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Mixed mobile ion effect in borosilicate glasses doped with cadmium sulfoselenide and silver and copper iodides

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ABSTRACT

We report measurements of dynamic (a.c.) electrical conductivity in borosilicate glasses doped with cadmium sulfoselenide and copper and silver iodides in a wide temperature range below the glass transition temperature T_g and at different frequencies. The concentration of the mobile dopant ions is governed by specific heat treatment conditions of the glass samples leading to a creation of the CdSSe, AgI and CuI semiconductor nanocrystals. Investigations include different cases from a full solution of the dopant ions coming from a dissociation of the dopants during the glass preparation to their almost complete incorporation into the nanocrystals in the glass matrix. At temperatures higher than 150 °C–200 °C the a.c. conductivity in all the examined glasses exhibits the Arrhenius behavior. In this temperature range the mixed mobile ion effect is detected: the doped glasses have the low values of the conductivity compared to the undoped ones. In the low temperature range only weak temperature dependence is detected for all the samples. The mixed mobile ion effect is still presented for the CdSSe-doped glasses, whereas the AgI- and CuI-doped glasses exhibit the classical MMIE which is essentially absent at low temperatures.

1. Introduction

The doped borosilicate glasses are of interest for various applications, ranging from commercially available colored glass edge filters [1] to embedding of ensembles of semiconductor nanocrystals (NCs) [2]. Successful formation of the semiconductor NCs is achieved in the borosilicate glasses based on the Ba_2O_3–SiO_2 system which, except the network formers, contains the metal oxides serving as modifiers. The ionic conductivity of these glasses is due mainly to the metallic modifier ions of a high mobility. In the a.c. electrical response of ionically conducting glasses, as generally in disordered solid ionic materials, two kinds of contributions are commonly distinguished [3]. The first is a thermally activated response on a frequency scale which decreases when lowering the temperature [4]. It originates from the long-range displacements of charge carriers responsible for d.c. conduction. A second contribution to the a.c. response is characterized by a weak temperature dependence and an a.c. conductivity nearly linear in frequency [5]. This “nearly constant loss” (NCL) response is observed at high frequencies and/or low temperatures and originates from local movements of charged units. From many investigations on ionically conducting glasses, the thermally activated low-frequency contribution can be significantly affected by mixing different types of mobile ions. This mixed mobile ion effect (MMIE) is observed as a marked decrease in the glass properties related to ionic transport, in particular in the ionic conductivity, when one type of mobile ion is partially replaced by another type of mobile ion [6,7]. Experimental studies have shown that the strength of the MMIE depends on many factors, e.g. temperature, size and mass difference of the involved ions, see e.g. Refs. [6–12]. Simultaneous experimental and theoretical structural investigations indicate that its origin is of structural character associated with a mismatch effect where sites in the glassy network favorable for one type of mobile ion are unfavorable for other type of mobile ion [13]. The largest MMIE is typical for alkali glasses and in this case is often referred to as mixed alkali effect (MAE). For instance, in the $Li_x Rb_{1-x} PO_3$ glass system the conductivity at an intermediate composition is a few orders of magnitude lower than that of the single alkali glasses [12]. The $Ag_x Na_{1-x} PO_3$ glasses, however, serve as a model system showing anomalously low magnitude of the MMIE due apparently to the fact that the Ag^+ and Na^+ ionic radii are similar in magnitude [12].

In this paper the MMIE is investigated in borosilicate glasses doped with the components of the CdSSe, AgI and CuI semiconductor compounds by means of dynamic (a.c.) conductivity experiments. The glass samples differing by a concentration of the mobile dopant ions were prepared by a technique similar to the one described e.g. in Ref. [2,14]. This method is based on the fact that the borosilicate glasses are perfect host network structures for embedding the semiconductor nanocrystals (NCs) [2]. For the same doped borosilicate glass ingot, the relevant heat treatment process allows to get a series of samples having a different concentration of the dissolved dopant ions. We

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present here much more detailed conductivity investigations as previously in [15] for the CdSSe- and AgI-doped glasses. Besides, similar measurements are reported in CuI-doped glasses.

2. Experimental procedure

The borosilicate glass ingots were prepared originally by means of a conventional melt-quenching technique [2]. The batches (SiO_2 – 59.5%, B_2O_3 – 20.5%, Al_2O_3 – 8.5%, Na_2O – 9.5%, K_2O – 1.2%, Sb_2O_3 – 0.8% + 1.3 wt.% of CdO, 0.5 wt.% of Se, and 0.65% wt.% of S for CdSSe containing glass, SiO_2 – 52.5%, B_2O_3 – 26.5%, Al_2O_3 – 7.5%, Na_2O – 12.5%, K_2O – 0.7%, Sb_2O_3 – 0.3% + 0.8 wt.% of $AgNO_3$ and 1.3 wt.% of NaI for AgI containing glass, and SiO_2 – 54.5%, B_2O_3 – 27.5%, Al_2O_3 – 8.5%, Na_2O – 7.8%, K_2O – 1.2%, Sb_2O_3 – 0.5% + 1.2 wt.% CuI for CuI containing glass) were molten at a temperature 1300 °C for 1 h in Al_2O_3 crucibles. The standard investigations, such as the optical absorption measurements and the TEM studies, indicate that the dopants are fully dissolved in the glass matrix. Below we label the respective samples as S_h (the CdSSe-doped sample), A_h (the AgI-doped sample) and C_h (the CuI-doped sample). Similarly, the notations S_v, A_v, and C_v are reserved for the virgin glasses which are fabricated from three different batches mentioned above but without any semiconductor additions. Besides, we deal with other sample sets, which undergo an extra heat treatment. Namely, after the rapid melt-quenching (to the room temperature) process the doped glass ingots are annealed additionally in the gradient temperature furnace (where the temperature ranges from 400 °C to 750 °C) and then are cut into pieces according to their colors. During the above heat treatment process a diffusion of the dopant ions leads to a formation of the semiconductor NCs in the glass network matrix [2]. Furthermore, the samples belonging to the same set differ from each other in (average) size of created NCs. This fact is confirmed by the optical absorption measurements performed in the relevant photon energy range and the TEM investigations as well. Bellow we focus on four specific samples S_i ($i = 1–4$) of the CdSSe-doped glass, the three AgI-doped samples A_i ($i = 1–3$) and the CuI-doped samples C_i ($i = 1–3$). For the samples belonging to the above sets, the absorption spectra are presented in Fig. 1 together with the typical TEM images as examples. The absorption spectra exhibit the quantum confinement effects: pronounced excitonic peaks and a blue shift with respect to the bulk gap energy [2]. Moreover, a blue shift differs from sample to sample within the same set that indicates a change of the (average) size of the embedded NCs. Remember that a blue shift of the exciton line in zero-dimensional system is the larger the smaller is a NC.

Basing on the results presented in (main panels) Fig. 1 we therefore come to the following conclusions. (i) For the samples belonging to S_i set, the CdSSe NCs grow in size from sample S_1 to S_2, to S_3 and finally to S_4, as is clearly seen in Fig. 1a. Furthermore, the sample S_4 contains evidently the bulk-like NCs, since no blue shift with respect to the bulk gap energy is observed in this case. These findings are confirmed by the respective TEM investigation: the sample S_4 mostly contains the large (rod-like) NCs with long axes about 70 nm–80 nm, see the upper inset in Fig. 1a. For the sample S_1, on the contrary, the small (nearly spherical) NCs with the radii of 1 nm–2 nm are detected, see the lower inset in Fig. 1a. (ii) For the samples belonging to the A_i set, a size of the AgI NCs increases from sample A_1 to A_2 and to A_3, as is seen in Fig. 1b. Similarly, the CuI NCs in samples C_i grow in size from sample C_1 to C_2 and to C_3. (Note that the Z_{12} peaks and the other two H_1 and H_2 peaks seen in Fig. 1c refer to the wurtzite and hexagonal modification of the CuI crystals [16].) The TEM investigations now show that for both the A_i set and the C_i set the NCs are mostly of a spherical form. For the largest NCs in the A_i and C_i samples the TEM images are shown in the insets in Fig. 1b, c and the respective radii are estimated to be around 8 nm and 5 nm, respectively.

For the electrical measurements, the examined samples were squared in cross section about 10 mm × 10 mm × 1 mm thick, and the silver paint electrodes were used. The electrical conductivities were measured with the help of the selective nanovoltmeter UNIPAN 237 in a frequency range from 10Hz to 10^5 Hz at different temperatures from the ambient temperature to (close) the glass transition temperature T_g. For clarity, remember that the main properties of the borosilicate glass samples used here in the a.c. conductivity experiments are the following. Firstly, we have the virgin glass samples S_v, A_v and C_v which contain no dopants, but differ by the batch composition. The conductivity in these samples is mainly due to the metallic Na^+ ions serving as the network modifiers. Next there are the doped glass samples S_h, A_h and C_h which have the same batch composition as for the S_v, A_v and C_v samples, respectively. They contain also the mobile ions coming from a dissociation of the dopants during the glass preparation, for example the Cd^{2+} (in S_h sample), Ag^+ (in A_h sample) and Cu^+ (in C_h sample) cations. It is natural to assume that these ions are homogenously distributed over the sample. Finally, we examine the S_i, A_i and C_i sets of the glass samples in which a part of the dopant ions forms the semiconductor NCs during a specific heat treatment process. Evidently, a concentration of the mobile dopants in these samples is lower than for the respective original samples S_h, A_h, and C_h. Moreover, one can generally suppose that a number of the dopant ions, which remain to be mobile and uniformly dissolved over the sample, is the lower the larger NCs were formed. A concentration of the mobile dopant ions then will vary from sample to sample decreasing from S_h to S_1, to S_2, to S_3, to S_4 and to S_v for the CdSSe-doped glasses, from A_h to A_1, to A_2, to A_3 and to A_v for the AgI-doped glasses, and finally from C_h to C_1, to C_2, to C_3 and to C_v for the CuI-doped glasses. Note that in the S_4, A_3 and C_3 samples the NC's sizes remain unchanged under further heat treatment, so that no mobile dopant ions are presented in these samples similar to the case of the undoped virgin glasses.

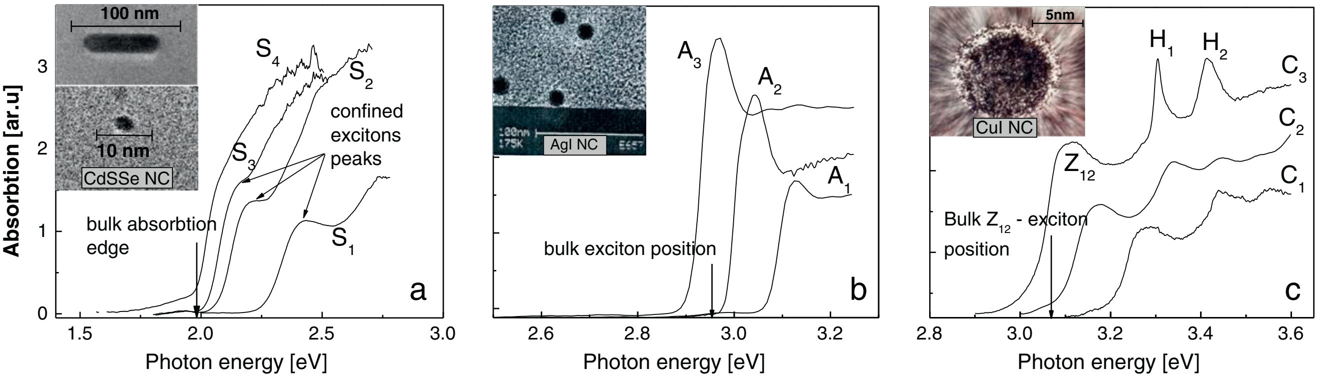

Fig. 1. Absorption spectra and TEM images: a) CdSSe-, b) AgI-, and c) CuI-doped samples.