the same procedure as described above except for the sintering condition. The sintering temperature was 2073 K, and holding time was prolonged by 50 min to ensure the uniformity of the specimen. $CaB_6$ and $SrB_6$, namely $x = 0$ and 1, respectively, were prepared by the same condition as that of alloys for comparison. We refer to the two specimens hereafter as $CaB_6^*$ and $SrB_6^*$ to distinguish them from the $CaB_6$ and $SrB_6$ prepared by shorter sintering. X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX) were used to characterize the specimens.

Electrical conductivity ($\sigma$) and Seebeck coefficient ($\alpha$) were measured by a standard four-probe method and a steady-state temperature gradient method, respectively. The thermal conductivity ($\kappa$) was calculated from the thermal diffusion coefficient and heat capacity measured by the laser flash method. Those measurements were carried out from room temperature to 1073 K. Hall measurements were made using the Van der Pauw method at room temperature by applying a magnetic field up to 1 T.

## 3. Results and discussion

Fig. 1 shows the temperature dependence of $\alpha$ and $\sigma$ for $CaB_6$, $SrB_6$, and $BaB_6$. The negative $\alpha$ indicates that the hexaborides prepared in this study are n-type materials. The $\sigma$ decreases with increasing temperature for all specimens, indicating metallic behavior. Although theoretical study [13] and angle-resolved photoemission measurement [14] suggested that the $CaB_6$ is essentially a semiconductor, such metallic behavior of $\sigma$ has been reported [14–16], and the values of $\sigma$ are scattered among the reports. The origin of the n-type carrier and differences in $\sigma$ appear to be attributable to impurity and defects in the hexaborides. As a result, the differences in $\alpha$ and $\sigma$ for the alkaline-earth hexaborides synthesized in the present study can be attributed to the difference in carrier concentration, $n$. We calculated $n$ of the hexaborides from the measured
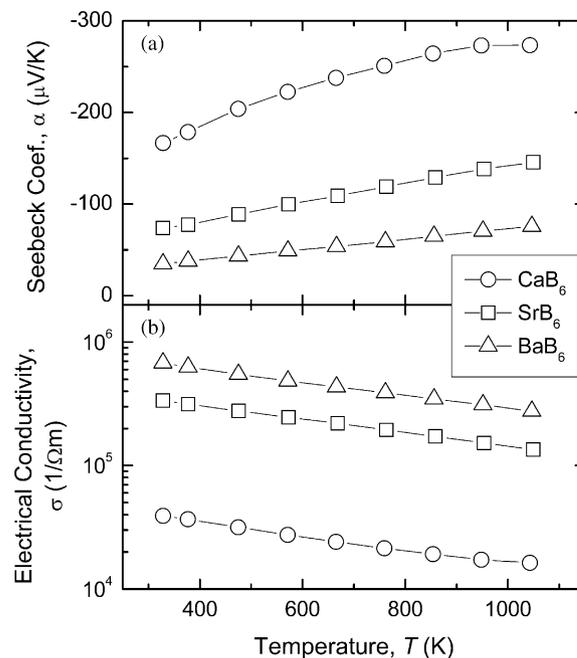


Fig. 1. Temperature dependence of (a) the Seebeck coefficient and (b) electrical conductivity for alkaline-earth hexaborides.

Hall coefficient, $R_H$, on the basis of the free electron approximation, $R_H = 1/en$. Fig. 2 shows the $\alpha$, $\sigma$, and power factor given by $\alpha^2\sigma$ as a function of $n$. These values were obtained at room temperature. The $\alpha$ decreases linearly with the increasing logarithm of $n$. The $\sigma$ lies in a straight line with a slope of 1, indicating almost the same Hall mobility for the three specimens. These results suggest that TE properties of the alkaline-earth hexaboride depend largely on carrier concentration, namely, on the quality of the specimen. Consequently, the power factor of the hexaboride appears to have a maximum value at a carrier concentration of around $2 \times 10^{26}\,\text{m}^{-3}$.

Thermal conductivity ($\kappa$) of the alkaline-earth hexaboride was higher than 10 W/m K even at 1073 K, which is relatively high compared with other TE materials, and lattice contribution to the $\kappa$ ($\kappa_{latt}$) was dominant [12]. The $\kappa$, particularly $\kappa_{latt}$, should be reduced to improve TE performance of the hexaboride. Alloying is an effective way to reduce $\kappa_{latt}$, and has been employed to improve the TE performance of materials such as Si–Ge system [17]. As discussed above, electrical properties of the alkaline-earth hexaboride appeared to be largely unaffected by constituent metal atoms, and hence, alloying of hexaboride using two or more alkaline-earth metals is expected to reduce $\kappa$ without seriously lowering the electrical performance.

We synthesized $(Ca,Sr)B_6$ alloys and confirmed that the alloys had hexaboride structures according to XRD spectra, and no phase separation was observed by SEM and EDX. Fig. 3 shows the temperature dependence of $\alpha$ and $\sigma$ for the $(Ca,Sr)B_6$ alloys together with those for $CaB_6^*$ and $SrB_6^*$ synthesized by the same condition as the alloys. The $\alpha$ and $\sigma$ of the alloys are intermediate between those of the $CaB_6^*$ and the $SrB_6^*$, and the values for all
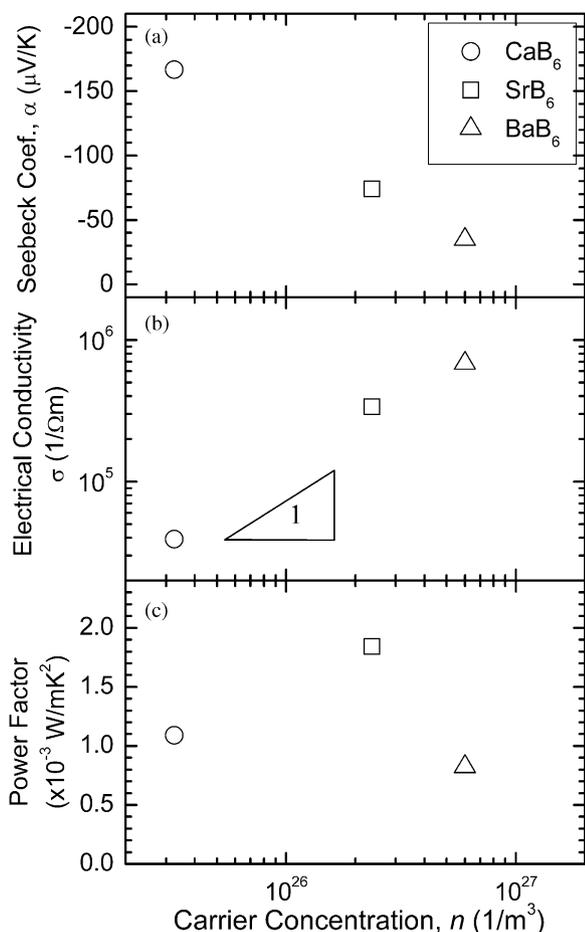
Fig. 2. (a) The Seebeck coefficient, (b) electrical conductivity, and (c) calculated power factor for alkaline-earth hexaborides as a function of carrier concentration. These values were obtained at room temperature.
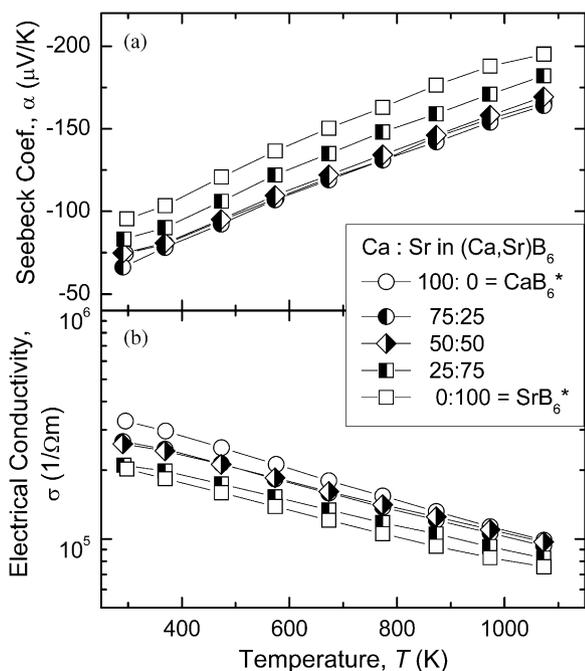


Fig. 3. Temperature dependence of (a) the Seebeck coefficient and (b) electrical conductivity for $(Ca,Sr)B_6$ alloys.
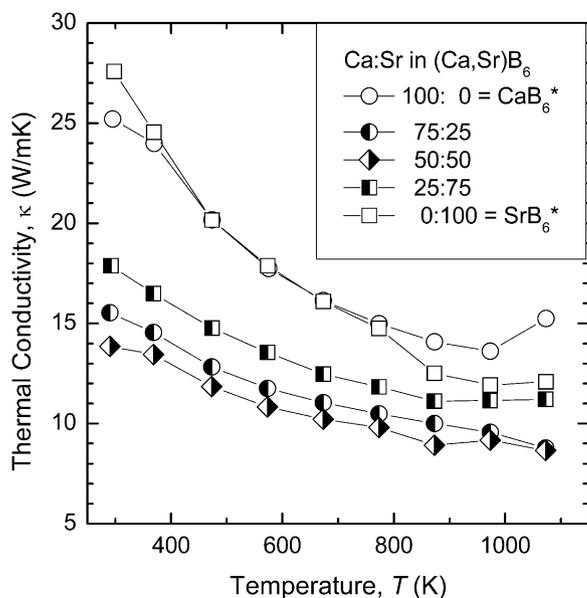


Fig. 4. Temperature dependence of thermal conductivity for $(Ca,Sr)B_6$ alloys.
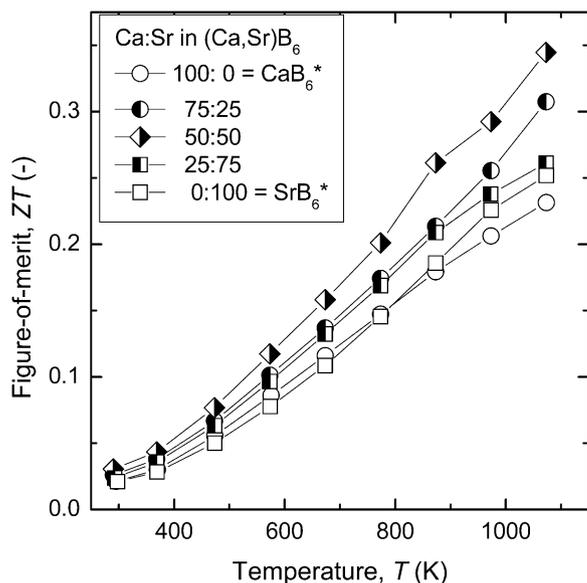


Fig. 5. Thermoelectric figure-of-merit, $ZT$, for $(Ca,Sr)B_6$ alloys.

specimens in this experiment are comparable with the ones for $SrB_6$ shown in Fig. 1. These results suggest that electrical performance was not seriously influenced by alloying. It should be noted that the $\alpha$ and the $\sigma$ of $CaB_6$* are quite different from those of $CaB_6$ but almost the same as those of $SrB_6$ shown in Fig. 1. These results indicate that the carrier concentration of $CaB_6$* is approximately one order of magnitude higher than that of $CaB_6$ due to higher defect density or impurity, but the mobility of the carrier is unchanged. Fig. 4 shows the temperature dependence of $\kappa$ for the alloys and non-alloyed specimens. All alloyed hexaborides have lower $\kappa$ values than those of $CaB_6$* and $SrB_6$*, indicating that $\kappa_{latt}$ was effectively reduced by alloying. The lowest $\kappa$ was obtained in the vicinity of Ca:Sr = 50:50. Fig. 5 shows the temperature dependence of

the figure-of-merit, $ZT$, calculated by Eq. (1). The $(Ca,Sr)B_6$ alloy with the lowest $\kappa$ possesses the highest $ZT$ value among the specimens we examined. The $ZT$ reaches 0.35 at 1073, which is, to the best of our knowledge, the highest value among n-type boron-rich solids.

## 4. Conclusion

We examined the TE and transport properties of alkaline-earth hexaborides: $CaB_6$, $SrB_6$ and $BaB_6$. We found that the Seebeck coefficient and electrical conductivity of these hexaborides depend largely on carrier concentration and that the highest electrical performance, i.e. power factor, can be obtained at around $2 \times 10^{26}\,\text{m}^{-3}$. Hall mobility was independent of constituent alkaline-earth metal, which implies that primarily the boron framework contributes to the electronic character of these hexaborides while each alkaline-earth atom only supplies two electrons to the framework. On the basis of this consideration, we synthesized alloys of $(Ca,Sr)B_6$ to reduce thermal conductivity while maintaining a high electrical performance as a TE material. Thermal conductivity was successfully reduced by alloying while electrical performance was almost the same as non-alloy hexaborides. As a result, the highest TE performance was obtained in the alloy. It is expected that alloying with two or more metals and carrier concentration adjustment will lead to further improvement in the TE performance of hexaborides.

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