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PHYSICAL AND CHEMICAL RESEARCH INTO $(2Bi_2O_3{\cdot}B_2O_3)_{100-x}$ – $(2\ Bi_2O_3{\cdot}3GeO_2)_x$ SYSTEM AND ELECTROPHYSICAL PROPERTIES OF OBTAINED ALLOYS

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Abstract: *The paper presents the results of studies into physical-chemical and electrophysical properties of alloys of the* $(2Bi_2O_3{\cdot}B_2O_3)_{100-x}$ – $(2\ Bi_2O_3{\cdot}3GeO_2)_x$ *system. Frequency dependences of electrical impedance (R), dielectric permittivity (ε') and dielectric losses (tg σ) in alternating current and different temperatures were studied. It found that in samples the conductivity is mainly hopping conductivity with lengths varied between localized states.*

Keywords: *conductivity, frequency dependence, composition, frequency, chemical analysis, temperature.*
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Introduction

Numerous applications of oxide materials including Bi_2O_3, B_2O_3, GeO_2 (SiO_2) and their alloys are related to characteristics of their properties [1-4]. Owing to optical transparency of dispersion of refractive index, chemical resistance and mechanical density, they can be used for preparation of various devices and microcircuits in electronics and microelectronics as scintillation materials in nuclear physics [5-6]. The need in bismuth-borate oxides makes it necessary to conduct a systematic study of the oxide materials. There are many works on the study of state diagram of the Bi_2O_3 - B_2O_3 system. For example, when analyzing the state diagram of the Bi_2O_3 - B_2O_3 system, authors of the research indicate the existence of 5 compounds (12: 1), (2:1), (3 :5), (1: 3) and (1 :4) which are in metastable state in the Bi_2O_3 - GeO_2 [7] system.

Authors [8] studied the Bi_2O_3 - GeO_2 system as regards compositions containing up to 22 мол% GeO_2. In addition, a stable state diagram of the Bi_2O_3 - B_2O_3 system has a phase separation area. In the works [4, 9] in specified concentration ranges we observed a wide region of solid solutions in the metastable state based on a high-temperature modification. They state that besides σ-Bi_2O_3 phase the system also contains stable phases $Bi_{12}GeO_{20}$ of selenite structure and $Bi_4(GeO_4)_3$ evlitine struture resulted in partial decay of the metastable solid solution.

Authors [10-11] researched a ternary system Bi_2O_3-B_2O_3-SiO_2 and analyzed electrophysical properties of obtained samples. In this system, the type of alloys conductivity with semiconducting properties was identified. At T=300-500K the values of dielectric permittivity and losses change in line with ranges of ε''=20-60; tgδ=0.02-0.06 and are relatively stable. Depending on the composition, the resistance changes into $\rho \geq 10^6$-10^{11} Om·cm to establish that some compositions of the system $(2Bi_2O_3{\cdot}3SiO_2)_{100-x}$–$(2Bi_2O_3{\cdot}B_2O_3)_x$ has practical value [12]. As is known, depending on the ratio of components in the $\frac{mB2O3}{nBi2O3}$ + x SiO_2 system many compositions of the alloys characterized by physical-chemical and physical properties were obtained [5, 14]. Study into properties of an alloy in the $(2Bi_2O_3{\cdot}B_2O_3)_{100-x}$ –

$(2Bi_2O_3{\cdot}3GeO_2)_x$ composition is of great interest [13].

Eariler we have conducted differential-thermal and X-ray analyses of alloys in the $2Bi_2O_3{\cdot}B_2O_3$-$2Bi_2O_3{\cdot}3GeO_2$ composition and temperature dependence of conductivity (σ), thermal conductivity (χ) and dielectric permittivity in the direct current. It is expected that the alloys in the $(2Bi_2O_3\ {\cdot}B_2O_3)_{100-x}$ – $(2Bi_2O_3{\cdot}3GeO_2)_x$, system have disordered cluster centers, so their composition grows as the concentration of B_2O_3 increases at high temperature (T= 460-480 K) where loosening and blurring of phase transition occur [13].

To obtain the precise and reliable results for high-impedance oxide materials, an analysis into electrophysical parameters in the direct current is insufficient: these paraemters must also be measured in the direct current. Aim of this work is a physical-chemical research into the $2Bi_2O_3{\cdot}B_2O_3$ -$2Bi_2O_3{\cdot}3GeO_2$ system and an analysis of frequency changes of conductivity (ρ), dielectric permittivity (ε′) and losses (tgσ) in the direct current to thus identify the conductivity mechanism and provide general characteristics of the properties of these systems.

Experimental part

Alloys of the $(2Bi_2O_3\ {\cdot}B_2O_3)_{100-x}$ – $(2\ Bi_2O_3\ {\cdot}3GeO_2)_x$ system were synthesized from Bi_2O_3 oxides of chemically pure GeO_2 – high purity and H_3BO_3 – analytical reagent grade in the furnace SNOL at 1273-1373K. Alloys were cast at a room temperature on a titanium plate. All samples were glassy from light brown to brock brown. Glasses were annealed at 673 K for 200 hours.

Note that objects of study were samples of the compositions: N1 x= 10 mol% ($2Bi_2O_3$ - $3GeO_2$); N2 x=15mol% ($2Bi_2O_3$-$3GeO_2$) and N3 x= 50 mol%($2Bi_2O_3$ -$3GeO_2$). Interaction in the system $(2Bi_2O_3$ - $B_2O_3)_{100-x}$ – $(2Bi_2O_3$ -$3GeO_2)_x$ was studied using the methods of differential-thermal, X-ray ohase analyses, as well as the measurement of density of compositions. DTA of system alloys was studied by derivatograph NETZSCH.STA 449 F3, STA 449F3A – 0,836 –M.

Also, X-ray phase analysis was conducted by diffractometer D2 Phaser Bruker.

Density of alloys was determined by hydrostatic weighing where distilled water was used as operating fluid.

Conductivity (σ) and dielectric permittivity ε′ and dielectric losses tgσ were studied at different frequencies in the alternating current at 300, 385 and 430K.

Thickness of samples were d=2-4 mm; width – b=8mm and length l=14mm

Results and discussion

Fig. 1 shows the results of DTA for the sample N1.

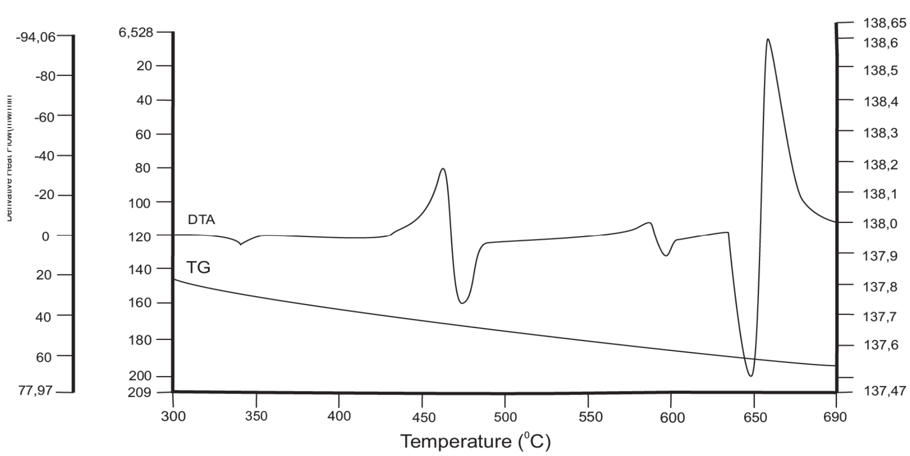

Fig.1. Results of DTA for the sample N1 - 10 mol% $2Bi_2O_3{\cdot}3GeO_2$

As can be seen from the figure 1, at T_1 = 340 ° C a weak endothermic peak is observed, i.e. weak association occurs (with the covalent bond being fixed). At T_2 - (450-460)°C, an exothermic reaction occurs with a transition and with an increase in covalent bond. At temperatures T_3≈470°C, T_4≈590°C and T_5≈650°C, endothermic effects are observed.

Frequency dependences of electrical impedance (R), dielectric permittivity (ε′) and dielectric losses tgσ were studied in samples of the $(2Bi_2O_3 \cdot B_2O_3)_{100-x}$ – $(2Bi_2O_3 \cdot 3GeO_2)x$ system with the following compositions: N1 x=10; N2 x=15; N 3-x=50 mol% $2Bi_2O_3 \cdot 3GeO_2$. Fig. 2 shows the results of frequency dependence of conductivity in the sample N1 (10mol% 2Bi2O3 ·3GeO2). According to Fig. 2, at T=300K the change of R-1(υ) in the frequency range (from 10-1 to10^5 Hz) occurs by the law $R^{-1} \sim \upsilon^{0.5}$ with the gorwth of υ in relatively low frequencies. With higher frequencies in the frequency range of $10^3 \leq \upsilon \leq 10^5$ the conductivity changes by the law $R^{-1} \sim \upsilon^{0.8}$, i.e. the conductivity grows exponentially with the increase of frequency of oscillating electrical field. At high temperatures (T=380K), frequency dependences of conductivity are weakened (Fig. 2, 3) and conductivity changes by the law $R^{-1} \sim \upsilon^{0.3}$ at $\upsilon \geq 10^3$Hz.

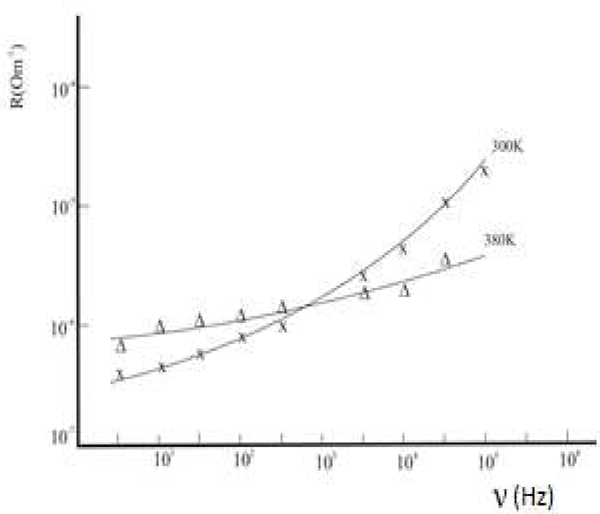

Fig.2. Frequency dependences of conductivity in the sample N1- 10 mol% $(2Bi_2O_3 \cdot 3GeO_2)$

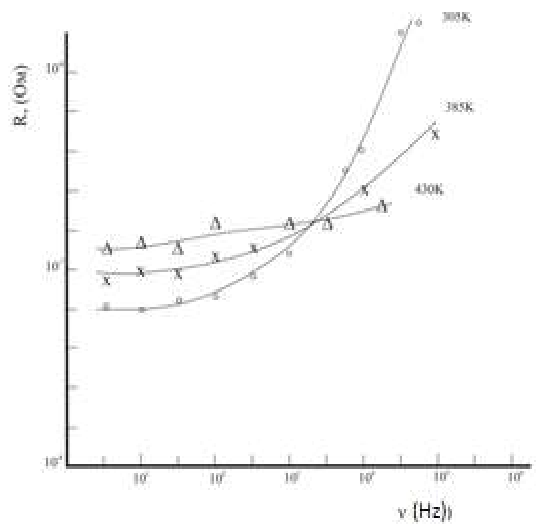

Fig.3. Frequency dependences of conductivity of the sample N3- 50mol% $(2Bi_2O_3 \cdot 3GeO_2)$

Similar measurements were conducted with the sample N3 (Fig.3, N3- 50mol% $(2Bi_2O3 \cdot 3GeO_2)$. According to Fig. 3, dependence $R^{-1}(\upsilon)$ substantially differs from values of sample N1 (Fig. 2). At lower frequencies, $\upsilon \leq 10^3$Hz conductivity changes by the law $R^{-1} \sim \upsilon^{0.4}$ if higher than $\upsilon > 10^3$ Hz. Also, strong growth of conductivity from frequency $R^{-1} \sim \upsilon^{2.0}$ is observed where values of conductivity correspond to our values obtained in the constant current [13] (Fig. 2. circuit 3). At high temperatures up to (T= 385K) the frequency dependence of conductivity in the alternating current weakens and changes in line with the law $R^{-1} \sim \upsilon^{0.6}$. Note that weak exponential growth remains to quantitatively differ from measured ones in the constant current [13]. Measurements of conductivity higher than T>400K show that in frequency range of $\upsilon \leq 10^5$ Hz conductivity remains practically constant ($R^{-1} \approx$ const) (Fig.3 curve 3 T=430K). Apparently, the conductivity mechanism is effective due to the transition of carriers of excited, yet in non-localized state close to the valence-band edge [14]. Apparently, the mechanism of conduction is due to the transfer of carriers of excited but nonlocalized states near the valence band [14].

In these samples (samples N2, N3), the frequency dependences of dielectric permittivity $\varepsilon'(\upsilon)$ and dielectric losses in the sample N3 were measured. The results are given in Fig. 4. According to samples N2 $\varepsilon'(\upsilon)\sim\upsilon^{-0.68}$ N3 $\varepsilon'(\upsilon)\sim\upsilon^{-1.04}$, depending on frequency the dielectric permittivity $\varepsilon'(\upsilon)$ sharply falls in the frequency region $10^{-1}\leq\upsilon\leq10^{2}$Hz; however, subsequent rise in frequency to 10^{5}Hz it weakens and decreases. None that sharp decrease at low frequencies (from 10^{-1} to 10^{2} Hz), by the law $\varepsilon'(\upsilon)\sim\upsilon^{-1.44}$ is possibly due to additional migration mechanism of polarization in the macroscopic nonhomogeneous structure and mixtures. This migration polarization occurs in lower frequencies due to considerable electric energy dissipation. Occurrence of this polarization is explained as being due to cluster centers with different conductivity.

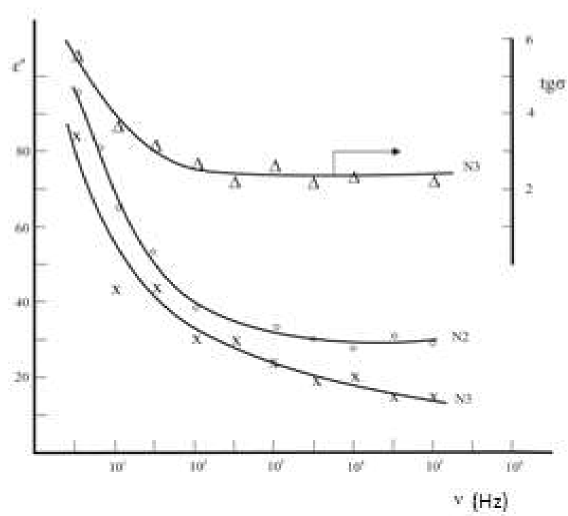

Fig.4. Frequency dependence of dielectric permittivity of samples N2 and 3 and dielectric losses (tg σ) of the sample N3, T=300K

Fig. 4 shows frequency dependence of dielectric loss in the sample N3. Dielectric loss (tgσ) in low frequencies sharply falls to $\upsilon\leq10^{2}$ Hz with a value of tgσ≈2.3. In the course of further increase of frequency up to 10^{5} Hz, it remains constant.

Thus, the study of samples at alternating current and a wide frequency range at room temperature confirms our assumption [13] that the studied compositions contain disordered cluster centers and their content increases with increasing Bi_2O_3 concentration. With increasing temperature, loosening occurs and a phase transition is observed at T → 460 K. However, research into alternating current in the wide range of frequency showed that during destruction of cluster centers the migration polarization related to non-homogeneity of the structure occurs in alloys besides dipole – relaxation polarization. Note that the migration polarization is observed at low frequencies $10^{-1}\leq\upsilon\leq10^{2}$ Hz (Fig.4.) by partial hopping conductivity with different wavelengths between chaotic distributed cluster centers. With increase of field frequencies, the dipole-relaxation polarization by migration polarization that arises in dissociation of cluster centers has a dominant role [13].

Conclusion

1) Conductivity mechanism in the $(2Bi_2O_3 \cdot B_2O_3)_{100-x}$ – $(2\ Bi_2O_3 \cdot 3GeO_2)_x$ system occurs due to non-localized excited carriers close to valence-band edge. At high temperatures the conductivity intensifies due to disorder in cluster centers.

2) Samples contain cluster centers and their number increases with growth of Bi_2O_3 concentration. Softening occurs at high temperatures but at T→460K gentle slopes of phase transitions are observed.

3) It is expected that during the decomposition of cluster centers in alloys the dipole-relaxation polarization is formed and the migration polarization which is related to non-homogeneity of bulk structures appears additionally.

References

1. Egorshev A.V., Volodin V.D., Skorikov V.M. Glass formation in system Bi_2O_3-B_2O_3- BaO. *Inorganic materials*. 2008, vol. 44, no. 11, pp. 1397-1401.
2. Becker P. Thermal and optical properties of glasses of the system $Bi_2O_3 \cdot B_2O_3$. *Cryst.Res Technol*. 2003, vol. 38**,** no.1, pp.74-82.
3. Kuzmicheva G.M., Melnikova T.I. Structural peculiarities of bismuth borates in system $nBi_2O_3 \cdot B_2O_3$. *Russian Journal of Inorqanic Chemistry*. 2009, vol. 54, no. 1, pp. 74-81.
4. Kargin Yu.F., Foal V.P., Egorysheva A.V. Phase diagram of metastable states of the Bi_2O_3 • B_2O_3 system. *Russian Journal of Inorqanic Chemistry*. 2002, vol. 47, no. 8, pp. 1362-1364.
5. Yarvale S.P., Rakade S.V. D.c. conductivity and hopping mechanism in Bi_2O_3-B_2O_3 glasses. *J.Mater.Sci*. 1993, vol. 28, pp. 5451-5455.
6. Kargin Yu.F., Burkov V.I., Maryin A.A. et al. $Bi_{12}M_xO_{20} \pm \delta$ crystals with sillenite structure. Synthesis, structures, propertie. Moscow. 2004, p. 316.
7. Kargin Yu.F., Egorysheva A.V. Synthesis and structural features of Bi24B2O39 with sillenite structure. *Inorganic Materials*. 1998, vol. 34, no.7, pp. 859-863.
8. Van Houten S. Semiconduction in $Li_xNi_{1-x}O$. *Journal of Physics and Chemistry of Solids*. 1960, vol. 17, pp. 7-17.
9. Irtyugo L.A., Denisova V.M., Foal V.P. et al. High-temperature heat capacity of bismuth borate glasses. *Journal of the Siberian Federal University. Chemistry*. 2011, vol. 4, no.4, pp. 344-349.
10. Bananyarly S.I, Gasimova R.N, Ismayilov Sh.S., Chernisheva N.V. Nonlinear variations of electrical resistance and dielectric properties (ἐ and tgδ) of glasses of the system $2Bi_2O_3 \cdot 3SiO_2$ - $Bi_2O_3 \cdot B_2O_3$. *International Journal of Advanced Scientific and Technical Research*. 2015, vol. 3, issue 5, pp.65-69.
11. Bananyarly S.I, Gasimova R.N., Ismayilov Sh.S. Temperature dependence of dielectric permittivity of glasses of $2Bi_2O_3 \cdot 3SiO_2$-$Bi_2O_3 \cdot B_2O_3$ system. *Chemical Problems*. 2013, no. 2, pp. 185-189.
12. Bananyarly S.I, Ismayilov Sh.S., Gasimova R.N. Electroresistance and dielectric characterictics of glasses of $2Bi_2O_3 \cdot 3SiO_2$ – $Bi_2O_3 \cdot B_2O_3$ (0-50 mol.% $Bi_2O_3 \cdot B_2O_3$) system. *Chemical Problems*. 2008, no. **2**, pp. 363-366.
13. Bananyarly S.I., Ismayilov Sh.S., Halilova L.A., Mehdiyeva I.F., Kulizade E.S. Physicochemical study of alloys of the system (2 Bi2O3 • B2O3) - (2Bi2O3 • 3GeO2). Conference New Science: Theoretical and Practical Perspective. Sofia, Bulgaria, 2018, pp. 9-18.

14. Mott N., Davis E. Electronic processes in non-crystalline substances. Moscow: Mir Publ.,1982, vol. 1, p. 368.

$(2Bi_2O_3{\cdot}B_2O_3)_{100-X}$ $(2Bi_2O_3{\cdot}3GeO_2)_X$ SİSTEMİNİN FİZİKİ-KİMYƏVİ TƏDQİQİ VƏ ALINAN ƏRİNTİLƏRİN ELEKTROFİZİKİ XASSƏLƏRİNİN ÖYRƏNİLMƏSİ

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Bu məqalədə $(2Bi_2O_3{\cdot}B_2O_3)_{100-x}$ – $(2\ Bi_2O_3{\cdot}3GeO_2)_x$ sistemi ərintilərinin fiziki –kimyəvi və elektrofiziki xassələrinin tədqiqinin nəticələri verilmişdir. Dəyişən cərəyanda və müxtəlif temperaturlarda elektromüqavimətin (R), dielektrik nüfuzluğun (ε') və dielektrik itkinin (tg σ) tezlik asılılıqları öyrənilmişdir.Müəyyən edilmişdir ki, tədqiq etdiyimiz nümunələrin elektrik keçiriciliyi mexanizmi əsasən səviyyələr arası sıçrayışlı keçid hesabına baş verir.
Açar sözlər: *elektrokeçiricilik, tezlik asılılığı, tərkib, tezlik, kimyəvi analiz,temperatur.*

ФИЗИКО- ХИМИЧЕСКОЕ ИССЛЕДОВАНИЕ СИСТЕМЫ $(2Bi_2O_3{\cdot}B_2O_3)_{100-X}$ $(2Bi_2O_3{\cdot}3GeO_2)_X$ И ИЗУЧЕНИЕ ЭЛЕКТРОФИЗИЧЕСКИХ СВОЙСТВ ПОЛУЧЕННЫХ СПЛАВОВ

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В статье представлены результаты исследования физико-химических и электрофизических свойств сплавов системы $(2Bi_2O_3{\cdot}B_2O_3)_{100-x}$ – $(2\ Bi_2O_3{\cdot}3GeO_2)_x$. Изучены частотные зависимости электросопротивления (R), диэлектрической проницаемости (ε') и диэлектрической потери (tg σ) при переменном токе и различных температурах. Выявлено, что в исследуемых образцах проводимость является в основном прыжковой проводимостью, но с различной длиной между локализованными состояниями.
Ключевые слова: *электропроводность, частотная зависимость, состав, частота, химический анализ, температура.*