ANALYSIS OF ACOUSTIC ATTENUATION SPECTRA OF PHOSPHATE ION CONDUCTING GLASSES BEFORE AND AFTER DEHYDRATION

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Abstract: In this paper, acoustic attenuation measurements are used to detect structural changes due to chemical processes related to dehydration. This paper presents the initial acoustic measurements conducted at a frequency of 13 MHz on a glass sample with composition $40Li_2O$-$10BaO$-$50P_2O_5$ (mol %) and in dehydrated after thermal treatment at 800 °C for increasing time lengths. The analysis revealed that the notable peak within the mid-temperature range was decreased after 1 and 3 hours of the dehydration process, and by the 6-hour, it was no longer present in the dehydrated sample.

Keywords: acoustic attenuation measurements, dehydration, phosphate ion conductive glasses.

1. INTRODUCTION

Ion conducting phosphate glasses are regarded as valuable materials with numerous applications in today's technological landscape. The chemical stability of phosphate glasses can be improved by addition of metal oxides. In comparison with silicate glasses, phosphate glasses exhibit excellent UV light transmittance, which currently makes them dominate high-power laser applications and they are increasingly used in optoelectronics, biomedical research or for radioactive waste storage. Their other industrial application is as insulation materials for radioactive waste products.

Phosphate glasses are promising materials for several technical applications, such as host material in optical devices (Langar et al., 2017), electrolytes in solid-state batteries (Huang et al., 2015) and vitrification of nuclear wastes (Stoch et al., 2016). Also, phosphate glasses are suitable candidates in tissue engineering due to the biocompatibility and degradation behaviour (Weiss et al., 2014).

Owing to these interesting properties, such as its high coefficient of thermal expansion, lower melting and softening temperatures compared with other types of oxide glasses (Jlassi et al., 2017), and optical transparency in UV region (Hejda et al., 2017), phosphate glasses have been attractive materials in the scientific community and are subject of the extensive research. However, the relatively poor chemical durability of phosphate glasses limits them in the wider development of technological applications (Muñoz-Senovilla et al., 2014). Other applications of phosphate glasses are as solid electrolytes in devices such as Li-ion batteries (Muñoz, 2012). Chemical durability can be improved by incorporation of high ionic field strength cations (Delahaye et al., 1998) or the addition of another glass former oxide. Phosphate glass fibers are also used in muscle tissues, and they also serve as a delivery system for antibacterial agents to the human body. Moreover, these phosphate glasses can be prepared as fibers, which could be used for soft tissue engineering and as fibrous reinforcement for resorbable polymers such as poly-(lactic acid) for fracture fixation applications (Sharmin et al., 2017).

In this paper, we focus on the study of temperature dependence of acoustic attenuation in ionic conductive glass samples before and after dehydration.

2. EXPERIMENTAL

As it has been shown in the past, acoustic waves are not only suitable for the study of composite materials (Danihelová et al., 2013), but can also be used to study the material properties of magnetic fluids (Kúdelčík et al., 2015), liquid crystals (Veveričík et al., 2017) and amorphous glasses (Hockicko et al., 2013, 2015).

2. 1. Preparation of investigation materials

A batch of 100 g of glass with composition $40Li_2O$-$10BaO$-$50P_2O_5$ (mol %) was prepared by mixing Li_2CO_3, $BaCO_3$ and $NH_4H_2PO_4$ reagent grade raw materials. The batch was calcined in a porcelain crucible up to 250 °C overnight then melted at 900 °C for 1 hours in air. The melt was poured onto a preheated brass plate and annealed in a muffle furnace by slowly cooling the liquid below 400 °C. The as-melted glass was the non-dehydrated sample. To obtain dehydrated glasses, a remelting under N_2 flow was done with 25 g of the previous glass in a graphite mold and following the procedure described in (Muñoz et al., 2019). In this case, the remelting was done at 800 °C for 1, 3 and 6 hours. The resultant glasses were thus well annealed, homogeneous and free of defects.

2. 2. Acoustic attenuation measurements

Our task was to determine whether we are able to detect the effect of dehydration of the glass sample, more precisely using the acoustic attenuation spectrum, by acoustic measurements. From previous experiments in the referred work (Muñoz et al., 2019), it was demonstrated that the content of water, in the form of hydroxyl ions, reduces progressively with the increase of the remelting time.

Longitudinal acoustic waves with a frequency of 13 MHz generated by a MATEC 7700 modulator and receiver (pulse, width of ~ 3 μs) and a $LiNbO_3$ transducer acoustically coupled directly to the sample were used to investigate individual glass samples. Acoustic measurements were performed at temperatures ranging from 290 K to 590 K at a heating rate of 0.5 K/min. The prepared sample was of cylindrical shape (thickness h = 1.45 - 4.81 mm). The ends of the surfaces were polished to be flat and parallel.

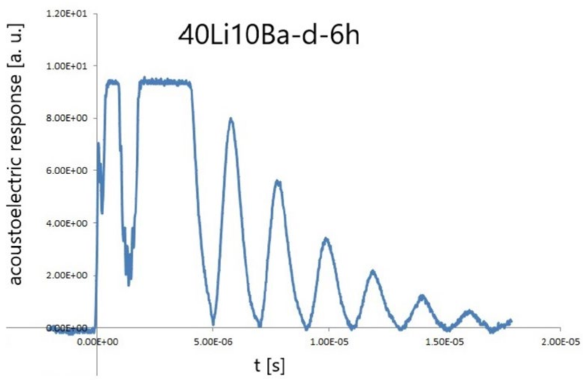

Fig. 1: Temporal behavior of subsequently reflected acoustic impulses, the first two peaks are connected with generated pulse, the following peaks characterize the attenuation of the acoustic waves after reflection in the sample.

Figure 1 illustrates the temporal behaviour of subsequently reflected acoustic impulses in the investigated sample 40Li10Ba-d-6h at room temperature.

Acoustic attenuation as a function of temperature was determined from the positions of the acoustic pulses (3^{rd} and 4^{th}, the first two peaks are connected with generated pulse in Figure 1) for whole investigated samples. The velocity of acoustic wave for dehydrated sample 40Li10Ba-d-6h: v = 4735 m/s was calculated from the positions of the acoustic pulses (3^{rd} and 4^{th}, that were no longer affected by the generating pulse) at room temperature, too (Figure 1). Compared to the non-dehydrated sample, a lower acoustic wave velocity v = 4204 m/s was found for the sample 40Li10Ba.

Figure 2 shows the measured acoustic spectra of the investigated glasses: non-dehydrated sample 40Li10Ba and dehydrated samples for 1 h: 40Li10Ba-d-1h, 3 h: 40Li10Ba-d-3h and 6 hours: 40Li10Ba-d-6h. From the temperature dependences of the acoustic attenuation and peak positions, the activation energy values of the dominant processes were determined.

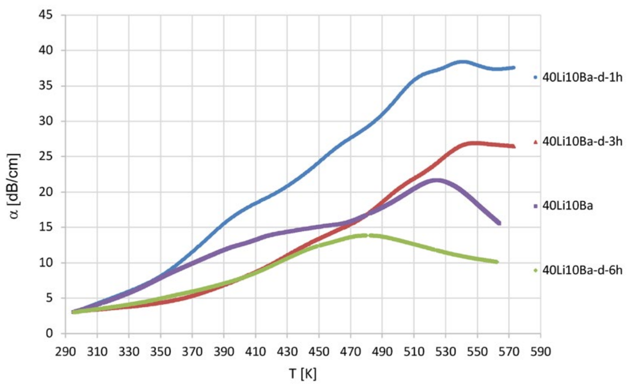

Fig. 2: Analysis of acoustic attenuation spectra of phosphate ion conducting glass samples before and after dehydration during 1, 3 and 6 hours.

As seen from the measured attenuation spectrum of the non-dehydrated sample and the dehydrated samples for 1 and 3 h, the main attenuation peak at higher temperatures is located in the 520-540 K range. Also, another peak is observed at a temperature around 400 K in the non-dehydrated sample and the dehydrated samples for 1 and 3 hour; however, this peak is eliminated with the dehydration time. In the case of sample dehydrated for 6 hours, the peak observed in the previous samples at 400 K disappeared.

Initial acoustic measurements of our samples before and after dehydration suggest that using the temperature dependence of the acoustic attenuation measurements we are able to detect changes that are related to the reduction of the water content that was retained within the glass after the melting.

Using Double Power Law (DPL) model (Muñoz-Senovilla et al., 2016; Hockicko, 2018), the individual relaxation processes were detected (Figure 3) and the activation energies of processes were calculated.

Calculated activation energies of each process together with the ratio of the areas belonging to the first and second relaxation processes are summarized in Table 1.

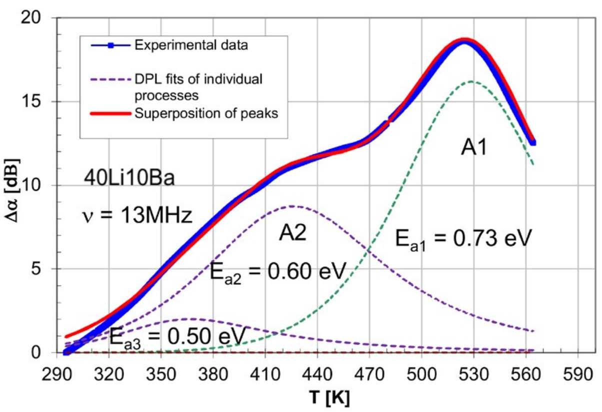

Fig. 3: Analysis of acoustic attenuation spectra of phosphate ion conducting glass sample and individual relaxation processes using DPL model.

sample	h [mm]	E_{a1} [eV] ± 0.01 eV	E_{a2} [eV] ± 0.01 eV	E_{a3} [eV] ± 0.01 eV	A2/A1
40Li10Ba	1.45	0.73	0.60	0.50	0.66
40Li10Ba-d-1h	4.68	0.75	0.59	0.50	0.37
40Li10Ba-d-3h	4.81	0.76	0.60	-	0.14
40Li10Ba-d-6h	1.61	0.66	-	0.51	-

Tab. 1: Sample thickness and calculated activation energies of individual relaxation processes

As we can see from Table 1, the area under the second peak (A2) connected with second relaxation process (E_{a2}) is eliminated with the increase of dehydration time. We can assume that this relaxation process in the studied set of samples may be related to the water content, which decreases in the dehydrated samples, until fully disappear for the 6 h dehydrated sample.

3. CONCLUSIONS

Initial acoustic measurements at 13 MHz of a glass sample of composition $40Li_2O$-$10BaO$-$50P_2O_5$ (mol.%) without and with subsequent dehydration during 1, 3, and 6 hours show that acoustic attenuation measurements are able to detect structural changes occurring due to chemical processes related to dehydration.

Due to dehydration, the prominent peak in mid-temperature interval was eliminated after 1 and 3 hours process of dehydration and no longer present in the dehydrated samples after 6 hours.

We anticipate that measurements on additional samples and at different frequencies will help us to investigate and better understand the processes related to the dehydration of the investigated materials.

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