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Polaron hopping conduction in manganese borosilicate glass

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ABSTRACT

A study on a novel material - manganese borosilicate glass without alkali metals, was reported. It was found that the obtained samples containing high amount of manganese oxide ($60MnO–xSiO_2–(40-x)B_2O_3$, x = 5, 10, 15, 20 and 30 mol%) were amorphous and homogeneous. XPS measurements showed that most of manganese ions are at oxidation level of Mn^{2+} ions and the mean oxidation level slightly moves toward higher value, with increasing in SiO_2 content. The conductivity was described in the terms of thermally activated polaron hopping with a charge carrier centred on Mn ions. It was shown, that the conductivity strongly depends on the mean Mn–Mn distance.

1. Introduction

Borosilicate glass exhibits low thermal expansion coefficient, high chemical durability and useful optical properties. To improve these properties, additives like transition metal oxides are mixed with a base compound. For instance, an addition of ZnO decreases thermal expansion coefficient [1], whereas an addition of MnO increases a chemical durability, changes the spectrum of optical absorption and modifies the microstructure [2–6]. Another examinations show an impossibility to incorporate Mn into $SiO_2–B_2O_3$ glass without addition of alkali atoms [3,5,7], while it is known that homogeneous $xB_2O_3–(100-x)MnO$ and $xSiO_2–(100-x)MnO$ glasses are possible to obtain if x does not exceed 50 mol% or 44 mol% respectively [3,5,8].

Glasses containing high concentration of transition metal ions are electronic conductors with conductivity in the range from 10^{-4} to 10^{-11} S/cm at 300 K [9,10]. Typical mobility of charge carriers in that system is very low, in the most cases is below 10^{-4} cm^2/V s at room temperature, what is explained by strong interaction between electrons and the lattice [9,10]. One of theories describing the mechanism responsible for electrical conduction is thermally activated polaron hopping. It states that electron (with the accompanying local lattice deformation) is hopping from transition metal ion at lower to neighbouring ion at higher oxidation level [11–13].

In the previous work [14] we showed that the conductivity of the glass of a composition of $xMnO–(80-x)SiO_2–20B_2O_3$, where x = 40, 50 and 60 mol%, strongly increases with increase in MnO content. According to the polaron hopping theory [12,13], such increment in conductivity can be observed as an effect of a decrement in the mean distance between transition metal ions or as an increment in $M^{x+1}/(M^{x+1}+M^x)$ (concentration of transition metal ions) ratio. The aim of the present study was to prepare a series of glass samples with a constant amount of manganese (i.e. 60 mol% MnO), and to evaluate influence of each effect on the process of electrical conductivity.

2. Experimental

Glasses of a composition of $60MnO–xSiO_2–(40-x)B_2O_3$ where x = 5, 10, 15, 20 and 30 mol% (further referred to as 60.x.(40 – x)), were prepared using appropriate amounts of analytical grade MnO_2 (Sigma-Aldrich), SiO_2 (POCH) and H_3BO_3 (POCH) powders. The stoichiometric compositions were mixed manually in an agate mortar and heated in a muffle furnace in platinum crucibles. The mixtures were melted in air for 30 min at 1400 K. The melts were quenched by pouring on a preheated to about 500 K brass plate and pressing by another plate to obtain flat circular pellets of 1–1.3 mm thickness and 10–20 mm in the diameter. In order to study properties related to the bulk material, before each measurement a surface layer of pellets was removed by grinding with a dry sand paper.

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Glass density was measured by the Archimedes method using kerosene as a reference fluid. The nominal mean distance between Mn atoms was then calculate using Eq. (1):

$$R_{Mn-Mn} = \sqrt[3]{\frac{M_{sample}}{d \cdot N_A}}, \quad (1)$$

M_{sample} is here a nominal molar mass, d is a density, and N_A is the Avogadro constant. XPS analyses were carried out with X-ray photoelectron spectrometer (Omicron NanoTechnology) with a 128-channel collector. The X-ray manganese source was operated at 15 kV and 300 W, and the vacuum was maintained below $1.1 * 10^{-8}$ mBar. The spectrometer dispersion was adjusted to give a binding energy of 284.8 eV for C1s [15]. The kinetic energy of photoelectrons was determined with a hemispheric analyser set to pass energy of 50 eV for both, wide and high-resolution spectra. Data analysis was performed with the CASA XPS software package using a Shirley background subtraction and least-square Gaussian-Lorentzian curve fitting algorithm. All aforementioned measurements were performed at room temperature.

To determine the glass transition temperature, differential scanning calorimetry (DSC) measurements were done. The thermal analysis was performed on about 5 mg of powdered samples in a flowing synthetic air (20% O_2 and 80% N_2) current of 40 cm^3 min^{-1} using Netzsch STA 449F1. The heating rate was maintained at 15 K min^{-1} in the temperature range from 400 K to 1150 K. Electrical properties were examined by impedance spectroscopy measurements, which were carried out in the temperature range of 175 K–475 K with a Novocontrol Concept 40 broadband dielectric spectrometer. The frequency range used was from 10 mHz to 1 MHz and the ac signal was 1 V_{rms}. Before the measurements, pellets of glasses were polished to obtain plane parallel circular samples. Circular electrodes of 9–12 mm in the diameter were prepared by sputtering gold on sample basal surfaces in vacuum.

3. Results

The obtained pellets were black and shining, without any signs of a phases separation. The results of density measurements are presented in Table 1. An amorphous structure of the samples were confirmed by XRD and SEM measurements.

X-ray photoelectron spectra of Mn2p, B1s and Si2p ranges are given in Figs. 1, 2 and 3. Identified manganese maxima are marked at around 642 eV and 653 eV for $Mn2p_{3/2}$ and $Mn2p_{1/2}$ respectively, with a $2p_{3/2}$ to $2p_{1/2}$ splitting of 11.8 eV [15,18,19]. The asymmetric $Mn2p_{3/2}$ main peak is found to have a low intensive shoulder on the high energy side of the maximum corresponding to the presence of the MnO satellite feature. Position of Si2p and B1s main peaks were determined around 102 eV and 192 eV, respectively [16–18]. However, as it can be seen in Figs. 2 and 3, Si2p peak is composed of two

Table 1
Compositions and properties of glass samples including: density, activation energy of electronic transport calculated on the basis of dc conductivity ($E_{a,\sigma}$) and relaxation time ($E_{a,\tau}$), dc conductivity of samples at 445 K (σ_{dc}), nominal mean distance between neighbouring Mn atoms (R_{Mn-Mn}), and glass transition temperature (T_g).

Sample	60.05.35	60.10.30	60.15.25	60.20.20	60.30.10
MnO_2	60	60	60	60	60
SiO_2	5	10	15	20	30
B_2O_3	35	30	25	20	10
Density (g/cm^3)	3.36(2)	3.47(3)	3.59(3)	3.57(3)	3.73(4)
R_{Mn-Mn} (Å)	3.86	3.81	3.78	3.76	3.69
T_g (K)	831	825	819	820	825
$E_{a,\sigma}$ (eV)	0.95(2)	0.92(2)	0.91(1)	0.90(1)	0.86(3)
$E_{a,\tau}$ (eV)	0.94(21)	0.96(16)	0.94(12)	0.91(8)	0.88(11)
$\sigma_{dc\,445\,K}$ (10^{-10} S/cm)	0.28(1)	1.4(1)	2.2(1)	3.2(1)	11(1)

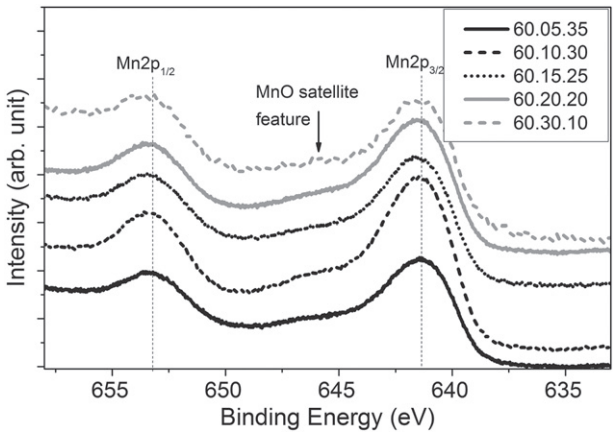

Fig. 1. Measured XPS spectra of the peak related to electron $Mn2p_{1/2}$ and $Mn2p_{3/2}$ orbitals.

maxima related to a presence of SiO_2 and $MnO–SiO_2–B_2O_3$ [16,17], while B1s peak is composed of two maxima related to a presence of B_2O_3 and $MnO–SiO_2–B_2O_3$ [18].

The results of DSC measurements are presented in Fig. 4 and Table. 1. The glass transition temperature (T_g) is estimated between 819 and 831 K. Similar values of T_g were observed in $50MnO\text{-}50B_2O_3$ (818 K) glass [3,5], what suggests that a silicon does not significantly change ability to vitrification of the material in the considered composition range. However, detailed analysis of T_g and exothermic peaks above 850 K shows more interesting phenomena. A strong exothermic peak around 950 K (T_k) correlated with a crystallisation process is seen for all compositions. For samples containing 15 mol% SiO_2, a shoulder on the low temperature side of the crystallisation peak is seen and its intensity increase in next samples with increase in SiO_2 content, while for the same composition T_g reach its minimum and starts to increase with increase in SiO_2 content. For 60.30.10 sample is found two more exothermic peaks around 875 K and 990 K.

Electric properties of a material can be described using different electric functions. To determine parameters of conductivity and to distinguish processes of the charge transport, the permittivity and conductivity representations are chosen. The plots of real part of permittivity shown in Fig. 5 at 445 K could be divided into three regions: a high frequency plateau, a step-like increment and a fast increment of permittivity with decrease in frequency. For instance at

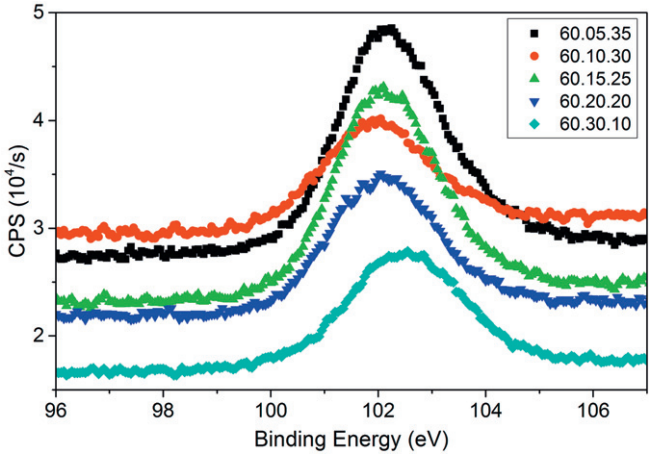

Fig. 2. Measured XPS spectra of the peak related to electron Si2p orbital. Positions of reference SiO_2, $MnO–B_2O_3$, peaks were based on literature [16,17].