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Amorphous Materials Obtained in Lead-Manganese-Borate Systems

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Abstract. Glasses based on the PbO-MnO-B_2O_3 system are classified as nanocomposites due to their properties characteristic of amorphous-matrix nanocomposite materials. It is proposed that the amorphous materials obtained in this system contain several types of structural units, which can be viewed as nanoscale inclusions. This study demonstrates how the ratio and size of these inclusions influence the dilatometric curves and volumetric electrical resistivity of the resulting materials. *© 2025 Bull. Georg. Natl. Acad. Sci.*

Keywords: manganese-containing borate glasses, lead borate glasses, amorphous matrix nanocomposites

Introduction

Recent studies on both simple and complex glass systems have established their classification as nanocomposites with amorphous and sub-micro-crystalline phases discernible within an amorphous matrix (Miller, 2008; Movahedi, 2016). These glasses often form the basis of materials exhibiting new functional properties, including glass-crystalline and porous materials. It is noteworthy that these inherently microheterogeneous glasses also behave as nanocomposites, with their properties dependent on the degree and fraction of the second phases.

The present research investigates the PbO-MnO-B_2O_3 glass system as part of a broader study on multi-manganese glasses conducted at Georgian Technical University. This work builds upon previous studies (Cheishvili, 2005; Gordeladze & Sarukhanishvili, 2005) and more recent developments (Karmakar et al., 2016).

Methodology

The characterization of materials was performed using a thermogravimetric analyzer (TGA), an atomic absorption spectrometer, Fourier-transform infrared (FT-IR) spectroscopy, and electron microscopy.

Results and Discussion

The study identified glass-forming regions and evaluated the properties of glasses within the PbO-MnO-B_2O_3 system. Notably, glass formation was

Table 1. Ion concentration and structural-chemical compositions of glass

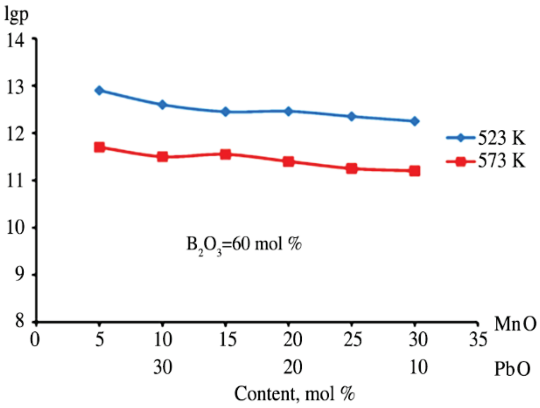
Glass compositions, Mol %	Ion concentration, mol/cm^3				Structural - chemical composition, mol %				
	[Pb^{2+}]	[Mn^{2+}]	[Mn^{4+}]	[B^{3+}]	$Pb(BO_{4/2})_2$	$MnO_{4/2}$	$Pb^{2+}Pb^{2-}O_{4/2}$	$BO_{3/2}$	$Mn(BO_{4/2})_2$
Glass series xPbO*(60-x)MnO*40B$_2$O$_3$									
50 PbO*50MnO*40B$_2$O$_3$	19.06	2.54	1.25	30.48	66.7	3.3	16.7	-	13.3
40 PbO*20MnO*40B$_2$O$_3$	15.86	5.28	2.64	31.74	53.0	6.7	13.3	-	26.6
30 PbO*30MnO*40B$_2$O$_3$	12.53	8.34	4.17	33.44	40.0	10.0	10.0	-	40.0
20 PbO*40MnO*40B$_2$O$_3$	8.34	11.13	5.56	33.48	27.7	13.4	6.6	-	55.3
10 PbO*50MnO*40B$_2$O$_3$	4.25	14.19	7.09	34.07	13.3	16.7	3.3	-	66.7
Glass series xPbO*(50-x)MnO*50B$_2$O$_3$									
40 PbO*10MnO*50B$_2$O$_3$	15.06	2.50	1.24	37.64	77.5	3.2	-	6.5	12.8
30 PbO*20MnO*50B$_2$O$_3$	12.06	5.33	2.68	40.19	56.2	6.6	-	12.7	24.9
20 PbO*30MnO*50B$_2$O$_3$	8.28	8.28	4.14	41.44	36.4	9.0	-	18.2	36.4
10 PbO*40MnO*50B$_2$O$_3$	3.25	11.07	5.53	41.53	15.0	11.5	-	26.2	47.0
Glass series xPbO*(40-x) MnO*60B$_2$O$_3$									
30 PbO*10MnO*60B$_2$O$_3$	11.12	2.47	1.12	44.55	48.7	2.4	-	38.1	10.8
20 PbO*20MnO*60B$_2$O$_3$	7.64	5.09	2.54	45.86	36.5	5.2	-	42.3	20.3
10 PbO*30MnO*60B$_2$O$_3$	4.01	8.01	4.01	48.09	15.4	7.7	-	46.2	30.7

observed even in compositions previously believed incapable of forming glass, despite the potential of Pb^{2+} ions as glass-formers.

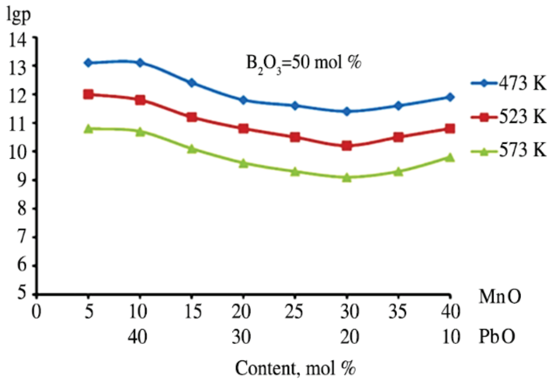
It was found that manganese enters the glasses primarily as divalent Mn^{2+} ions and potentially as tetrahedrally coordinated Mn due to favorable crystal-chemical parameters. Structural analysis suggests the presence of units such as $Pb(BO_{4/2})_2$, $Pb^{2+}Pb_2–O_{4/2}$, $MnO_{4/2}$, $Mn(BO_{4/2})$, and $BO_{3/2}$. These units directly influence properties such as thermal expansion and electrical resistivity.

Ion concentrations and structural-chemical compositions were derived using Müller's ion-atom valence theory (Müller, 1965). Table 1 summarizes these data.

Figures a-c illustrate the significant variation in electrical resistance (lgρ) based on composition.



a



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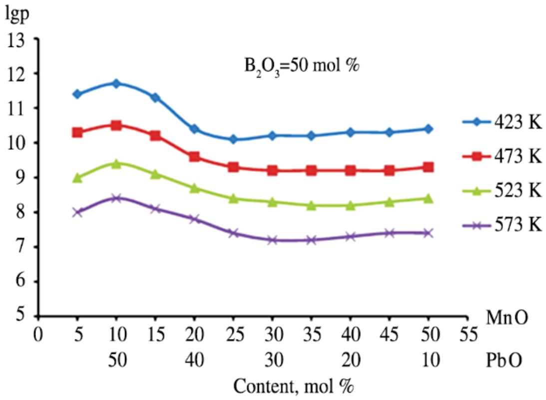

c

Figure. Dependence of electrical resistance (lgρ) on composition: a) B_2O_3 = 60 mol%; b) B_2O_3 = 50 mol%; c) B_2O_3 = 40 mol%.

Glasses with 60 mol% B_2O_3 showed the highest resistivity, while those with 40 mol% exhibited the lowest. Intermediate values were found in compositions with 50 mol% B_2O_3. Substituting MnO for PbO led to a slight but consistent decrease in lgρ, particularly pronounced in the composition $20PbO\cdot30MnO\cdot50B_2O_3$, which showed a minimum, followed by an increase.

The differences in resistivity are attributed to the absence or presence of $BO_{3/2}$ structural units. At 40 mol% B_2O_3, $BO_{3/2}$ is notably absent – contradicting earlier reports stating complete $BO_{3/2}$ to $BO_{4/2}$ transition is thermodynamically limited without sufficient oxygen contributors (Awad et al., 2023).

In such cases, lead tends to form structural units ($Pb^{2+}Pb_2–O_{4/2}$) that do not integrate well into the boron-manganese matrix, creating isolated units that hinder charge transport. As MnO content increases, the degree of blocking decreases, and the ratio of polar groupings shifts favorably for conductivity.

Glasses with 50 mol% B_2O_3 exhibited moderate conductivity with a notable presence of manganese-based polar complexes that may form linear groupings or "chains." At 60 mol%, the structure likely consists of nonpolar lead-borate and manganese-borate complexes, contributing to higher resistivity values and enhanced nanoinhomogeneity.

Conclusion

Electron microscopy confirms that the majority of the investigated glasses resemble amorphous manganese nanocomposites in morphology, showing a direct link between structural arrangement and material properties. By tailoring the composition, it is possible to engineer glasses with specific functional characteristics. This understanding is essential for the development of advanced amorphous matrix nanocomposites, especially when incoporating foreign nanoscale inclusions.

ქიმიური ტექნოლოგია

ტყვია-მანგანუმ-ბორატის სისტემებში მიღებული ამორფული მასალები

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ნაშრომში PbO-MnO-B_2O_3 სისტემაზე დაფუძნებული მინები განიხილება ნანოკომპოზიტებად, რადგან ისინი ავლენენ ამორფული მატრიცის ნანოკომპოზიტური მასალებისთვის დამახასიათებელ თვისებებს. ნავარაუდევია, რომ აღნიშნულ სისტემაში მიღებული ამორფული მასალები შედგება რამდენიმე ტიპის სტრუქტურული ერთეულისგან, რომლებიც შეიძლება ჩაითვალოს ნანოზომის ჩანართებად. კვლევა აჩვენებს, თუ როგორ მოქმედებს ამ ჩანართების თანაფარდობა და ზომა დილატომეტრული მრუდების ბუნებასა და მიღებული მასალების მოცულობით ელექტრულ წინაღობაზე.

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