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HEAT CAPACITY AND HEAT CONTENT OF $BiNb_5O_{14}$

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The heat capacity and the heat content of bismuth niobate $BiNb_5O_{14}$ were measured by the relaxation time method, DSC and drop method, respectively. The temperature dependence of heat capacity in the form C_{pm}=455.84+0.06016T–7.7342·10^6/T^2 (J K^{-1} mol^{-1}) was derived by the least squares method from the experimental data. Furthermore, the standard molar entropy at 298.15 K S_m=397.17 J K^{-1} mol^{-1} was derived from the low temperature heat capacity measurement.

Keywords: *$BiNb_5O_{14}$, bismuth niobate, heat capacity, heat content*

Introduction

Phase relations in the binary system Bi_2O_3–Nb_2O_5 were thoroughly investigated by Roth *et al*. [1]. They observed five mixed oxides with stoichiometry $Bi_5Nb_3O_{15}$, $BiNbO_4$, $Bi_8Nb_{18}O_{57}$, $BiNb_5O_{14}$ and $Bi_2Nb_{12}O_{33}$. They reported that the phase $BiNb_5O_{14}$ is stable at the room temperature and decomposes at approximately 1095°C to $Bi_8Nb_{18}O_{57}$ and $Bi_2Nb_{12}O_{33}$. Bryntse [2] synthesized the non-stoichiometric phase $BiNb_{5.4}O_x$. This phase was orthorhombic with lattice parameters a=17.676, b=17.207 and c=3.9610 Å. According to XRD patterns this phase is identical with the phase $BiNb_5O_{14}$ described by Roth *et al*. [1].

In the course of a systematic study of thermochemical properties of complex oxides in the system Bi_2O_3–SrO–Nb_2O_5, we have recently measured the heat capacity and the heat content of $BiNbO_4$ [3] and $Bi_2SrNb_2O_9$ [4]. The aim of this paper is the measurement of the heat capacity and the heat content of $BiNb_5O_{14}$.

Experimental

A powder sample of $BiNb_5O_{14}$ was prepared by conventional solid-state reaction from high purity binary oxides Bi_2O_3 (99.9%, Aldrich) and Nb_2O_5 (99.85%, Alfa Aesar). The appropriate amounts of binary oxides were ground in an agate mortar and heated up to 900°C in a platinum crucible in the air atmosphere for 120 h. After reground and homogenization, the mixture was treated at 950°C in air for 120 h. The phase composition was determined using X-ray powder diffraction analysis (PANalytical X'Pert PRO) and the ratio of the metal elements was detected using X-ray fluorescence spectroscopy (Thermo ARL 9400 by Thermo Electron Corporation).

The PPMS facility (Quantum Design) was used for the heat capacity measurement in the temperature range of 2–190 K. It is fully automated equipment using a hybrid adiabatic relaxation technique. The PPMS software employs a two-tau relaxation time method to evaluate the C_p values. The accuracy of heat capacity measurement is estimated to be better than ±2%.

The Micro DSC III calorimeter (Setaram) was used for the heat capacity determination in the temperature range of 258–350 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 0.4–1 g. The uncertainty of heat capacity measurements is estimated to be better than ±1%.

Heat content determinations were carried out by the drop method using the high temperature calorimeter Multi HTC 96 (Setaram). 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 ($BiNb_5O_{14}$ 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. Endother-

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mic effects are detected and the relevant peak area is proportional to the heat content of the dropped specimen. The measurements were performed at temperatures 721–1373 K on samples with the masses 90–190 mg. The delays between two subsequent drops were 40–50 min. Estimated overall accuracy of the drop measurements is ±3%.

Results and discussion

The XRD analysis (Fig. 1) revealed that the prepared sample consists of single phase oxide with orthorhombic structure. No other diffraction lines from the unreacted precursors or other phases are observable. Recorded diffraction pattern of our sample is compared to the reference (JCPDS 48-0986) from Bryntse [2] that was measured in a narrow range of 2θ up to 55°. The metal atoms ratio determined by the XRF analysis is Nb/Bi=5.08/1.00. Thus the composition of our sample corresponds to the stoichiometric formula $BiNb_{5.08}O_{14.20}$ in which oxygen stoichiometry was calculated with respect to the valency of metal ions Bi^{3+} and Nb^{5+}. Nevertheless, the stoichiometric formula $BiNb_5O_{14}$ is used in the whole paper for simplicity.

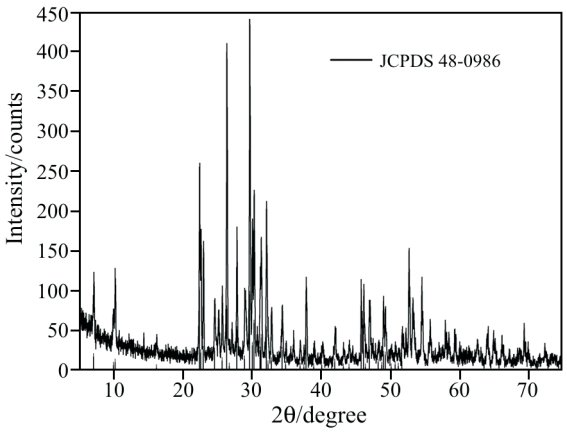

Fig. 1 X-ray diffraction pattern of $BiNb_5O_{14}$

The measured C_{pm} data (99 points from relaxation time and 45 points from DSC) are plotted in Fig. 2. The heat content data are listed in Table 1 and shown in Fig. 4.

The raw data were analyzed in two separate steps using the least-square method with different weights for individual points. In the first run, relaxation time data in the temperature range 99.6–190.1 K and DSC data were fitted using an empirical equation in the following form:

$$C_{pm} = -(26.145\pm4.732)+(2.1302\pm0.0478)T- -(0.00250\pm0.00011)T^2 \quad (1)$$

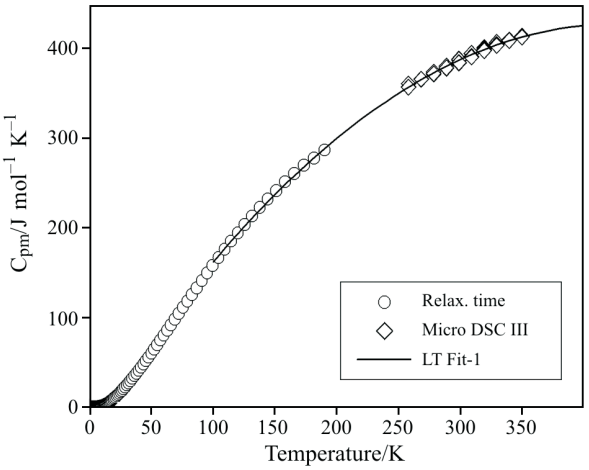

Fig. 2 Temperature dependence of the heat capacity of $BiNb_5O_{14}$; (LT Fit – calculated according to Eq. (1))

Table 1 Heat content of $BiNb_5O_{14}$

T/K	$H_m(T)-H_m(298.15)$/J mol^{-1}		δ/%
	experimental	integration of Eq. (2)	
721.60	198700	190792	4.1
721.63	187353	190806	–1.8
772.43	220218	215541	2.2
772.63	223254	215639	3.5
822.59	233840	240202	–2.6
822.60	236989	240207	–1.3
872.62	276513	265020	4.3
872.65	279007	265035	5.3
922.77	292397	290107	0.8
922.77	292698	290107	0.9
972.77	324195	315319	2.8
972.78	320460	315324	1.6
1023.05	346305	340866	1.6
1023.05	337271	340866	–1.1
1073.09	355094	366479	–3.1
1073.16	371624	366515	1.4
1123.28	388372	392352	–1.0
1123.36	382207	392393	–2.6
1172.40	396864	417846	–5.0
1173.21	406249	418268	–2.9
1223.30	454685	444442	2.3
1223.31	452809	444447	1.9
1272.98	473121	470572	0.5
1273.00	464952	470582	–1.2
1322.92	480971	497006	–3.2
1322.94	497277	497017	0.1
1372.40	533924	523362	2.0
1372.55	509739	523442	–2.6

C_{pm}(298.15 K)=386.67 J K^{-1} mol^{-1} was calculated using Eq. (1) and this value was subsequently used as constraints for high-temperature data processing.

In the second run, the DSC heat capacity data and the heat content data from drop calorimetry were treated simultaneously. Different weights assigned to individual points were calculated as $1/\delta^2$ where δ are absolute errors of the each point derived from overall accuracies of the measurements (1% for DSC and 3% for drop). Thus the temperature dependence of the molar heat capacity of solid $BiNb_5O_{14}$ can be expressed by the following equations (T=298.15–1500 K):

$$C_{pm}=(455.84\pm10.60)+(0.06016\pm0.01604)T-\\-(7.7342\pm0.5521)\cdot10^6/T^2\ (\mathrm{J\ K^{-1}\ mol^{-1}}) \quad (2)$$

Temperature dependence of the heat capacity of $BiNb_5O_{14}$ according to Eq. (2) is shown in Fig. 3. The dependence calculated according to the empirical Neumann–Kopp's rule [5] is given there for comparison. It is obvious that the Neumann–Kopp's prediction gives a good approximation for this mixed oxide.

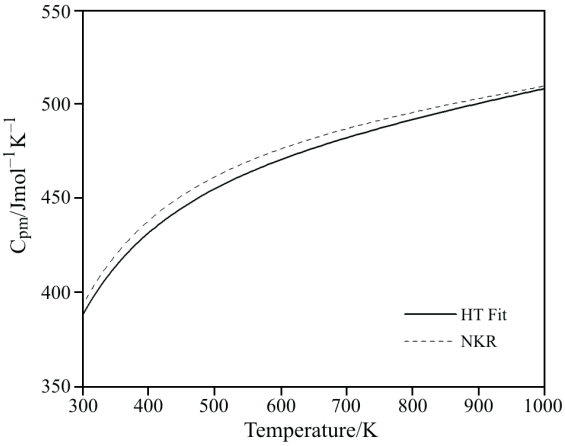

Fig. 3 Temperature dependence of the heat capacity of $BiNb_5O_{14}$; (HT Fit – calculated according to Eq. (2), NKR – calculated according to the Neumann–Kopp's additive rules)

The value of standard molar entropy of $BiNb_5O_{14}$ at 298.15 K was derived from the low-temperature C_{pm} data integrating the C_{pm}/T function from zero up to 298.15 K. A numerical integration was used for the 0–100 K range whereas an analytical integration of Eq. (1) was applied from 100 to 298.15 K. This value as well as the standard entropy of formation from the constituent binary oxides, $\Delta S_{f,ox}$, are summarized in Table 2. The values of $\Delta S_{f,ox}$ for other mixed oxides in the system Bi_2O_3–SrO–Nb_2O_5 are also listed in Table 2 for comparison.

According to the literature [1] $BiNb_5O_{14}$ is stable up to temperature of 1368 K. As the value of $\Delta S_{f,ox}$ is negative, the stability of $BiNb_5O_{14}$ should be considered as a result of exothermic nature of the formation reaction

$$Bi_2O_3(s)+5Nb_2O_5(s)=2BiNb_5O_{14}(s) \quad (3)$$

Unfortunately, there is no experimental value of $\Delta H_{f,ox}$ (the standard enthalpy of formation from the constituent binary oxides) in the literature to justify this hypothesis.

Table 2 Standard molar entropies and 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 [6]	
SrO	53.58 [7]	
Nb_2O_5	137.30 [8]	
$BiNb_{5.08}O_{14.20}$	397.17[a]	–25.82
$BiNbO_4$	147.86[b]	4.96
$Bi_2SrNb_2O_9$	327.15[c]	–12.23
$Sr_2Nb_2O_7$	232.37[d]	–12.09
$Bi_2Sr_4O_4$		–12[e]
$Bi_2Sr_2O_5$		–24[e]
$Bi_2Sr_3O_6$		–7[e]

[a]This work; [b]based on low-temperature C_{pm} data [3]; [c]based on low-temperature C_{pm} data [4]; [d]based on low-temperature C_{pm} data [9]; [e]thermodynamic assessment [10]

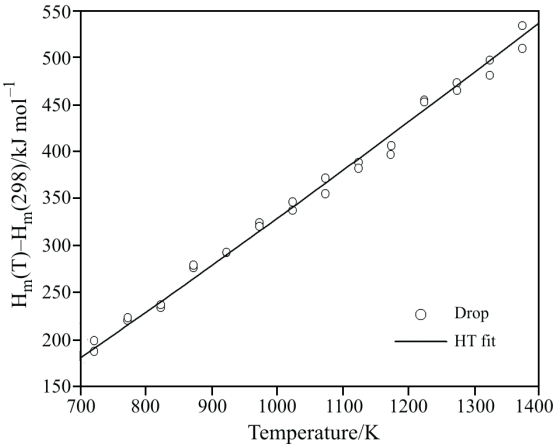

Fig. 4 Heat content of $BiNb_5O_{14}$; (HT Fit – integration of Eq. (2))

Conclusions

The heat capacity and heat content of bismuth niobate $BiNb_5O_{14}$ were measured and the temperature dependence of high temperature heat capacity was derived. The value of the standard molar entropy at 298.15 K was evaluated from the low temperature C_{pm} measurement.

Acknowledgements

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