

Enhanced thermoelectric properties of samarium boride

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Abstract

SmB₆₂ single crystals were successfully grown by the floating zone (FZ) method. The high-temperature thermoelectric properties were investigated, together with magnetic properties and specific heat at low-temperature. The electrical resistivity, ρ , shows variable-range-hopping (VRH) behavior with significantly lower values than other rare-earth RB₆₂ (RB₆₆) compounds. An effective magnetic moment, μ_{eff} , of 0.42 μ_B /Sm was estimated, which if straightforwardly taken indicates a mixed valency for SmB₆₂ with Sm²⁺:Sm³⁺ = 1:1, which is the first ever indicated for RB₆₆-type compounds. Localization length of the VRH at the Fermi level, ξ , was estimated to be 3.33 Å indicating that carriers in SmB₆₂ are much less localized than in YB₆₆ which has 0.56 Å. The thermoelectric behavior of SmB₆₂ is striking, with ρ reduced by two orders of magnitude while maintaining large Seebeck coefficients, and as a result the power factor is ~30 times higher than other rare-earth phases. Overall the figure of merit ZT amounts to ~0.13 at 1050 K, with an extrapolated value of ~0.4 at 1500 K, an expected working temperature for topping cycles in thermal power plants; that gives a ~40 times enhancement for Sm. Since there are few thermoelectric materials applicable for very-high temperature applications, this discovery gives new interest in the samarium higher borides.

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1. Introduction

Thermoelectric materials are being actively investigated throughout the world now, due to the potential large societal benefits through the direct conversion of waste heat to electricity. One need exists to develop high temperature thermoelectric materials which can utilize the high temperature waste heat in thermal power plants, steelworks, factories, and incinerators, etc. and also the conversion of concentrated solar power CSP [1,2]. The performance of thermoelectric materials can be evaluated by the figure of merit $ZT = S^2T/\rho\kappa$, where S , ρ , κ and T are the Seebeck coefficient, electrical resistivity, thermal conductivity and temperature, respectively.

Boron cluster compounds are attractive candidates as high temperature thermoelectric materials because of their material stability and generally large Seebeck coefficients [3–5]. Furthermore, they have been found to typically possess intrinsic low thermal conductivity [6–8], which is a built-in advantage for thermoelectrics. This property is quite interesting since the boron cluster compounds are strongly covalently bonded solids with high sound velocities. Several mechanisms, such as symmetry mismatch effect or degrees of freedom of boron dumbbells in the B₈₀ cluster, in addition to the well-known crystal complexity first demonstrated by Slack [8], have been proposed to be the origin of this intrinsic low thermal conductivity [5,9,10]. Many of the boron cluster compounds follow the variable range hopping (VRH) transport mechanism [11] which is advantageous at high temperatures, since the electrical conductivity and Seebeck coefficient have a positive temperature coefficient [3,4]. Another attractive feature of such boron cluster compounds in general is that the network structures and physical properties have been found to

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be controllable to some degree through incorporation of metal atoms in the voids of clusters, and also by the addition of third elements like C, N, Si which can act as bridging sites of the cluster framework [12].

Up to now, there has been active investigation into the thermoelectric properties of boron cluster compounds such as boron carbide [2,13–15], rare earth borocarbonitrides $RB_{15.5}CN$, $RB_{22}C_2N$, and $RB_{28.5}C_4$ (R = rare earth) [16–19], doped β -boron [20–22], B_6S_{1-x} [23], RB_{66} [24,25], $RB_{44}Si_2$ [3,8,26,27], $MgAlB_{14}$ [28,29], $Y_xAl_yB_{14}$ [30–32], and a recent re-examination of the prospects of B_6O by Slack [33].

RB_{66} is an interesting boride [12], with a complex structure with more than 1600 atoms in the unit cell, and it was discovered to be a crystalline material with glass-like thermal conductivity [5,6], which can be considered as a precursor to the famous phonon glass electron crystal (PGEC) concept. A view of the crystal structure is given in Fig. 1, together with a simplified view. The crystal structure can be represented by three structural units; the $(B_{12})_{13}$ supericosahedra, B_{80} cluster, and the rare earth atoms. As a representative expression of the compound, RB_{66} is typically used, but the congruent composition has been reported to be RB_{62} , for example, and in some

cases the composition is also used to express the compound (like in this paper).

Among rare-earth series of compounds, phases with Yb and Sm have been discovered to sometimes exhibit anomalous properties for different reasons, related e.g. to mixed valency [34]. Mixed valency has previously been reported in the case of SmB_6 [35–37]. Recently, SmB_6 has attracted increasing interest as a topological insulator [38–45]. Topological insulators have been reported to have enhanced thermoelectric properties [46].

With these developments in mind, we revisited the PGEC RB_{66} compound and investigated the samarium phase in detail by growing high quality single crystals of SmB_{62} . RB_{66} (congruent composition of RB_{62}) had previously been reported to be a poor thermoelectric material [24,25] but we discovered that SmB_{62} has a ~ 40 times higher ZT than its yttrium and erbium counterparts. At 1050 K it amounts to 0.13, or extrapolated to 1500 K (an expected working temperature for topping cycles in thermal power plants) a value of ~ 0.4 , which is a promising start as a new high temperature material. This discovery of a dramatic increase in performance in a well-known boride by investigating the samarium phase, is exciting and shows the still untapped potential of these materials.

2. Experimental

SmB_{62} crystals were synthesized by the Floating Zone (FZ) method with focused light from four Xenon lamps. The feed and seed rod for the crystal growth were synthesized by the borothermal reduction method [12], starting from samarium oxide and boron powder.

The borothermal reduction method was carried out by mixing Sm_2O_3 (99.95% Wako) and Boron (99.9% SB Boron) with ratios of B: Sm_2O_3 of 127:1 and 123:1 to make the composition Sm:B to be 1:62 and 1:60, respectively. We used a composition of SmB_{62} , since this has been shown to be the congruent composition for YB_{66} , and we therefore, tried to grow a slightly samarium-rich crystal also. The constituents were mixed in agate mortars for 20 min in ethanol to ensure homogeneity. After drying the mixture overnight under a halogen lamp, it was compacted with a Cold Isostatic Press (CIP) apparatus at 2500 kg/cm^2 to form solid rods. Then the solid rods were heated in an induction furnace for 8 h at $\sim 1700 \text{ }^\circ\text{C}$ under vacuum. The temperature was controlled manually with a pyrometer.

The rods were then crushed with a mortar and compacted by CIP and heated again by induction furnace. The process was repeated 3 times to be certain to reduce Sm_2O_3 completely and form the samarium boron solid rod. BO gas was observed to emanate during heating, with the most intense gas evaporation observed during the first heating sequence, but reduced considerably for following sequences. At the end of the borothermal reduction process, the rods were dense and ready to be used as feed and seed rod for FZ crystal growth. A part of the rod was crushed and characterized by powder X-ray diffraction (XRD) using a Rigaku Ultima III X-ray

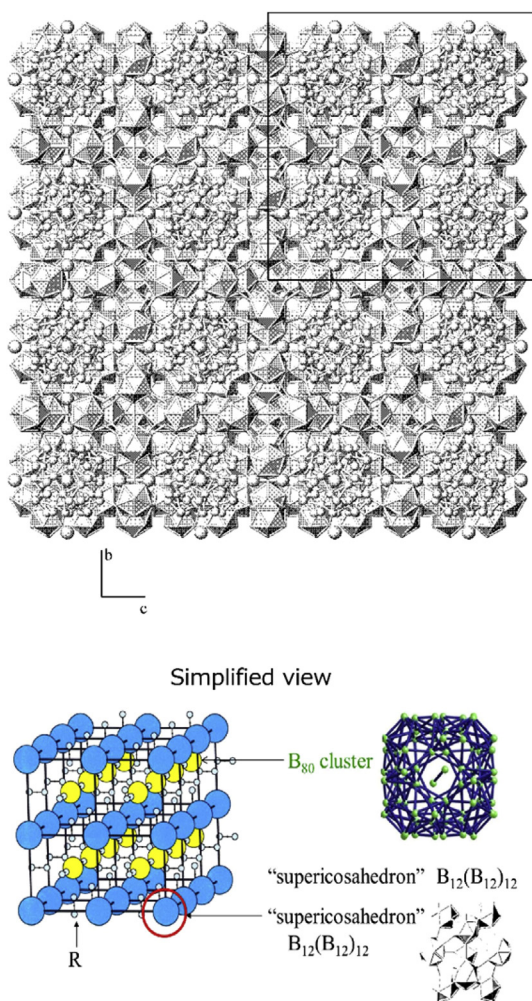


Fig. 1. Crystal structure of RB_{62} (RB_{66}).

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