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Multifunctional material $Bi_4Ge_3O_{12}$: thermodynamic properties

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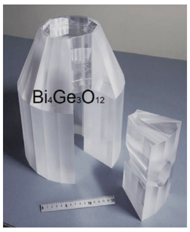
Thermodynamic characteristics of a single crystal of bismuth orthogermanate ($Bi_4Ge_3O_{12}$), which are necessary to improve device portfolio, have been studied. It has been shown that bismuth orthogermanate is thermodynamically stable against decomposition into binary oxides at 50 °C, which gives us grounds to consider this compound promising for various applications.



Keywords: Czochralsky technique, bismuth germanate, single crystal, calcium germanate, solution calorimetry, formation enthalpy.

As is known, compounds on the basis of bismuth oxide, in particular, single crystal of bismuth orthogermanate $Bi_4Ge_3O_{12}$ (BGO), possess scintillation properties enabling to apply these materials in nuclear physics, high energy physics, low background spectrometry, positron emission tomography *etc*.[1–6] Significant progress in obtaining large sized BGO crystals has been achieved at Nikolaev Institute of Inorganic Chemistry SB RAS.[3] To further improve the technology for growing large sized bismuth germanate crystals, it is necessary to obtain additional information about thermodynamic properties of this material.

To date, the standard formation enthalpy of bismuth germanate ($Bi_4Ge_3O_{12}$) single crystals has not been investigated. Thermodynamic data for single crystals are more reliable than those for ceramic materials, inasmuch as ceramic materials may contain amorphous phases which cannot be determined by X-ray powder diffraction, whereas in crystals these phases are absent.

Previously, the thermodynamic properties of ceramic compounds in the Bi_2O_3–GeO_2 system have been studied by electromotive force (EMF) method and differential scanning calorimetry (DSC).[7,8]

The aim of this research was to study thermodynamic properties of $Bi_4Ge_3O_{12}$ and reactions involving it by direct calorimetric measurements. Direct calorimetric measurements represent the most reliable approach to determine the formation enthalpies compared with measurements performed by electromotive force (EMF) method.[9–11]

In our study, bismuth oxide, calcium germanate and bismuth orthogermanate were used for calorimetric[†] experiments.[12–14] A single crystal of $Bi_4Ge_3O_{12}$ which was grown specifically for calorimetric measurements is presented in Figure 1.

Solution calorimetry was chosen to study thermochemical properties of bismuth orthogermanate.

Initially, it seemed that the most direct way to obtain the formation enthalpy of bismuth germanate by solution calorimetry would be dissolving of bismuth oxide, germanium oxide and bismuth orthogermanate that would allow us to get the formation enthalpy of $Bi_4Ge_3O_{12}$ from simple oxides. However, the only solvent, in which all substances are dissolved, is hydrofluoric acid, while our calorimeter is not designed to operate with HF. And furthermore, calorimeters for working with HF have a number of drawbacks. It is known that bismuth oxide and bismuth orthogermanate dissolve satisfactorily in hydrochloric acid at a temperature of 50 °C. Hence, one could try to develop a cycle using $GeCl_4$. Nevertheless, working with germanium chloride is dangerous because its boiling point is 83 °C. In addition, it is difficult to select a solvent for $GeCl_4$; this compound is hydrolyzed in dilute HCl while its solubility is extremely low in concentrated hydrochloric acid.

Therefore, we settled on choice of thermochemical cycle which included dissolution of bismuth oxide, bismuth

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[†] Bismuth oxide was obtained at Nikolaev Institute of Inorganic Chemistry SB RAS *via* oxidation of bismuth melt with oxygen in a rotating reactor by the method developed earlier.[13] Analysis for elements Na, Mg, Al, Si, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Ge, Ag, Te and Sb showed that content of each element did not exceed 10^{-5}%.

Bismuth orthogermanate was grown by low-temperature-gradient Czochralsky technique with weight control from bismuth oxide and germanium oxide specifically for calorimetric measurements according to technology described previously.[12] The crystal had a cubic structure, evlitine. Space group *J*43*d*, lattice parameter a = 10.52 Å.

A sample of bismuth orthogermanate for calorimetric studies was cut from the central part of the grown single crystal. The sample did not have visible inclusions as well as any color tint. A charge containing mixture of germanium and bismuth oxides in stoichiometric ratio was used to grow a single crystal. The impurity level of crystalline sample was beyond the detection limits of the instruments. $Bi_4Ge_3O_{12}$ had the evlitine structure and melted congruently at 1049 °C.

Calcium germanate ($CaGeO_3$) was synthesized from germanium dioxide and calcium carbonate (GeO_2, Strem 6N; $CaCO_3$, Ventron, ASC) by solid phase synthesis. The stoichiometric mixture was heated to a temperature of 1000 °C for 70 h, and then, after grinding, it was held at a temperature of 1200 °C for 40 h. X-ray phase analysis showed that the sample was single-phase. A triclinic modification of calcium germanate was revealed.

The phase purity was analyzed by X-ray diffraction (Shimadzu XRD-7000, CuKα1 radiation). Contents of bismuth and germanium were determined by fluorescence analysis. According to the results of the analysis the compound had the formula $Bi_4Ge_3O_{12}$ (accuracy ~0.01%).

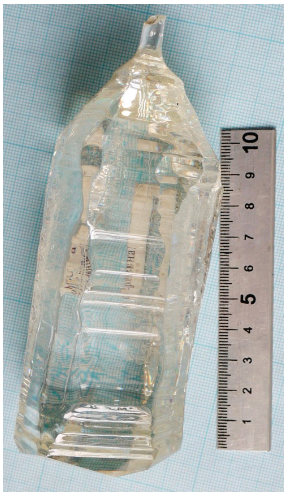

Figure 1 Single crystal of $Bi_4Ge_3O_{12}$.

orthogermanate and calcium germanate. The formation enthalpy of calcium germanate was measured by A. Navrotsky[15] *via* reaction calorimetry and by Grebenshchekov *et al*.[16] *via* solution calorimetry in hydrofluoric acid. The obtained values are well consistent and a reliable value of the formation enthalpy of calcium germanate based on these data is given in the handbook.[17]

A 2M HCl solution was used as a solvent. The scheme of calorimetric reactions is presented below.

$$2Bi_2O_3\ (s) + \text{solution I} = \text{solution II} + 2\Delta_{sol}H_1^0, \quad (1)$$

$$3CaGeO_3\ (s) + \text{solution II} = \text{solution III} + 3\Delta_{sol}H_2^0, \quad (2)$$

$$3CaO\ (s) + \text{solution I} = \text{solution IV} + 3\Delta_{sol}H_3^0, \quad (3)$$

$$Bi_4Ge_3O_{12}\ (s) + \text{solution IV} = \text{solution III} + \Delta_{sol}H_4^0. \quad (4)$$

Further, the summation of thermochemical reactions gives us:

$$2Bi_2O_3\ (s) + 3CaGeO_3\ (s) = 3CaO\ (s) + Bi_4Ge_3O_{12}\ (s) + \Delta_r H_5^0, \quad (5)$$

where $\Delta_r H_5^0 = 2\Delta_{sol}H_1^0 + 3\Delta_{sol}H_2^0 - 3\Delta_{sol}H_3^0 - \Delta_{sol}H_4^0$.

The experiments were carried out in solution calorimeter with isothermal shell in 2M HCl solution at 50 °C. A detailed description of the design of calorimeter and experimental procedure has been published earlier.[18–19] The dissolution enthalpies of bismuth oxide, calcium oxide and bismuth germanate were determined as the average of six experiments and comprised:

$$\Delta_{sol}H_1^0\,(Bi_2O_3) = -114.4 \pm 1.6\ \text{kJ mol}^{-1},$$

$$\Delta_{sol}H_2^0\,(CaGeO_3) = -75.4 \pm 1.9\ \text{kJ mol}^{-1},$$

$$\Delta_{sol}H_3^0\,(CaO) = -195.7 \pm 1.4\ \text{kJ mol}^{-1},$$

$$\Delta_{sol}H_4^0\,(Bi_4Ge_3O_{12}) = -91.2 \pm 3.5\ \text{kJ mol}^{-1}.$$

Uncertainties were calculated for 95% confidence interval using Student's coefficient.

Calculated enthalpy of the reaction (5) was 223.3 ± 8.5 kJ mol^{-1}. Using the formation enthalpy from oxides for triclinic modification of $CaGeO_3$ from the reference book,[17] we calculated the formation enthalpy from oxides for $Bi_4Ge_3O_{12}$ by the reaction:

$$2Bi_2O_3(s) + 3GeO_2(s) = Bi_4Ge_3O_{12}\ (s). \quad (6)$$

It was -92.9 ± 8.5 kJ mol^{-1}.

The standard formation enthalpy of germanium oxide is -580.2 ± 1.42 kJ mol^{-1} and the standard formation enthalpy of bismuth oxide is -577.8 ± 4.2 kJ mol^{-1}.[17] Using these data and the value we obtained for reaction (5), we calculated the standard formation enthalpy of $Bi_4Ge_3O_{12}$ as -2988.5 ± 10.7 kJ mol^{-1}.

Based on our experimental data and entropies of all the compounds involved in reaction (6), it can be concluded that bismuth orthogermanate is thermodynamically stable with respect to decomposition into binary oxides.

As mentioned above, free Gibbs energy for $Bi_4Ge_3O_{12}$ was determined[7] by electromotive force (EMF) method in the temperature range of 900–1000 K. These data can not be compared with our results since the measurements were done[7] in the different temperature range.

In this paper, we for the first time measured solution enthalpy for bismuth orthogermanate and calcium germanate in 2M HCl at 50 °C. The standard formation enthalpy and formation enthalpy from simple oxides were calculated on the basis of data obtained. Thermodynamic stability of bismuth orthogermanate with respect to decomposition into simple oxides at 50 °C makes it prospective for use in different applications.

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