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THERMOCHEMICAL STUDIES ON $Bi_4Ge_3O_{12}$ AND $Bi_4Ti_3O_{12}$ SINGLE CRYSTALS

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The specific heat values of $Bi_4Ge_3O_{12}$ and $Bi_4Ti_3O_{12}$ single crystals have been studied using a DSC instrument in the temperature range from 323 to 1273 K. The temperature range at which the anomaly associated with transition from polarized to non-polarized phase in $Bi_4Ti_3O_{12}$ occurred, has been estimated using the shape of the $Bi_4Ge_3O_{12}$ heat capacity curve as a "normal" one. The heat effect and the entropy change of the transition were evaluated.

Keywords: $Bi_4Ge_3O_{12}$ and $Bi_4Ti_3O_{12}$ single crystals, phase transition, specific heat

Introduction

Due to their optical, piezoelectric and photoconductive properties, the compounds of the Bi_2O_3-GeO_2 and Bi_2O_3-TiO_2 systems have a wide variety of applications and, therefore, are of great interest.

The phase diagram of Bi_2O_3-GeO_2 systems shows three crystalinne compounds with the mole ratios 6:1, 2:3 and 1:3 [1] as well as the Bi_2O_3–TiO_2 system representing three compounds with mole ratios 6:1, 2:3 and 1:4 [2]. For isomorphous bcc $Bi_{12}GeO_{20}$ and $Bi_{12}TiO_{20}$ (6:1) compounds the results of differential scanning calorimetry (DSC) above room temperature and of non-isothermal kinetic analysis for the formation processes have been reported earlier [3, 4]. If the mole ratio Bi_2O_3:MO_2 is changed to 2:3, the compounds $Bi_4Ge_3O_{12}$ and $Bi_4Ti_3O_{12}$ with different types of crystal structure form, namely, $Bi_4Ge_3O_{12}$ with cubic structure of eulytine type and $Bi_4Ti_3O_{12}$ with tetragonal structure including perovskite-like layers.

$Bi_4Ge_3O_{12}$ possesses intense scintillation properties and is used as an energy detector for high energy ($\bar{e}$, X-ray, γ-radiation) signals and may be utilized at high temperatures [5]. The ferroelectric $Bi_4Ti_3O_{12}$ is characterized by the high stability of piezoelectric and dielectric properties, and also by high electric Curie point (943 K) [6]. This compound is spontaneously polarized below this temperature

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and an anomaly is to be expected in the heat capacity near the Curie point, where the transition from polarized to nonpolarized configuration occurs.

In this paper the results of specific heat measurements on $Bi_4Ge_3O_{12}$ and $Bi_4Ti_3O_{12}$ single crystals by DSC are presented. On this basis the thermodynamic characteristics of the phase transition in $Bi_4Ti_3O_{12}$ are evaluated.

Experimental

Single crystals of $Bi_4Ge_3O_{12}$ and $Bi_4Ti_3O_{12}$ for DSC measurements have been prepared by A. S. Kalutskov and Yu. F. Kargin (Kurnakov Institute of General and Inorganic Chemistry, the USSR Academy of Sciences). The $Bi_4Ge_3O_{12}$ samples for the measurements were obtained by cutting from the grown bouls of the disc specimens of about 1 mm in thickness and 5 mm diameter; the sample weight was 250–280 mg. The $Bi_4Ti_3O_{12}$ samples were composed of two or three discs of single crystals of about 1.5 mm total thickness; the sample weight was 120–180 mg.

A Netzsch high temperature DSC 404 equipped with platinum furnace and platinum/rhodium sample carrier was used for the measurements. A large contact area was ensured between the flat surface of the single crystal specimens studied and the platinum crucible.

To calculate the specific heat, three DSC scans were required. The experiments were conducted at a heating rate of 20 deg·min^{-1} from 323 to 1473 K. The first scan was run with empty pan to establish the baseline, the second scan was for sapphire as a standard to determine the sensitivity and the third one was for the sample examined.

The average deviation of the experimental specific heat values from the smoothed ones did not exceed 1% for both curves presented.

The temperature control of DSC 404 was provided by Netzsch programmer 413 and controller 413. Data acquisition and instrument control were provided by a computer system with peripheral units and appropriate software.

X-ray diffraction patterns of the samples were obtained using a 'Geigerflex' X-ray diffractometer with Cu–K_α radiation.

Results and discussion

The results of the specific heat measurements for $Bi_4Ge_3O_{12}$ and $Bi_4Ti_3O_{12}$ are presented in Table 1. They are approximated as a function of temperature by a polynomial equation.

Table 1 Specific heat values, approximated by Eq. $C_p(\pm\partial) = a + bT + cT^2 + dT^3$, J g^{-1} K^{-1}

Compound	$a \cdot 10^{-2}$	$b \cdot 10^{-4}$	$-c \cdot 10^{-7}$	$d \cdot 10^{-10}$	∂
$Bi_4Ge_3O_{12}$ (323–1173 K)	18.57⁺0.58	5.37⁺0.25	5.19⁺0.33	1.85⁺0.14	0.0030
$Bi_4Ti_3O_{12}$ (323–873 K)	20.2 ⁺2.4	6.5 ⁺1.3	8.4 ⁺2.2	4.5 ⁺1.2	0.0042

The heat capacity curve of $Bi_4Ge_3O_{12}$ was estimated preliminarily as an additive value in relation to the contributions of the heat capacities of $Bi_{12}GeO_{20}$ and GeO_2 [7] according to the equation:

$$C_p(Bi_4Ge_3O_{12}) = \frac{1}{3} C_p(Bi_{12}GeO_{20}) + \frac{8}{3} C_p(GeO_2).$$

For this estimate we used the heat capacity values of $Bi_{12}GeO_{20}$ single crystal studied in our recent work [3]. For this $Bi_{12}GeO_{20}$ sample the electronic contribution in the heat capacity associated with thermally induced electronic excitation, was believed to be very small as compared to the lattice contribution. The experimental and estimated C_p values of $Bi_4Ge_3O_{12}$ agreed well (Fig. 1). This result allows to propose that there are some peculiarities similar for both $Bi_{12}GeO_{20}$ and $Bi_4Ge_3O_{12}$. We came to the conclusion that in spite of the different crystal structure, the crystal lattice was characterized by (GeO_2)-tetrahedra bound by the bismuth polyhedra.

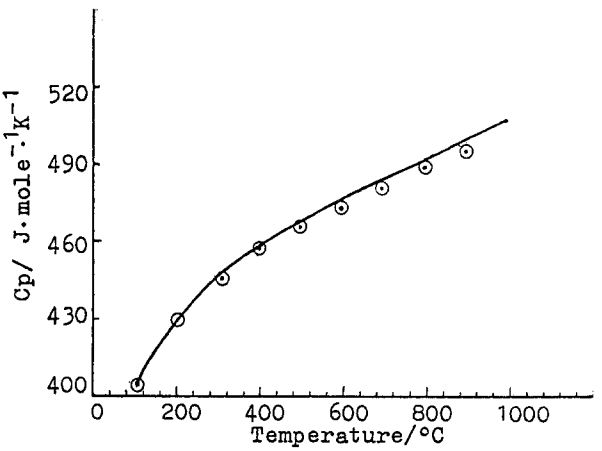

Fig. 1 Heat capacity of $Bi_4Ge_3O_{12}$: experimental curve: (o) estimated values

Since the heat capacity is sensitive to structural rearrangements, it is of interest to compare the heat capacity values of $Bi_4Ge_3O_{12}$ with those of $Bi_4Ti_3O_{12}$.

The heat capacity curve of $Bi_4Ti_3O_{12}$ is typical for ferroelectrics. The temperature at which the heat capacity reaches a maximum, the transition temperature, was studied during heating and cooling. On heating the transition temperature is taken as 943 K. This transition occurred with some hysteresis that may be associated with the structural rearrangement taking place at temperatures just above the Curie point.

The temperature scanning over the range above the Curie point resulted in an unexpected character of the specific heat curve which involved the gradual decrease of values till approximately 1173 K and further increase with some anomalies. This abnormal behaviour may be caused by the structural rearrangements as well as by the process of bismuth reduction typical for bismuth containing oxides at high temperatures. As a matter of fact the single crystal specimens heated at high temperatures lost their transparency. The data obtained for the high temperature phase were reproducible within ±2.5% only. For these reasons the C_p curve for the high temperature phase was not determined, but we pointed out that the average values of the specific heat approached those $Bi_4Ge_3O_{12}$ contrary to the differences between the low temperature data of titanate and germanate.

Heat of transition

Since the transition occurs as visually estimated over a wide temperature range, the determination of values for the heat effect and entropy changes associated with the transition is difficult. To estimate a 'normal' heat capacity, the C_p values of $Bi_4Ti_3O_{12}$ and $Bi_4Ge_3O_{12}$ were compared (Fig. 2).

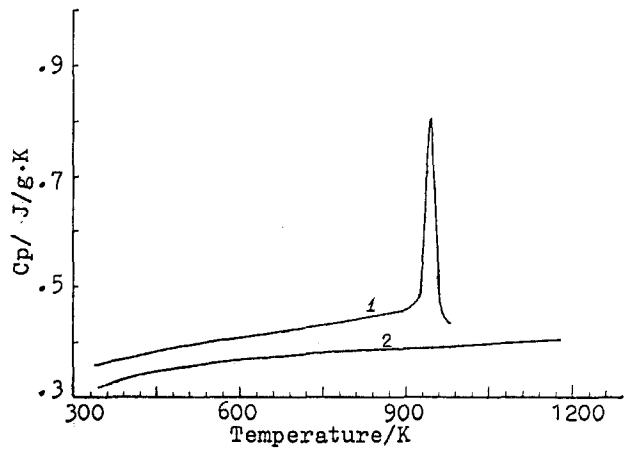

Fig. 2 Heat capacity of $Bi_4Ti_3O_{12}$ (1) and $Bi_4Ge_3O_{12}$ (2)

Assuming for the interpolated 'normal' heat capacity curve the same course as for $Bi_4Ge_3O_{12}$, the temperature range from 783 to 973 K of 'anomaly' was es-

timated. Such an estimate gives possibility to subtract the 'normal' value from the total heat content obtained for this region from the heat capacity data and thus to evaluate the enthalpy change associated with the transition itself.

The value thus obtained $\Delta H = 10.9 \pm 0.1$ kJ·mol^{-1}. But we have to stress that there is no evidence provided by the present data that this is the only possible shape for a 'normal' curve.

Entropy of transition.

The total entropy change for the transition region was found by the equation.

$$\Delta S^{\text{trans.}} = \frac{\Delta H^{\text{trans.}}}{T}$$

For better accuracy the small increments of $\Delta H/T$ in the region of the anomaly were used. The total entropy change was found to be 11.62 J·mol^{-1} K^{-1}. The entropy transition may be associated with an order-disorder transformation in the crystal structure occurring with spontaneous polarization loss. The entropy change observed was close to the entropy change which could be expected from the equation $\Delta S = R \ln 4$. This value allowed to propose the increase of the orientation positions four times during the change from oriented to the random configuration. The experimentally observed entropy change may include the contribution associated with volume changes in the transition region. But some uncertainty in the estimation of the 'normal' heat capacity over the transition region makes a comparison of the theoretical and experimental results difficult.

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Zusammenfassung — Mittels DSC wurde im Bereich 323 bis 1273 K die spezifische Wärme von $Bi_4Ge_3O_{12}$- und $Bi_4Ti_3O_{12}$-Einkristallen untersucht. Unter Zuhilfenahme des "normalen" Wärmekapazitätskurvenverlaufes für $Bi_4Ge_3O_{12}$ wurde derjenige Temperaturbereich bestimmt, in dem in $Bi_4Ti_3O_{12}$ die anomale Umwandlung von einer polarisierten in eine unpolarisierte Phase verläuft. Wärmeeffekt und Entropieänderung für diese Umwandlung wurden ermittelt.