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Journal of Solid State Chemistry 179 (2006) 77–80

JOURNAL OF SOLID STATE CHEMISTRY

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Heat capacity, enthalpy and entropy of bismuth niobate and bismuth tantalate

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Received 21 July 2005; received in revised form 26 September 2005; accepted 27 September 2005
Available online 27 October 2005

Abstract

The heat capacity and the heat content of bismuth niobate $BiNbO_4$ and bismuth tantalate $BiTaO_4$ were measured by the relaxation method and Calvet-type heat flux calorimetry. The temperature dependencies of the heat capacities in the form $C_{pm} = 128.628 + 0.03340\,T - 1991055/T^2 + 136273131/T^3$ $(\mathrm{J\,K^{-1}\,mol^{-1}})$ and $133.594 + 0.02539\,T - 2734386/T^2 + 235597393/T^3$ $(\mathrm{J\,K^{-1}\,mol^{-1}})$ were derived for $BiNbO_4$ and $BiTaO_4$, respectively, by the least-squares method from the experimental data. Furthermore, the standard molar entropies at 298.15 K $S_m(BiNbO_4) = 147.86\,\mathrm{J\,K^{-1}\,mol^{-1}}$ and $S_m(BiTaO_4) = 149.11\,\mathrm{J\,K^{-1}\,mol^{-1}}$ were assessed from the low temperature heat capacity measurements. To complete a set of thermodynamic data of these mixed oxides an attempt was made to estimate the values of the heat of formation from the constituent binary oxides.

Keywords: $BiNbO_4$; $BiTaO_4$; Bismuth niobate; Bismuth tantalate; Heat capacity; Heat content; Entropy; Heat of formation

1. Introduction

In the recent years, new ceramic materials have attracted much attention due to their outstanding dielectric or ferroelectric properties. Formerly used materials, such as $(Zn,Sn)TiO_4$, $Ba_2Ti_9O_{20}$, possess good dielectric properties but too high sintering temperatures for applications in multilayer microwave integrated devices with regard to the low melting points of Ag or Cu metallization. Therefore, $BiNbO_4$ and $BiTaO_4$ with low sintering temperatures are considered as promising dielectric materials [1,2]. Another application is the manufacturing of ferroelectric memories using these oxides as buffer layers between Si bulk and functional layers of $Bi_2SrTa_2O_9$ or $Bi_2SrNb_2O_9$.

Thermophysical properties of these oxides have not been studied so far. As a part of the systematic study on the thermodynamic properties and phase equilibria in the system Bi–Sr–Nb–Ta–O, heat capacity and heat content of $BiNbO_4$ and $BiTaO_4$ were measured. Moreover, values of the standard molar entropies at temperature of 298.15 K have been evaluated by integration of C_{pm}/T functions in the temperature range of 0–298.15 K.

2. Experimental

The samples of $BiNbO_4$ and $BiTaO_4$ were synthesized by conventional solid-state reaction from high-purity binary oxides Bi_2O_3 (99.9%, Aldrich) and Nb_2O_5 (99.85%, Alfa Aesar), Bi_2O_3 and Ta_2O_5 (99.85%, Alfa Aesar), respectively. Appropriate amounts of binary oxides were mixed and ground in agate mortar. The Bi_2O_3–Nb_2O_5 mixture was treated at 800 °C in air for 80 h while the Bi_2O_3–Ta_2O_5 mixture was fired first at 700 °C in air for 12 h and after reground it was reheated at 850 °C in air for 65 h. X-ray powder diffraction patterns were recorded on DRON 3 apparatus.

The PPMS® facility (Quantum Design) was used for the heat capacity measurements in the temperature range of 2–322 K. It is fully automated equipment using a hybrid

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0022-4596/$ - see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2005.09.042

adiabatic relaxation technique. The PPMS software employs a two-tau relaxation method to evaluate the C_p values. The accuracy of heat capacity measurements is estimated to be better than $\pm 1\%$.

The Calvet-type Setaram C-80 calorimeter was used for the heat capacity determination in the temperature range of 305–570 K. The measurements were carried out in the incremental temperature scanning mode with a number of 5–10 K steps (heating rate 0.2 K min^{-1}) followed by isothermal delays of 9000 s. The synthetic sapphire, NIST Standard reference material No. 720, was used as the reference material. The typical mass of samples was 13–16 g. The accuracy of heat capacity measurements is estimated to be better than $\pm 2\%$.

Heat content determinations were carried out by the drop method using the high-temperature calorimeter Setaram (Multi HTC 96). All measurements were performed in air by alternating dropping of the reference material (small pieces of synthetic sapphire, NIST Standard reference material No. 720) and of the sample ($BiNbO_4$ or $BiTaO_4$ pellets, 5 mm in diameter, thickness of 1.5–2.5 mm) being initially held at room temperature (T_0) through a lock into the working cell of the preheated calorimeter. Endothermic effects are detected and the relevant peak area is proportional to the heat content of the dropped specimen. The measurements were performed at temperatures 670–1170 K on samples with the masses 230–380 mg. The delays between two subsequent drops were 40–50 min. In order to check for the accuracy of the present measurement, the heat content of platinum was measured first and compared with published values [3–5]. Estimated overall accuracy of the drop measurements is $\pm 2\%$.

3. Results and discussion

The XRD analysis revealed that the prepared samples consist of single phase $BiNbO_4$ or $BiTaO_4$. Both phases were present in low temperature orthorhombic structure (α-modification) and they were the only phases present without any observable diffraction lines from unreacted precursors or other phases. The following lattice parameters of the prepared samples were evaluated by Rietveld refinement: $a = 5.6893$ Å, $b = 11.728$ Å and $c = 4.9915$ Å for α-$BiNbO_4$ and $a = 5.6394$ Å, $b = 11.776$ Å and $c = 4.9626$ Å for α-$BiTaO_4$. They are in good agreement with the values published recently by Lee et al. [6].

The molar heat capacity data are plotted in Figs. 1 and 2 for $BiTaO_4$ and $BiNbO_4$, respectively. Temperature dependencies of C_{pm} derived by Neumann–Kopp's additive rule are given in these figures for comparison. The heat content data are listed in Tables 1 and 2.

3.1. Low-temperature heat capacity

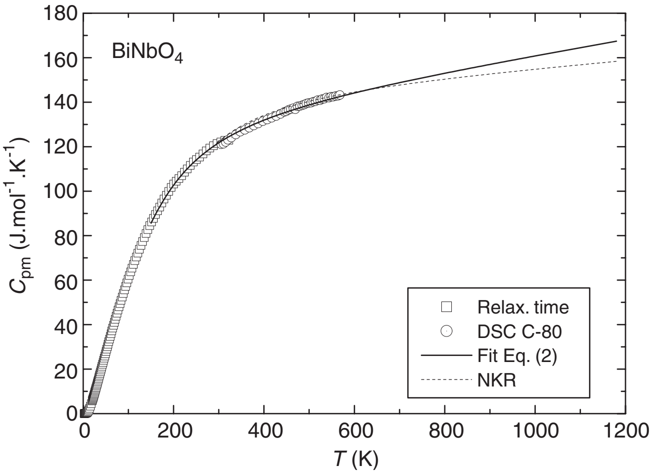

Fig. 1. Temperature dependence of the heat capacity of $BiNbO_4$ (NKR—calculated according to the Neumann–Kopp's additive rules).

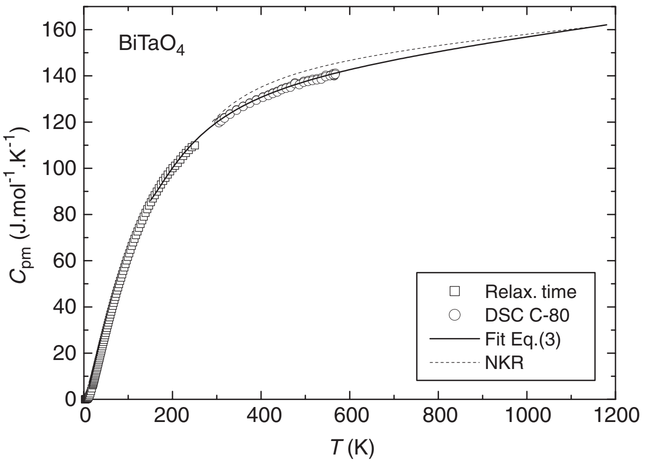

Fig. 2. Temperature dependence of the heat capacity of $BiTaO_4$ (NKR—calculated according to the Neumann–Kopp's additive rules).

A total number of 120 C_{pm} values in the temperature range 2.0–322.2 K for $BiNbO_4$ and 111 C_{pm} values in the temperature range 2.3–250.5 K for $BiTaO_4$ were measured. The temperature dependence of C_{pm} in the low-temperature region (2–250 K) was approximated by the superposition of Debye and Einstein equations with three Debye and 15 Einstein discrete normal vibration modes

$$C_{V\mathrm{m}} = 9\mathbf{R}\left(\frac{T}{\Theta_{\mathrm{D}}}\right)^3 \int_0^{\Theta_{\mathrm{D}}/T} \frac{x^4 \mathrm{e}^x}{(\mathrm{e}^x - 1)^2}\,\mathrm{d}x + 3\mathbf{R}\sum_{i=1}^{n-1} \frac{(\Theta_{\mathrm{E_i}}/T)^2 \mathrm{e}^{\Theta_{\mathrm{E_i}}/T}}{(\mathrm{e}^{\Theta_{\mathrm{E_i}}/T} - 1)^2} \qquad (1)$$

The characteristic temperatures Θ_{D}, Θ_{E1}, Θ_{E2}, Θ_{E3} and Θ_{E4}, as well as the degeneracies of the respective Einstein modes were assessed by trial and error method to obtain a satisfactory fit with the experimental points. The selected total number of 18 normal modes corresponds to $3N$ degrees of freedom for $N = 6$ atoms per formula unit. This

Table 1
Heat content of $BiNbO_4$

T (K)	$H_m(T)$—H_m (298.15 K) (J mol^{-1}) experimental	$H_m(T)$—H_m (298.15) (J mol^{-1}) integration of Eq. (2)	δ (%)
670.3	53321	50927	4.5
670.4	51969	50931	2.0
723.5	58029	58823	−1.4
723.6	58492	58844	−0.6
773.1	64515	66312	−2.8
773.2	63888	66320	−3.8
823.2	73621	73976	−0.5
823.3	73214	73985	−1.1
872.9	84023	81675	2.8
873.0	84344	81681	3.2
923.3	89328	89582	−0.3
923.3	91395	89582	2.0
973.1	92915	97489	−4.9
973.2	93891	97498	−3.8
1023.2	105397	105532	−0.1
1023.3	104058	105558	−1.4
1073.4	113553	113688	−0.1
1073.4	112425	113693	−1.1
1123.3	120929	121906	−0.8
1123.4	122100	121909	0.2
1123.4	118964	121911	−2.5
1173.2	128364	130190	−1.4
1173.3	130438	130205	0.2
1173.3	131245	130208	0.8

Table 2
Heat content of $BiTaO_4$

T (K)	$H_m(T)$—H_m (298.15 K) (J mol^{-1}) experimental	$H_m(T)$—H_m (298.15) (J mol^{-1}) integration of Eq. (3)	δ (%)
670.5	48840	50307	−3.0
670.6	50431	50319	0.2
723.3	57125	58036	−1.6
723.5	56635	58064	−2.5
773.1	64778	65426	−1.0
773.2	66108	65440	1.0
822.8	74656	72879	2.4
822.9	77172	72885	5.6
823.1	73225	72916	0.4
872.5	79733	80418	−0.9
872.6	76861	80426	−4.6
873.0	79955	80493	−0.7
923.0	89466	88159	1.5
923.0	89908	88164	1.9
973.0	97400	95901	1.5
973.0	97183	95907	1.3
1023.1	104930	103739	1.1
1023.2	103907	103760	0.1
1073.1	111043	111637	−0.5
1073.2	112920	111648	1.1
1123.1	118490	119610	−0.9
1123.2	120926	119614	1.1
1123.2	115329	119620	−3.7
1123.2	124313	119620	3.8
1173.0	125869	127627	−1.4
1173.1	131535	127642	3.0
1173.2	122829	127653	−3.9
1173.2	123229	127653	−3.6

is indeed a simplification, since the real structure contains four formula units per unit cell giving rise to 72 independent normal modes. However, as it is not reasonable to use higher number of adjustable parameters, the Einstein oscillators simulating the optical branches of the real phonon spectrum were grouped into four modes with different degeneracies. The fitted parameters are summarized in Table 3. Unfortunately, it is not possible to compare the obtained values with the Raman spectra [6], since the group theory analysis of the phonon symmetry is not yet available.

Although, strictly speaking, Eq. (1) holds for lattice contribution of heat capacity at constant volume, the difference between C_{pm} a C_{Vm} is unimportant in the temperature range 0–298.15 K and Eq. (1) can be thus used for the isobaric heat capacity. Using the following data for $BiTaO_4$ at 298.15 K: $V_m = 51.35 \times 10^{-6}\,m^3\,mol^{-1}$, $\alpha = 2 \times 10^{-5}\,K^{-1}$ [7], $\beta \approx 1.5 \times 10^{-11}\,Pa^{-1}$ [8], one can calculate a dilatation term $C_{pm} - C_{Vm} = 0.41\,J\,K^{-1}\,mol^{-1}$, which represents 0.35% from the value of $C_{pm}(298.15\,K) = 119.29\,J\,K^{-1}\,mol^{-1}$. The values of standard molar entropies of $BiNbO_4$ and $BiTaO_4$ were obtained by numerical integration of C_{pm}/T dependence using the fitted curves in the temperature range 0–298.15 K. These values as well as the standard entropies of formation from the constituent binary oxides, $\Delta S_{f,ox}$ are summarized in Table 4. The values of $\Delta S_{f,ox}$ are positive and relatively small.

3.2. High-temperature heat capacity and heat content

The raw data were simultaneously analyzed using the least-squares method with different weights for individual points. These weights were assessed as reciprocal values of absolute errors of the individual measurements. In order to smoothly link the high and low temperature data, 29 points in the temperature range 150–322 K for $BiNbO_4$ and 28 points in the temperature range 150–250 K for $BiTaO_4$ were included in the fit procedure. A four parameters fitting equation including the T^{-3} term was used to attain higher flexibility around the room temperature. Thus, the temperature dependence of the molar heat capacity of solid $BiNbO_4$ and $BiTaO_4$ can be expressed by the following equations ($T = 150-1200\,K$):

$$C_{pm}(BiNbO_4) = 128.628 + 0.03340\,T - \frac{1{,}991{,}055}{T^2} + \frac{136{,}273{,}131}{T^3}\,(J\,K^{-1}\,mol^{-1}), \tag{2}$$

$$C_{pm}(BiTaO_4) = 133.594 + 0.02539T - \frac{2{,}734{,}386}{T^2} + \frac{235{,}597{,}393}{T^3}\,(J\,K^{-1}\,mol^{-1}). \tag{3}$$

Table 3
Characteristic temperatures of the low-temperature C_{pm} fit. The numbers in parentheses represent the degeneracies of the respective phonon modes selected arbitrarily taking into account the total number of $3N$ normal modes

Oxide	Θ_D (K) (3)	Θ_{E1} (K) (3)	Θ_{E2} (K) (3)	Θ_{E3} (K) (5)	Θ_{E4} (K) (4)
$BiNbO_4$	132	193	381	418	990
$BiTaO_4$	130	178	350	440	1080

Table 4
Standard entropies of formation of mixed oxides from the constituent binary ones

Oxide	S_m(298.15 K) ($J K^{-1} mol^{-1}$)	$\Delta S_{f,ox}$(298.15 K) ($J K^{-1} mol^{-1}$)
Bi_2O_3	148.5 [9]	
Nb_2O_5	137.30 [10]	
Ta_2O_5	143.09 [10]	
$BiNbO_4$	147.86	4.96
$BiTaO_4$	149.11	3.31

According to the phase diagram of the Bi_2O_3–Nb_2O_5 system [11] α-$BiNbO_4$ is stable up to the transformation temperature ≈1300 K. As the value of $\Delta S_{f,ox}$ is relatively small, the stability of α-$BiNbO_4$ must be considered as a result of exothermic nature of the formation reaction

$$\tfrac{1}{2}Bi_2O_3(s) + \tfrac{1}{2}Nb_2O_5(s) = BiNbO_4(s). \quad (4)$$

Unfortunately, there is no experimental value of $\Delta H_{f,ox}$ (the standard enthalpy of formation from the constituent binary oxides) in literature and so the only way is to estimate it on the basis of some empirical method. A simple method for estimation of $\Delta H_{f,ox}$ suggested by Smith [12] is based on the following relation:

$$\Delta H_{f,ox} = -(h(A) - h(B))^2, \quad (5)$$

where h(A) and h(B) are empirical parameters for acidic and basic oxides and $\Delta H_{f,ox}$ is expressed per one atom of oxygen in a basic oxide. Only the parameter $h(Bi_2O_3) = -3.7$ is given in the original paper [12] so the parameter $h(Nb_2O_5)$ has to be derived from published values of the heats of formation for other niobates [13,14]. We derived the following values: $h(Nb_2O_5) = 1.52 \pm 0.20$ and $\Delta H_{f,ox}(BiNbO_4) = -40.9 \pm 3.1\,kJ\,mol^{-1}$. To examine the reliability of this procedure $\Delta H_{f,ox}(SbNbO_4) = -3.5 \pm 3.1\,kJ\,mol^{-1}$ was calculated and compared with the experimental value of $\Delta H_{f,ox}(SbNbO_4) = 2.4 \pm 1.4\,kJ\,mol^{-1}$ [15]. The values are in acceptable agreement. Using the same procedure and the published data for other tantalates [16] we obtained $h(Ta_2O_5) = 2.38 \pm 0.96$ and $\Delta H_{f,ox}(BiTaO_4) = -55.5 \pm 17.5\,kJ\,mol^{-1}$. Due to a large uncertainty of the parameter $h(Ta_2O_5)$ the calculated values of $\Delta H_{f,ox}(BiTaO_4)$ should be considered much less reliable.

4. Conclusions

The heat capacities and heat contents of bismuth niobate and tantalate were measured and the temperature dependencies of high-temperature heat capacities were derived. The values of the standard molar entropies at 298.15 K were evaluated from the low temperature C_{pm} measurements. In order to get a complete set of thermodynamic data of these mixed oxides an attempt was made to estimate the values of the heat of formation from the constituent binary oxides. However, the resulting values are not much plausible and so the experimentally obtained data are necessary for an accurate calculation of the Gibbs energies of these substances.

Acknowledgments

This work was supported by the Ministry of Education of the Czech Republic (Research Projects Nos. MSM6046137302 and MSM6046137307).

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