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STUDY OF $3Bi_2O_3{\cdot}5B_2O_3$-$Nd_2O_3{\cdot}3B_2O_3$ SYSTEM AND DEPENDENCE OF ELECTROPHYSICAL AND HEAT PROPERTIES OF OBTAINED ALLOYS ON THE COMPOSITION

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The $3Bi_2O_3{\cdot}5B_2O_3$-$Nd_2O_3{\cdot}3B_2O_3$ system was studied using DTA, XRD, and electrical conductivity and heat properties measured. A new ternary compound was revealed in the system. Formation of a new compound expands an area of glass formation towards non-glass forming boundary binary compounds. It found that obtained materials possess semiconductor properties as distinct from initial $3Bi_2O_3{\cdot}5B_2O_3$, $Nd_2O_3{\cdot}3B_2O_3$

Keywords: *electric resistance, system, dielectric loss, phonons, dependence, frequency.*
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Introduction

Materials based on boric oxide are of a great practical importance. High dielectric borate glasses are widely used in different fields of technology (microelectronics) as high melting coatings which provide isolation of main operating materials from external influence. Laser borate crystals which are used in microelectronics are very important materials [1-6].

Composition of studied alloys consists of binary-, ternary-, tetra- and sometimes multicomponent mixtures. Production of new materials and improvement of their properties are possible by studying phase diagrams of multicomponent systems. Phase diagrams are closely connected with composition-property diagrams.

Earlier, we studied phase equilibriua and some physical properties of the $BaO{\cdot}2B_2O_3$-$La_2O_3{\cdot}2B_2O_3$, BaO-La_2O_3-$2B_2O_3$,$2B_2O_3{\cdot}3SiO_2$-$Bi_2O_3{\cdot}B_2O_3$, $2Bi_2O_3{\cdot}B_2O_3$– $2Bi_2O_3{\cdot}3GeO_2$ and $3Bi_2O_3{\cdot}5B_2O_3$ - $Nd_2O_3{\cdot}3B_2O_3$and systems to establish areas of glass formation therein [7-10]. From this point of view, the data on studying Bi_2O_3-B_2O_3-Nd_2O_3 triple system, the research of internal section in the triple system by physical-chemical methods, the border of Bi_2O_3-B_2O_3-Nd_2O_3 triple system – binary systems Bi_2O_3-B_2O_3 Nd_2O_3- Bi_2O_3 and Nd_2O_3- B_2O_3 are less known in literature sources [11-15].

It is known that 5 compounds are generated in Bi_2O_3-B_2O_3 system: Bi_2O_3-$3B_2O_3$ (melting temp. (981K), $3Bi_2O_3$-$5B_2O_3$ (995K), Bi_2O_3-B_2O_3 (963K), $2Bi_2O_3$-B_2O_3 (948K) and $3Bi_2O_3$-B_2O_3(908K) [1,2].

It was determined that 3 compounds had been formed in Nd_2O_3- B_2O_3 system: $Nd_2O_3{\cdot}3B_2O_3$ (1428K), $Nd_2O_3{\cdot}B_2O_3$ (1885K), $3Nd_2O_3{\cdot}B_2O_3$ [3]. In Bi_2O_3-Nd_2O_3 system formation of solid solution and one compound at 1:1 ratio based on primary compounds are shown in literature source.

In the present work we continued physical-chemical research of $3Bi_2O_3{\cdot}5B_2O_3$-$Nd_2O_3{\cdot}3B_2O_3$ system and gave analysis of values typical for some electro-physical parameters of alloys [9].

Experimental part

Samples were prepared from oxides (Bi_2O_3, Nd_2O_3) of elements and borate acid. Borate acid was decomposed at 723K:

$$H_3BO_3 \overset{723K}{\Longleftrightarrow} B_2O_3 + H_2O$$

We used chemically pure reagents in the synthesis of samples in the research work. Synthesis was conducted at 1273÷1373K8-10 hours in platinum crucibles. The compositions (those with high concentration of Nd_2O_3) with high melting temperature were synthesized by solid phase synthesis method 40-50 hours at 1273K in platinum crucibles [8-9].

Synthesized samples were studied by differential-thermal analysis (DTA), X-ray phase analysis methods. Differential thermal analysis (DTA) was performed on a derivatograph with a Pt-Pt / Rh thermocouple in platinum crucibles with a heating rate of 10º/min.X-ray phase analysis was conducted on diffractometer «D 2Phazer» (CuK_{α} ray, Ni – filter).

According to the results of differential-thermal analysis we determined that softening temperature of synthesized glasses was in the range of 773÷ 873K, melting temperature – 973÷ 1073K, and hardening temperature – 943÷1043K. Optimum crystallization condition for glasses was selected and crystallization process conducted at 923K 100 hours.

Results and discussion

On the basis of differential-thermal and X-ray phase analysis phase diagram of $3Bi_2O_3{\cdot}5B_2O_3$-$Nd_2O_3{\cdot}3B_2O_3$ system was plotted (Fig. 1.) [9]. As is seen from diagram, $3Bi_2O_3{\cdot}5B_2O_3$-$Nd_2O_3{\cdot}3B_2O_3$ system was quasi-binary, and formation of new one compound in the system determined.

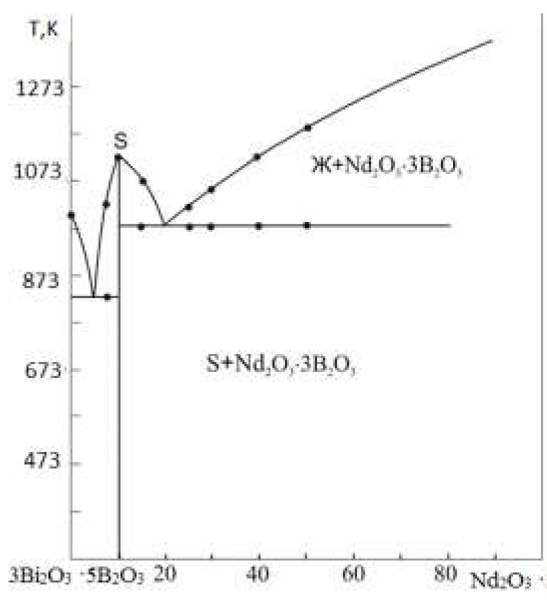

Fig. 1. Phase diagram of the $3Bi_2O_3{\cdot}5B_2O_3$-$Nd_2O_3{\cdot}3B_2O_3$ section.

The composition of the new compound conforms to 86 mol% $3Bi_2O_3{\cdot}5B_2O_3$ 14mol% $Nd_2O_3{\cdot}3B_2O_3$, it is glass-like, softening temperature is 773K, crystallization temperature – 943K, melting temperature – 1113K.

We determined eutectics between new compound and primary oxides: e_1= 93mol%, $3Bi_2O_3{\cdot}5B_2O_3$ – 7mol%, $Nd_2O_3{\cdot}3B_2O_3$ and e_2=

80mol%, $3Bi_2O_3 \cdot 5B_2O_3$ – 20 mol%, $Nd_2O_3 \cdot 3B_2O_3$, melting temperature is 813÷973K correspondingly.

Also, 10, 20, 30, 50 and 70 mol% $Nd_2O_3 \cdot 3B_2O_3$ containing alloys of $3Bi_2O_3 \cdot 5B_2O_3$-$Nd_2O_3 \cdot 3B_2O_3$ system were synthesized additionally. Some physical parameters of samples synthesized in the range of T=300÷600K: composition dependence of electrical resistance (R), volt-ampere characterization (VACh), heat conductivity coefficient (ε) and heat resistance values were calculated and their diagrams drawn and analyzed.

Fig. 2 shows the dependence of the electrical resistance (R) on the composition at a room temperature. As is seen from Fig., when moving from primary substance ($3Bi_2O_3 \cdot 5B_2O_3$) to 10 mol% of Nd_2O_3 oxide containing composition, R resistance dropped approximately by one order R= $8.5 \cdot 10^{11}$ Ohm.

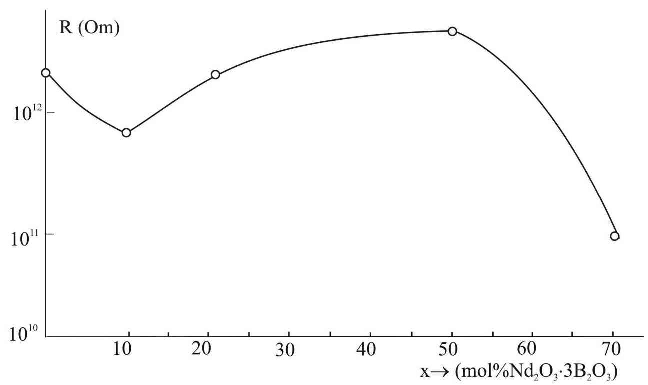

Fig. 2. Structural dependence of electric resistance (R) of the $(3Bi_2O_3 \cdot 5B_2O_3)_{100-x}$-$(Nd_2O_3 \cdot 3B_2O_3)_x$ system T= 300K

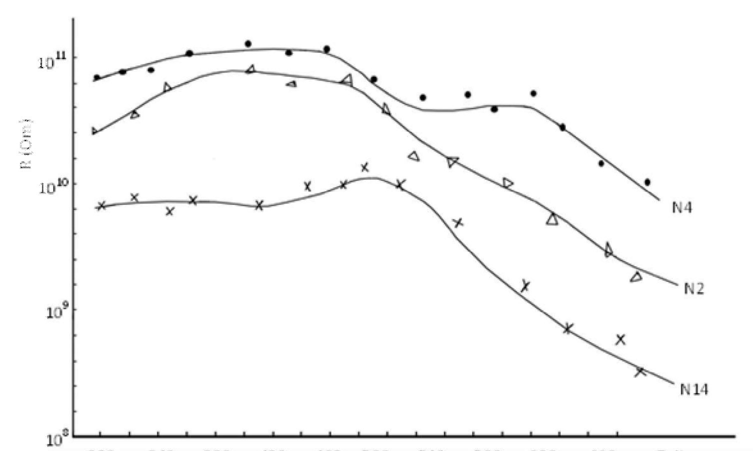

Fig. 3. Temperature dependence of electric resistance of $(3Bi_2O_3 \cdot 5B_2O_3)_{100-x}$-$(Nd_2O_3 \cdot 3B_2O_3)_x$
N2 - x = 10 mol%; N4 - x = 20 mol%; N14 - x = 70 mol%

This reduction is explained by the formation of optimal maximum structure in the composition. Increase of $Nd_2O_3{\cdot}3B_2O_3$ component up to 25mol% occurred due to the formation of additional dispersion center and value of electric resistance in 50:50mol% was maximum ($9.8{\cdot}10^{12}$ Ohm). In the system, this sample (50 mol %) was a material with maximum resistance. In following increase of the second component ($Nd_2O_3{\cdot}3B_2O_3$) the value of electric resistance is reduced approximately to ~$5{\cdot}10^{10}$Ohm·sm.

We may come to the conclusion that alloys of $(3Bi_2O_3{\cdot}5B_2O_3)_{100-x}$- $(Nd_2O{\cdot}3B_2O_3)_x$ system pertained to high resistive active dielectric row.

Fig. 3 shows temperature dependences of electric resistances of x=10(N2); x=20(N4) and x=70(N14) mol% $Nd_2O_3{\cdot}3B_2O_3$ sample from $(3Bi_2O_3{\cdot}5B_2O_3)_{100-x}$-$(Nd_2O_3{\cdot}3B_2O_3)_x$ system alloys. Measurements were performed in the temperature range of T=300÷680K. As is seen from the chart, in the temperature range of T=300÷460K and in x=20 and 70 mol% samples R(T) dependences were relatively stable and had values of R=$8.5{\cdot}10^9$÷$8{\cdot}10^{10}$ohm.

Fig. 4 shows the dependence of dielectric permittivity (ε) and dielectric loss (tgδ) of 30mol% $(3Bi_2O_3{\cdot}5B_2O_3)$ + 70mol% -$(Nd_2O_3{\cdot}3B_2O_3)$ samples on space frequency. According to Fig. 4, at T = 300 K and a frequency of f = 10 Hz, the dielectric constant ε '= 54, at f = 100 Hz, the ε decreased to 40. In the range of $f=10^3÷10^5$ Hz it is relatively stable within experimental error and in the course of further increase of space frequency ($f>10^5$ Hz) it decreased slightly. As for the value of dielectric loss, the situation is different: in the range of $f=50÷10^5$ Hz it was tgδ ≈const≈6. But in the range of $f\geq10^5$ Hz dielectric loss increased. The values of electric resistances and dielectric constants of this composition at T=300÷460K and in $f\leq10^5$ Hz frequencies were relatively stable.

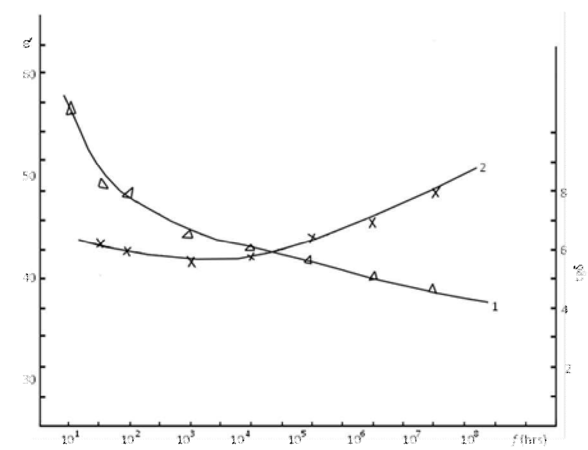

Fig. 4. The dependence of dielectric permittivity (ε') (1) and dielectric loss (tgδ) (2) of 30 mol% $(3Bi_2O_3{\cdot}5B_2O_3)$ + 70 mol% -$(Nd_2O_3{\cdot}3B_2O_3)$ sample on dielectric space frequency. T=300K.

Fig. 5 shows the volt-ampere characteristics (VACh) for the alloys of the composition (N2: x=10 mol% $Nd_2O_3{\cdot}3B_2O_3$, N4 x=20 mol% и N14 x=70mol%). The measurements were carried out at a room temperature and electric field voltage in the range E = 0 ÷ 450 V / cm. According to Fig. 5, the volt-ampere characteristic has a different shape. A sample with composition x = 70 mol% in the range U = 0 ÷ 150 V (in other words, at low voltage values), had a semiconductor property, its resistance at a room temperature is R ≈$8.5 \cdot 10^{10}$ Ohm, and in a wide temperature range (T = 300 ÷ 460 K) it had dielectric properties, relatively low dielectric constant and at U=0-150V, its volt-ampere characteristic corresponds to semiconductors.

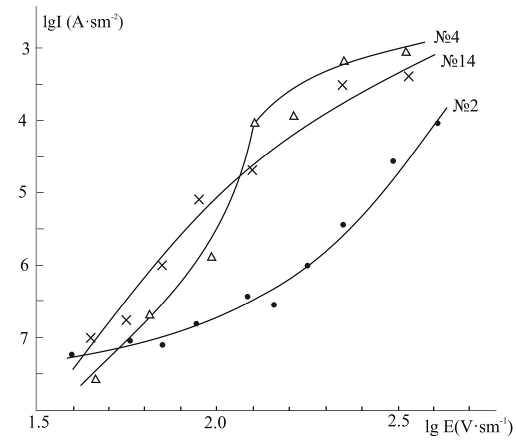

Fig. 5. Volt-ampere characteristics (VACh) for alloys of the $(3Bi_2O_3 \cdot 5B_2O_3)_{100-x}$ - $(Nd_2O_3 \cdot 3B_2O_3)_x$ system. N2-x = 10 mol%; N4-x = 20 mol%; N14-x = 70 mol%

The temperature dependences of the thermal conductivity χ and thermal resistance coefficient ω at compositions x = 30 and 50 mol% are also studied.As can be seen from figure 6, in the temperature range T = 300÷420 K, the χ values of the sample N1 are relatively stable and equal to $\chi_1 \approx 10.8 \cdot 10^{-3}$ Vt / cm · K, while in sample N2, in the temperature range T = 300 ÷ 500 K is relatively stable and equal to $\chi_2 \approx 12 \cdot 10^{-3}$Vt / cm · K. With a further increase in temperature (T ≥420K) in the sample N2-x = 30 mol%, the χ_2 value sharply decreases and at T = 620K, the $\chi_2 \approx 4 \cdot 10^{-3}$Vt / cm · K, and vice versa for the sample N1-x≈50 mol% , at T ≥420 K, the χ_1 decreases very slightly and at T = 620K corresponds to $\chi_1 = 5 \cdot 10^{-3}$Vt / cm · K. To identify the defective nature of these samples, the dependence of the electrical resistance on temperature was analyzed (Fig.6).

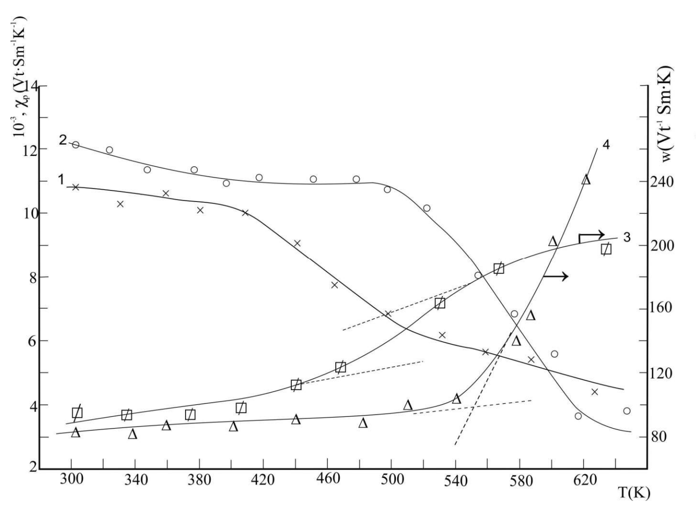

Fig.6. Temperature dependences of thermal conductivity (1.2) and heat resistance (3.4) in the $(3Bi_2O_3{\cdot}5B_2O_3)_{100-x}$ – $(Nd_2O_3{\cdot}3B_2O_3)_x$ system. 1 and 3 - x=50mol%; 2 and 4 - x=30 mol%

It was determined that in 300÷480K temperature range heat resistance was relatively stable (w=const.). (Fig. 6). w increases in different rates in the further increase of temperature (in 30 and 50 mol% of samples). Non-linear change of w for these samples is related to not only the dispersion of phonons from point defect, vacant centers, but also phonon-phonon interactions. In other words, low values and change of heat-conductivity χ and heat resistance win complex form were related to sharp increase of mixed dispersion mechanism. In other compositions (10, 20 and 70mol% of $Nd_2O\cdot 3B_2O_3$) similar processes occurred. But in these samples the change of χ in temperature range was weak, it was relatively stable within experimental error.

It was determined from analyses of heat conductivity coefficient and other kinetic parameters that unlike relevant properties of dielectric materials the change of parameters proved closer to relevant properties of semi-conducting materials.

Conclusion

Results of the complex study of the $3Bi_2O_3\cdot 5B_2O_3$-$Nd_2O_3\cdot 3B_2O_3$ system are presented and formation of one ternary compound revealed in the system. Based on analyses of heat conductivity coefficient and other kinetic parameters, we determined that unlike dielectric properties of starting components, parameters of intermediate alloys are close to properties of semiconductor materials.

The formation of a new compound increases the glass formation region towards non-glass-forming boundary binary components.

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$3Bi_2O_3 \cdot 5B_2O_3$-$Nd_2O_3 \cdot 3B_2O_3$ SİSTEMİNİN TƏDQİQİ VƏ ALINAN ƏRİNTİLƏRİN ELEKTROFİZİKİ VƏ İSTİLİK XASSSƏLƏRİNİN TƏRKİBDƏN ASILILIĞI

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Bu məqalədə DTA, RFA metodlarından istifadə edərək $3Bi_2O_3 \cdot 5B_2O_3$ - $Nd_2O_3 \cdot 3B_2O_3$ sistemi öyrənilmiş, elektrik və istilik parametrləri ölçülmüşdür. Sistemdə yeni üçlü birləşmənin meydana gəlməsi aşkar edilmişdir. Yeni birləşmənin əmələ gəlməsi şüşəəmələgəlmə sahəsini şüşəəmələgətirməyən ikili komponentlərə doğru genişləndirir. Müəyyən edilmişdir ki, parametrlərin dəyişməsi dielektrik maddələrin xüsusiyyətlərindən daha çox yarımkeçirici materiallara uyğundur.
Açar sözlər: *elekrik müqaviməti, sistem, dielektrik itkisi, fononlar, asılılıq, tezlik.*

ИЗУЧЕНИЕ СИСТЕМЫ $3Bi_2O_3 \cdot 5B_2O_3$-$Nd_2O_3 \cdot 3B_2O_3$ И ЗАВИСИМОСТИ ЭЛЕКТРОФИЗИЧЕСКИХ И ТЕПЛОВЫХ СВОЙСТВ ПОЛУЧЕННЫХ СПЛАВОВ ОТ СОСТАВА

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В статье представлены результаты исследования системы $3Bi_2O_3 \cdot 5B_2O_3$ - $Nd_2O_3 \cdot 3B_2O_3$ методами ДТА, РФА и измерения ее электрических и тепловых характеристик. В системе обнаружено образование нового тройного соединения. Образование нового соединения увеличивает область стеклообразования в сторону не образующих стекло пограничных двойных компонентов. Было установлено, что полученные материалы обладают полупроводниковыми свойствами в отличие от исходных $3Bi_2O_3 \cdot 5B_2O_3$, $Nd_2O_3 \cdot 3B_2O_3$.

Ключевые слова: *электрическое сопротивление, система, диэлектрические потери, фононы, частота.*