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Heat Capacity and Thermodynamic Properties of Crystalline SrB_4O_7

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Abstract—The heat capacity of a strontium tetraborate (SrB_4O_7) single crystal has been determined in the temperature range 55–300 K by adiabatic calorimetry, and its Debye characteristic temperature, entropy change, enthalpy increment, and phonon mean free path have been calculated as functions of temperature.

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INTRODUCTION

Strontium tetraborate (SrB_4O_7) crystals are a promising multifunctional material offering a unique combination of physical properties. They possess a fundamental absorption edge at very short wavelengths (~120–130 nm) [1, 2], large nonlinear optical coefficients compared to other borates, and a very high optical damage threshold [2, 3], which makes them extremely attractive for nonlinear optical frequency conversion to the deep-UV spectral region.

The use of SrB_4O_7 in nonlinear optics is only limited by the lack of phase matching because of its low birefringence [1]. Nevertheless, there is strong evidence that SrB_4O_7 crystals can be used in autocorrelation measurements of femtosecond pulses with nonlinear optical wavelength conversion down to 125 nm [2]. Oseledchik et al. [1] discussed the possibility of waveguide harmonic matching. Zaitsev et al. [4] observed extended domain structures in SrB_4O_7 single crystals, which allow such crystals to be used in various nonlinear optical processes [5–7].

The luminescence and thermoluminescence properties of rare-earth-doped strontium tetraborate have been the subject of extensive studies. The interest in SrB_4O_7 in this context is motivated by the possibility to stabilize a number of rare-earth elements (Eu, Sm, Yb, Tm, and Nd) in the divalent state [8–12]. Such doped crystals can be used as UV phosphors [13], high-pressure sensors [14], scintillators, and thermographic phosphors [11, 15].

Given that SrB_4O_7 has considerable potential for practical application, it is necessary to study its physical properties in detail. Its dielectric, optical, nonlinear optical, elastic, piezoelectric, and mechanical (fracture toughness) characteristics have already been investigated [1–3, 16, 17].

In a previous study [18], the thermal conductivity of a SrB_4O_7 single crystal was shown to be very high. Its lattice (phonon) thermal conductivity extrapolated to its melting point, T_m = 1273 K [19], considerably exceeds the level typical of T_m: 1–2 W/(m K). One of the key factors determining the thermal conductivity of a dielectric single crystal is its heat capacity [20]. In addition, the relatively low melting point of SrB_4O_7 crystals, related to their heat capacity through their characteristic temperature, does not correlate with their excellent elastic properties [16] and strength [17].

In this context, it is of practical interest to measure the heat capacity of SrB_4O_7. A literature search revealed no calorimetric studies of SrB_4O_7 crystals.

The purpose of this work was to study possible anomalies in the heat capacity of a SrB_4O_7 single crystal between liquid-nitrogen and room temperatures.

EXPERIMENTAL

A single crystal 20 g was grown by the Czochralski technique from a stoichiometric melt. The growth procedure was similar to that described elsewhere [4].

The heat capacity, C_p, of the crystal was measured at temperatures from 55 to 300 K by an adiabatic step-heating technique. The measurement system and procedure were similar to those described by Sirota et al. [21]. The uncertainty in our heat capacity measurements was within 1%.

RESULTS AND DISCUSSION

Curve *1* in Fig. 1 represents the $C_p(T)$ data. The data points are seen to fall very close to a straight line. The quadratic polynomial used to fit the $C_p(T)$ data had the form

$$C_p(T) = -1.062 \times 10^{-4} T^2 + 0.6156T - 18.943 \quad \text{J/(mol K)}.$$

In the temperature range studied, the heat capacity of the crystal increases by almost one order of magnitude. Near room temperature, the heat capacity per formula unit is 13 J/(mol K), that is, half the value predicted by the Neumann–Kopp law.

In this context, it is of interest to examine the temperature dependence of the Debye characteristic temperature, Θ, obtained by comparing the measured heat capacity to Debye values, $C_V(\Theta/T)$ [22].

The $\Theta(T)$ calculation results are well represented by the cubic polynomial

$$\Theta(T) = -4.256\times10^{-6}T^3 - 5.727\times10^{-3}T^2 + 4.6366T + 398.2 \text{ K}.$$

Curve *2* in Fig. 1 demonstrates that, in the temperature range studied, Θ increases by a factor of 2. At the same time, it increases very slowly near room temperature. At $T = 300$ K, Θ differs little from the melting point of the crystal (T_m).

Interestingly enough, crystals of other borates, such as LiB_3O_5 [23], α-BaB_2O_4, and β-BaB_2O_4 [24], have similar Θ values at $T = 300$ K, which also differ little from their T_m's, even though these borates differ markedly in crystal structure and mechanical properties from strontium tetraborate.

Figure 2 shows the temperature dependences of the entropy change and enthalpy increment found as

$$\Delta S(T) = S(T) - S(55\text{ K}) = \int_{55}^{T}\frac{C_p(T)}{T}dT;$$

$$\Delta H(T) = H(T) - H(55\text{ K}) = \int_{55}^{T}C_p(T)dT.$$

Knowledge of these characteristics helps to optimize crystal growth processes. As seen in Fig. 2, both $\Delta S(T)$ and $\Delta H(T)$ increase monotonically throughout the temperature range studied. Both quantities increase at an increasing rate. The data are well represented by the polynomials

$$\Delta S(T) = 8.298\times10^{-9}T^4 - 7.584\times10^{-6}T^3 + 2.702\times10^{-3}T^2 + 0.065T - 10.79 \quad \text{J/(mol K)}$$

and

$$\Delta H(T) = 0.2902T^2 - 16.433T \quad \text{J/mol}.$$

The present heat capacity data, in combination with the thermal conductivity of SrB_4O_7 measured previously at temperatures from 50 to 300 K [18], can be used to evaluate the phonon mean free path in crystals of this compound as a function of temperature from the well-known Debye relation. We calculated the phonon mean free path along the *b* axis, whose direction corresponded to the crystallographic setting proposed by Oseledchik et al. [1] for SrB_4O_7 crystals (sp. gr. $Pnm2_1$; unit-cell parameters $a = 4.4255(7)$, $b = 10.709(2)$, and $c = 4.2341(9)$ Å; density $\rho = 4.011$ g/cm^3 [3]). The mean phonon (sound) velocity was taken to be $v = 7$ km/s [16]. As seen in Fig. 3, *l* is a strong function of temperature. In the temperature range studied, *l* varies over two orders of magnitude. At room temperature, it is twice the *b* cell parameter. Near $T = 300$ K, the exponent *n* in $l(T) \sim T^{-n}$ exceeds 2.

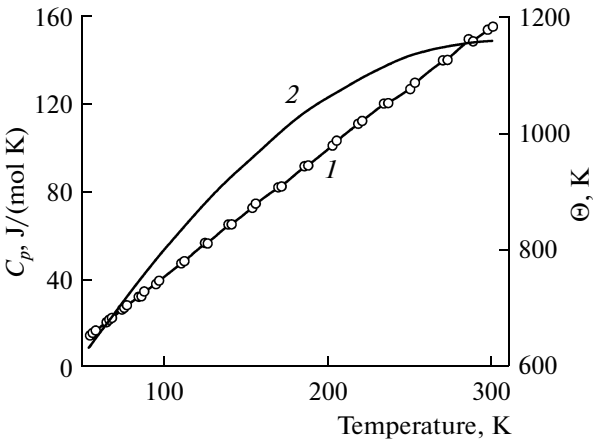

Fig. 1. Temperature dependences of the (*1*) molar heat capacity and (*2*) Debye characteristic temperature for a SrB_4O_7 single crystal.

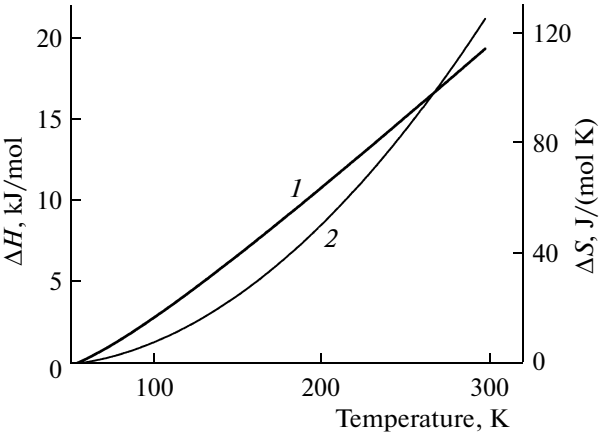

Fig. 2. Temperature-dependent (*1*) entropy and (*2*) enthalpy relative to those at $T = 55$ K for a SrB_4O_7 single crystal.

The dashed line in Fig. 3 represents extrapolation of calculated $l(T)$ to the melting point of SrB_4O_7. Since the extrapolation was made from low temperatures, where the lattice contribution to thermal conductivity is insignificant, the result seems to be quite credible. The highest temperature value, $l = 2.03$ Å, corresponds (is equal) to the average bond distance (average ionic diameter) in SrB_4O_7 crystals:

$$d = \sqrt[3]{\mu/12\rho},$$

where μ is the molecular mass of SrB_4O_7 and ρ is its density. It is worth pointing out that, even at the high-

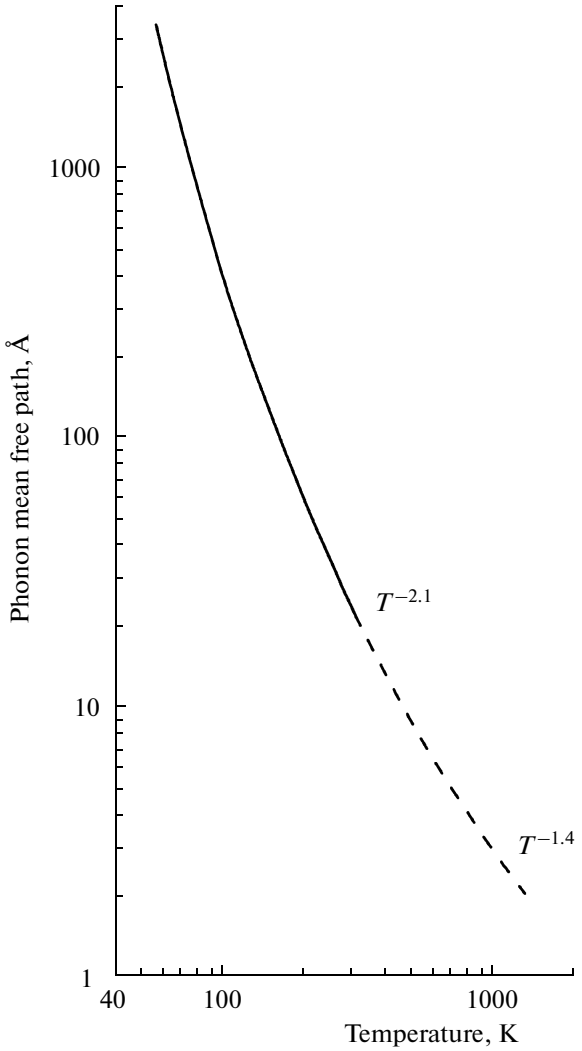

Fig. 3. Log–log plot of the phonon mean free path against temperature for single-crystal SrB_4O_7.

est temperatures examined, $l(T)$ varies more rapidly than T^{-1}. It is, therefore, reasonable to assume that the actual l values at T_m are even higher.

CONCLUSIONS

We performed what we believe to be the first calorimetric study of single-crystal strontium tetraborate, SrB_4O_7, a promising multifunctional material.

The heat capacity of a SrB_4O_7 single crystal was determined in the temperature range 55–300 K by adiabatic calorimetry, and its Debye characteristic temperature, entropy change, enthalpy increment, and phonon mean free path were calculated as functions of temperature.

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