Heat capacity and phase transition of bismuth niobate doped by rare earth elements

N I Matskevich¹, S V Stankus², D A Samoshkin¹,², V P Zaitsev¹,³ and E N Tkachev¹
1 Nikolaev Institute of Inorganic Chemistry SB RAS, 630090 Novosibirsk, Russia
2 Kutateladze Institute of Thermophysics SB RAS, 630090 Novosibirsk, Russia
3 Siberian State University of Water Transport, 630099 Novosibirsk, Russia
E-mail: nata.matskevich@yandex.ru

Abstract. The heat capacity of bismuth niobate doped by rare earth elements (R = Er, Lu) was measured by differential scanning calorimetry. It was found that there were phase transitions for investigated compounds at temperatures > 500 K. The temperatures of beginning phase transitions increased with decreasing of rare earth elements radii, which correlated with an increase in lattice energies.

1. Introduction
Compounds on the basis of delta form of bismuth oxide (δ-Bi₂O₃) are promising materials for fuel cells, oxygen ceramic generators, inorganic pigments, etc. [1–8]. The problem is that this modification is stable only in limited temperature range (1000–1100 K). In order to increase the stability of δ-Bi₂O₃ up to room temperatures, doping by various elements of fifth, sixth and third groups, in particular rare earth elements, is applied. Bismuth niobate, partially doped by yttrium (Bi₃Nb₀.₂Y₀.₈O₆.₂), is a promising ionic conductor [1]. To improve the functional and thermodynamic characteristics, it is advisable to study compounds based on bismuth niobate, doped by other rare earth elements.

In our earlier paper [6], we synthesized bismuth niobate, doped by dysprosium (Bi₃Nb₀.₂Dy₀.₈O₆.₂) and measured its heat capacity in the temperature range of 167–818 K.

2. Experimental
In this work we synthesized bismuth niobates doped by lutetium and erbium, measured heat capacity for these compounds and also systematically considered heat capacity and phase transitions for Bi₃Nb₀.₂R₀.₈O₆.₂ compounds (R = Lu, Er, Dy). The regularities of changing in phase transition temperatures when replacing one rare earth element by another were revealed.

High purity precursors were used to synthesize doped bismuth niobates: bismuth oxide (Bi₂O₃, purity > 0.9999), niobium oxide (Nb₂O₅, purity > 0.999), lutetium oxide (Lu₂O₃, purity > 0.999) and erbium oxide (Er₂O₃, purity > 0.999). Bismuth niobates doped by lutetium and erbium (Bi₃Nb₀.₂Lu₀.₈O₆.₂, Bi₃Nb₀.₂Er₀.₈O₆.₂) were synthesized by solid-phase reaction. A methodology, which allowed obtaining high-quality samples, that included mixing, pressing and annealing at high temperatures, was developed before synthesis.

The starting materials were mixed in a planetary mill Fritsch Pulverisette 6 for several hours (> 70 h), pressed in pellets and then annealed in furnace at temperature of more than 1000 K for about 50 h.
Characterization of compounds was carried out by X-ray powder diffraction (Shimadzu XRD-7000) and fluorescence analyses.

The heat capacity of bismuth niobates doped by lutetium and erbium was firstly measured by differential scanning calorimetry. This method with suitable calibration served to measure heat capacity with an accuracy of 1-3% [9-12]. DSC 404 F1 Pegasus calorimeter was applied to measure heat capacity for $\text{Bi}_3\text{Nb}_{0.2}\text{Lu}_{0.8}\text{O}_{6.2}$, $\text{Bi}_3\text{Nb}_{0.2}\text{Er}_{0.8}\text{O}_{6.2}$ in the temperature range of 320–965 K. The experimental technique was described in detail in papers [9-10].

3. Results and discussion

According to results of X-ray and fluorescence analyzes, the obtained compounds $\text{Bi}_3\text{Nb}_{0.2}\text{Lu}_{0.8}\text{O}_{6.2}$ and $\text{Bi}_3\text{Nb}_{0.2}\text{Er}_{0.8}\text{O}_{6.2}$ were individual phases without any impurity. Typical X-ray diffraction pattern was presented in figure 1. An analysis, performed using FullProf program, showed that compounds have cubic structure (space group Fm3m).

![Typical X-ray diffraction pattern for $\text{Bi}_3\text{Nb}_{0.2}\text{R}_{0.8}\text{O}_{6.2}$ (R = Er, Lu).](image)

Samples of compounds $\text{Bi}_3\text{Nb}_{0.2}\text{Lu}_{0.8}\text{O}_{6.2}$ and $\text{Bi}_3\text{Nb}_{0.2}\text{Er}_{0.8}\text{O}_{6.2}$ for measurement of heat capacity were prepared as follows. Cylinders with 5 mm diameter and 1.5 mm thickness were cut from synthesized tablets of doped bismuth niobates. Samples were weighed using AND GH-252 electronic balance with an uncertainty of no more than 0.3 mg. The weight of $\text{Bi}_3\text{Nb}_{0.2}\text{Er}_{0.8}\text{O}_{6.2}$ sample was 130.76 mg. The weight of $\text{Bi}_3\text{Nb}_{0.2}\text{Lu}_{0.8}\text{O}_{6.2}$ sample was 161.48 mg. Sapphire, weighing 63.44 mg, was used as a calibration sample. After all the measurements the weight of samples did not change.

The measurements were carried out using platinum crucibles with corundum inserts and platinum lids. The heating and cooling rate was 6 K min$^{-1}$. Previously, experiments were carried out with
different heating-cooling rates. As shown by results of preliminary experiments, the speed of 6 K min\(^{-1}\) provided the most precise measurements. The working volume of calorimeter was pumped out to high vacuum before measurements. The measurements were carried out in a high-purity inert gas (argon, purity more than 99.99%). The calorimeter was calibrated as indicated in paper [13].

Heat capacity measurements included three heating-cooling cycles. All heating and cooling curves were reproduced within uncertainties of measurements (2-3%). Beginning from temperatures above 590 K, dependences of heat capacities for samples Bi\(_3\)Nb\(_{0.2}\)Lu\(_{0.8}\)O\(_{6.2}\), Bi\(_3\)Nb\(_{0.2}\)Er\(_{0.8}\)O\(_{6.2}\) were non-monotonous. Such non-monotonic changing in indicated temperature range could be explained by phase transitions. The heat capacity increased by more than 20%. The results of first heating for both samples of bismuth niobate doped by lutetium and erbium differed from subsequent heating. The reason for this was that absorbed compounds from surface and stresses were removed at first heating.

The temperature dependence of Bi\(_3\)Nb\(_{0.2}\)Er\(_{0.8}\)O\(_{6.2}\) sample is presented in figure 2. The temperature dependence of Bi\(_3\)Nb\(_{0.2}\)Lu\(_{0.8}\)O\(_{6.2}\) has the similar character.

![Figure 2. Temperature dependence of heat capacity for Bi\(_3\)Nb\(_{0.2}\)Er\(_{0.8}\)O\(_{6.2}\).](image)

Monotonic changing of heat capacity for bismuth niobate doped by erbium from 231 J K\(^{-1}\) mol\(^{-1}\) up to 260 J K\(^{-1}\) mol\(^{-1}\) was observed in the temperature range of 320–590 K, and then a sharp increase in heat capacity was exhibited. For lithium niobate doped by lutetium a smooth changing of heat capacity was observed from 216 J K\(^{-1}\) mol\(^{-1}\) up to 258 J K\(^{-1}\) mol\(^{-1}\) in the temperature range of 320–630 K, and then phase transition occurred.

Earlier [6], we measured the temperature dependence of heat capacity for bismuth niobate doped by dysprosium with composition of Bi\(_3\)Nb\(_{0.2}\)Dy\(_{0.8}\)O\(_{6.2}\). The compound also had a cubic structure (space group Fm\(_{3m}\)). The heat capacity for this compound varied monotonically in the temperature range of 167–540 K, and then the phase transition occurred.
A joint consideration of experimental data on temperature dependences of heat capacity for compounds Bi$_3$Nb$_{0.2}$Dy$_{0.8}$O$_{6.2}$, Bi$_3$Nb$_{0.2}$Er$_{0.8}$O$_{6.2}$, Bi$_3$Nb$_{0.2}$Lu$_{0.8}$O$_{6.2}$ has shown the following. As could be seen, temperatures of phase transitions onset increased when radius of rare earth element decreased from Dy to Er and Lu [14]: r(Dy$^{3+}$) = 0.0912 nm; r(Er$^{3+}$) = 0.0890 nm; r(Lu$^{3+}$) = 0.0861 nm.

On the basis of modified Kapustinsky formula [15], it was possible to assume that the lattice energy should increase with decreasing radius of the rare earth element. Therefore, further we will calculate lattice energies for investigated Bi$_3$Nb$_{0.2}$Er$_{0.8}$O$_{6.2}$ and Bi$_3$Nb$_{0.2}$Lu$_{0.8}$O$_{6.2}$ compounds as well as for Bi$_3$Nb$_{0.2}$Dy$_{0.8}$O$_{6.2}$ compound that was studied earlier.

Here, the Born-Haber cycle was used to calculate the lattice energy. For such calculation, it was necessary to know standard formation enthalpies for bismuth niobates doped by rare earth elements, as well as formation enthalpies for following gaseous ions: Bi$^{3+}$, Nb$^{5+}$, Dy$^{3+}$, Er$^{3+}$, Lu$^{3+}$, O$^{2-}$. The standard formation enthalpies were taken from our paper [4], and data for gaseous ions were taken from reference book [16]. Based on above data, lattice energies for bismuth niobates doped by rare earth elements were calculated as follows: \( \Delta_{\text{lat}}E(\text{Bi}_3\text{Nb}_{0.2}\text{Dy}_{0.8}\text{O}_{6.2}) = 28460 \text{ kJ mol}^{-1} \); \( \Delta_{\text{lat}}E(\text{Bi}_3\text{Nb}_{0.2}\text{Er}_{0.8}\text{O}_{6.2}) = 28540 \text{ kJ mol}^{-1} \); \( \Delta_{\text{lat}}E(\text{Bi}_3\text{Nb}_{0.2}\text{Lu}_{0.8}\text{O}_{6.2}) = 28630 \text{ kJ mol}^{-1} \).

Further, the dependence of onset phase transition temperatures on lattice energies was constructed. The dependence was presented in figure 3. As could be seen, the temperature of phase transition onset increased with increasing lattice energy. On the basis of presented dependence, it may be stated that bismuth niobate doped by lutetium is the most promising material for application from the thermodynamic point of view.

![Figure 3. Dependence of onset phase transition temperatures on lattice energies for Bi$_3$Nb$_{0.2}$R$_{0.8}$O$_{6.2}$.](image)

The fact of increasing temperature of phase transition onset with increasing lattice energy is important for practice. The lattice energy can be calculated using Kapustinsky formula or Born-Haber
cycle. This will provide an opportunity to see direction in temperature of phase transition beginning. It should be noted here that the obtained regularities were found only for compounds with the same structures and low doping by rare earth elements.

Conclusion
The heat capacities of $\text{Bi}_3\text{Nb}_{0.2}\text{Er}_{0.8}\text{O}_{6.2}$, $\text{Bi}_3\text{Nb}_{0.2}\text{Lu}_{0.8}\text{O}_{6.2}$ compounds in the temperature range of 320–965 K have been measured by differential scanning calorimetry. The heat capacity for both compounds is shown to have nonmonotonic character, associated with phase transitions. A joint consideration of heat capacity temperature dependences for $\text{Bi}_3\text{Nb}_{0.2}\text{R}_{0.8}\text{O}_{6.2}$ compounds ($\text{R} = \text{Dy}, \text{Er}, \text{Lu}$) has been performed. The onset of the phase transition temperatures is demonstrated to increase with decreasing radii of rare earth elements. A correlation between lattice energy and temperature of phase transition onset has been found.

Acknowledgments
The research was supported by Russian Science Foundation (project 19-19-00095).

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