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SPECIFIC HEAT AND THERMAL CONDUCTIVITY OF DEUTERATED TRIGLYCINE FLUOROBERYLLATE

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ABSTRACT

The temperature dependence of the specific heat in deuterated triglycine fluoroberyllate (DTGFB) was measured over the range 294—375 K. The room temperature value was 0.317 cal g^{-1} K^{-1} and the jump in C_p between the ferroelectric and paraelectric phases is 0.048 cal g^{-1} K^{-1}. Measurements of the thermal conductivity along the principal crystallographic axes [010], [100], [001] and [110] were temperature independent and had average values of 1.22, 1.61, 1.24 and 1.46 $\times 10^{-3}$ cal s^{-1} cm^{-1} $°C^{-1}$, respectively. The effects of deuteration on these properties were also examined.

INTRODUCTION

The compounds triglycine fluoroberyllate (TGFB) and the deuterated form (DTGFB) have the general formula $(NH_{3-x}D_xCH_2COOH_{1-x}D_x)_3 \cdot H_{2-x}D_xBeF_4$, where x indicates the mole fraction of deuterium present in the crystal. These materials have attracted considerable attention because of their superior performance in IR thermal imaging systems [1—4]. The compounds crystallize in the monoclinic structure and exhibit a ferroelectric transition at about 345 K. The ferroelectric phase (space group $P2_2 - C_2^2$) is stable below 345 K and the paraelectric phase ($P2_1/m - C_{2h}^2$) is stable at higher temperatures [5]. Previous studies have given specific heat data on TGFB and DTGFB, where the deuteration level was 92% [6,7]. The present study reports measurements on the temperature dependence of the specific heat and thermal conductivity of DTGFB crystals with different deuterium concentrations.

EXPERIMENTAL

Single crystals of DTGFB were grown from saturated solutions by the temperature lowering method as previously reported [7]. Chemical analysis of the grown crystals indicated that impurity contents (with respect to transition elements) were less than 50 ppm. Samples were fabricated from the grown crystals in the form of small discs, 3 mm diameter by 1 mm thick for specific heat measurements, and as rods, 15 ± 0.01 mm diameter by lengths

10—15 mm for thermal conductivity measurements.

The specific heat data were obtained with a Perkin-Elmer Model DSC-2 differential scanning calorimeter interfaced to a Textronix Model 31 programmable calculator. The system is equipped with an Autoscan Zero minicomputer for automatic baseline corrections. The specific heat was measured from 294 to 375 K at a heating rate of 5 K min^{-1}. In order to obtain data at 294 K the scans were initiated from 274 K using an accessory refrigeration unit. Two sets of measurements were made on two different samples and the sample to sample variation was less than 1%. The mean values of the four sets of specific heat data were further refined by normalization to the NBS values for sapphire [8]. The temperature calibration of the DSC-2 was made using a pure indium standard (m.p. 429.78 K).

Thermal conductivity measurements were obtained with a commercial twin standard instrument [9], which utilizes a comparison method for determination of thermal conductivity (K). A sample of the material to be measured is sandwiched between two identical standards made from Corning type 7740 pyrex. Thermal contact is achieved using type Z9 silicone super heat sink compound [10]. A comparison of the thermal gradients (under equilibrium conditions) in the sample and standards permits the thermal conductivity of the sample to be determined. The heat flux through each of the three stacked components is given by

$$-q = \frac{KA\,\Delta T}{L} \tag{1}$$

where K is the thermal conductivity (cal sec^{-1} cm^{-1} $^\circ\text{C}^{-1}$), A is the area normal to heat flow, L is the length of the sample, and ΔT is the temperature difference along the section L. Assuming the radial heat losses are negligible or uniform down the stacked samples, then the average heat flux passing through the two standards can be taken as equal to the flux through the sample. Knowing the thickness of each component, the ratio of temperature drops across each and the K values of the standard, the average thermal conductivity of the sample can be calculated from

$$K_1 = K_0 \cdot \frac{\Delta T_0}{\Delta T_1} \cdot \frac{L_1}{L_0} \tag{2}$$

where the subscripts 0 and 1 refer to the standard and sample, respectively. Each thermal conductivity data point measurement required at least 18 h in order to permit the apparatus to attain thermal equilibrium. The thermal gradient across the samples during measurement was about 2.5°C over the temperature range 15—71°C. The apparatus was calibrated using a Corning 7740 Pyrex standard and measurements were within 2% of the cited value [11]. Considering all potential sources of error for this type of measurement technique, the thermal conductivity values are estimated to be accurate to 5%.

The deuterium concentrations of the DTGFB crystals were measured using a newly developed nuclear magnetic resonance (NMR) technique and are good to ±1%D [12].

RESULTS AND DISCUSSION

The temperature dependence of C_p for both TGFB and DTGFB (70%D) in the vicinity of the ferroelectric phase transition is shown in Fig. 1. The heat of transition (ΔH) was determined by integrating the area enclosed by the C_p curve and an extrapolated line connecting C_p in the ferroelectric and paraelectric phases. For calibration purposes, a crystal of pure TGS gave $\Delta H = 0.46 \pm 0.05$ cal g^{-1}, which is in excellent agreement with Hoshino et al.'s value of 0.464 cal g^{-1} [13]. The values of ΔH for DTGFB and TGFB were 0.83 cal g^{-1} and 0.96 cal g^{-1}, respectively. The C_p values for TGFB are about 20% higher than those previously reported [13]. There appears to be a slight increase in C_p of about 2% upon deuteration of TGFB. The shape of the C_p curves for TGFB and DTGFB is similar to TGS which undergoes a second order transition when going from the ferroelectric to paraelectric phase [14]. The calculated entropy of the transition for TGFB and DTGFB was 0.0027 and 0.0024 cal g^{-1} K^{-1}, respectively. The transition entropy (ΔS) was obtained by dividing ΔH by the transition temperature (taken as the peak in C_p curve), thus this approximation assumes that the transition occurs over a small temperature interval. These values are comparable with 0.0015 cal g^{-1} K^{-1} obtained for TGS [15]. The values of ΔH and ΔS are therefore upper bonds on the true latent heat and the entropy discontinuity at the ferroelectric transition for TGFB and DTGFB.

It is interesting to note that deuteration of TGFB results in a small shift of the ferroelectric phase transition (1°) as contrasted to similar type materials like TGS and DTGS which show an increase of 10° [15]. Other hydrogen bonded ferroelectrics representative of the KDP family exhibit increases in transition temperatures of about 100° upon deuteration [16]. This increase on deuteration occurs because the hydrogen bonding in these materials plays a dominant role in the ferroelectric transition mechanism. Therefore, the small effect observed in the TGFB—DTGFB system would imply that hydrogen

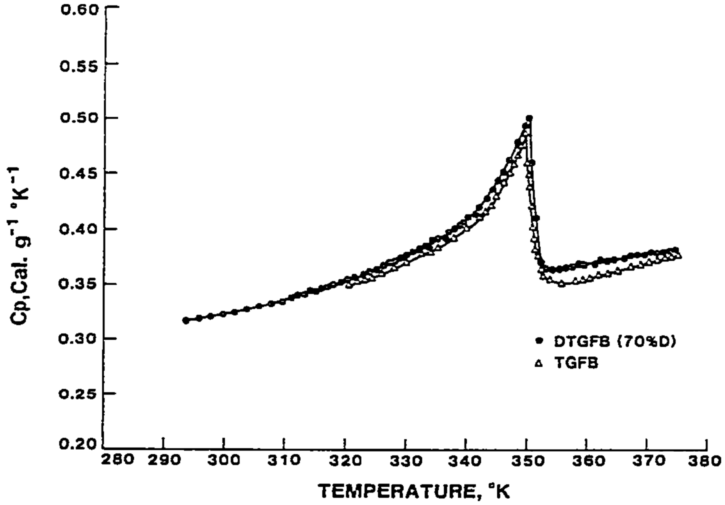

Fig. 1. Temperature dependence of C_p in DTGFB and TGFB.

TABLE 1

Anisotropic behavior of the thermal conductivity in DTGFB (70%) ($K \times 10^{-3}$ cal s^{-1} cm^{-1} °C^{-1} ± 0.05)

Temp. (°C)	[010]	[100]	[001]	[110]
23	1.22	1.61	1.24	1.46
32	1.22	1.62	1.23	1.47
44	1.20	1.60	1.22	1.44

bonding does not play a significant role in the transition and the mechanism must involve other molecular factors. A detailed study of the effects of deuteration on the electrical and thermal properties of TGFB is in preparation [17].

The results of the thermal conductivity measurements are summarized in Table 1. It is clear that K is slightly anisotropic in DTGFB. This confirms earlier observations on the lack of thermal spread in thermal images on a DTGFB pyroelectric vidicon target [18]. The temperature dependence of K in DTGFB for the orientations [010], [001], [100] and [110] are shown in Fig. 2. The K values for [010] and [001] are nearly equal. There is essentially no temperature dependence of K over the temperature interval measured. Calculation of the thermal diffusivity of DTGFB (at 40°C) using K, C_p and the density of the crystal results in a value of 2.0×10^{-3} cm^2 s^{-1} which is in excellent agreement with the reported value [1].

The effect of deuteration on K in DTGFB was measured and the data are given in Table 2. Within the experimental accuracy of the comparative mea-

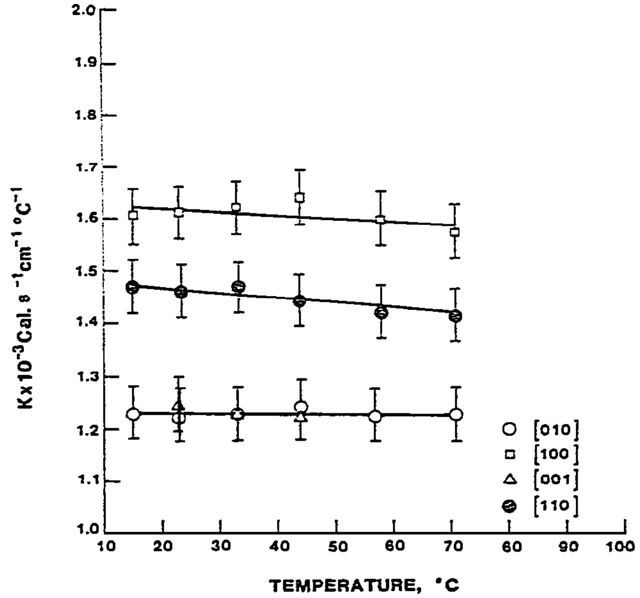

Fig. 2. Temperature dependence of thermal conductivity in DTGFB for principal orientations.

TABLE 2

Effect of deuteration on thermal conductivity in DTGFB
($K \times 10^{-3}$ cal s^{-1} $^{\circ}C^{-1}$ ± 0.05 [010])

Temp. (°C)	0%	60%	70%	90%
23	1.27	1.24	1.22	1.29
32	1.28	1.23	1.21	1.28
44	1.28	1.23	1.20	1.28

surement method, there exists no appreciable effect of deuteration on the thermal conductivity. The variation of K for a number of different crystals having the same deuteration level (70 ± 2%D) ranged from 1.17 to 1.26 × 10^{-3} cal s^{-1} cm^{-1} $^{\circ}C^{-1}$ for the [010] orientation.

CONCLUSIONS

The specific heat and thermal conductivity of DTGFB have been measured and the data indicate that deuteration has no significant effect on either of these thermal properties. There is a minor shift of the ferroelectric transition to higher temperatures. However, based on a comparison with other materials (TGS), this effect is also negligible. The thermal conductivity for DTGFB in four crystallographic orientations is independent of temperature over the range 15—70°C.

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