Characterization and photo-viscous changes in phosphate-based glasses doped by copper ions

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Abstract

Phosphate glasses represent a significant group of phosphorus and oxygen-containing glasses with several potential technological applications. These materials exhibit relatively high values of coefficient of thermal expansion with low glass transition temperature and other processing temperatures which is interesting for sealing (1). Some phosphate glasses with suitable chemical compositions, e.g. calcium phosphate glasses, are also applicable in the field of biomedicine (2). In addition, they also have the short wavelength absorption edge typically located in UV region and are able to incorporate into their structure a relatively high amount of transition metal ions (1,3). These properties make phosphate glasses promising for several hi-tech applications, such as solid-state lasers (4), low-frequency optical fibers (5) or optical data storage (6). The advantage of these materials from the point of view of sustainable development is also the potential immobilization of radioactive wastes (7).
Copper can exist in glassy structures in several different chemical forms, i.e. metallic Cu(0), Cu(+) or Cu(2+) ions with various coordinations, which differently determine/affect the materials' properties, e.g. optical characteristics (8). The chemical form of copper in glasses is subsequently given mainly by the chemical compositions of starting materials, which react together during the synthesis, and applied experimental conditions (8-10).

In this work, we focus on the substitution of Zn(2+) ions by Cu(n+) ions (where n = 1 or 2) in the phosphate glasses and the influence of this substitution on their structure and properties, i.e. optical and thermal properties including also photo-viscous changes. All bulk materials (i.e. with 0-11.6 mol% of starting CuO) were synthesized by classical melt-quenching technique in a corundum crucible.

The obtained bulk glasses were chemically stable in the ambient atmosphere. The amorphous character or the presence of crystalline phase in glasses was detected using X-ray diffraction analysis. The real chemical composition of prepared materials was checked employing X-ray fluorescence spectroscopy. The information on the structure of the anionic part of glasses, i.e. the present phosphate-based structural units, was obtained using two different methods: Raman and 31P nuclear magnetic resonance spectroscopy. The characterization of incorporated Cu(n+) ions (oxidation state, coordination) was performed by electron paramagnetic

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resonance spectroscopy. The effect of Cu(n+) ions on the optical properties was examined using UV/Vis spectroscopy in the range of λ = 300-900 nm. Glass transition temperature of prepared materials was determined by thermomechanical analysis.

The photo-viscous changes were examined similarly as in our previous work (11) employing a specially modified thermomechanical analyzer (TMA) with an optical transparent path (indenter) for *in-situ* laser illumination during the measurements. In this work, the photo-viscous changes were studied using two different approaches. The first approach is based on the measurement of the rate of indenter penetration into the sample (the change of penetrating indenter volume per time in the given time interval) during the isothermal measurements. The penetration rates for measurements with and without illumination were subsequently compared. In the second case, TMA was used for the common dilatometric measurements without and with illumination. For each illumination, solid state continuous-wave laser emitting at 808 nm (maximal laser power density incident on the samples $\approx$ 5.9 W/cm2) was used.

In this work, it was found that copper ions significantly affect the optical properties in the visible region due to the formation of a broad absorption band with maximum around 800 nm which intensity increases with the increasing amount of starting CuO. The values of glass transition temperatures have non-monotonous behavior affected by the amount of CuO and the structure of prepared materials. Illumination of the samples by 808 nm during penetration measurements at the same temperatures led to an increase in the penetration rate compared to that obtained without illumination. Based on the shift of penetration rates between illuminated and non-illuminated measurements, the local non-uniform overheating of the sample with $\approx$ 0.7 mol% of CuO induced by illumination is by $\approx$ 22 $\circ$C. Similarly, illumination causes the "apparent" decrease of glass transition temperature value compared to the dilatometric measurement without illumination which is for the same sample (0.7 mol% CuO) $\approx$ 20 $\circ$C corresponding well with the results obtained by penetration method. In addition, the magnitude of the difference between glass transition temperature without illumination and "apparent" glass transition temperature due to illumination increases with the increasing CuO content. The cause is probably higher overheating of materials as a result of the increasing absorbance at 808 nm associated with the increase of Cu(2+) ions content.

We believe that the results of this work could bring new findings from the point of view of the laser-solid state interactions and could help to determine the suitable Cu(2+) ions concentration for the successful laser micro-structuring (i.e. concave or convex microlenses formation) by synergy effect of the heat and continuous-wave laser in the visible part of the spectra. The laser micro-structuring of materials presents an interesting way for miniaturization of various devices.

References

(1) Brow, R.K., *Journal of Non-Crystalline Solids* **263-264** (2000) 1-28.

(2) Knowles, J., *Journal of Materials Chemistry* **13** (2003) 2395–2401.

(3) Schwarz, J., Ticha H., Tichy L., *Materials Letters* **61**(2) (2007) 520-522.

(4) Campbell, J.H., Suratwala T.I., *Journal of Non-Crystalline Solids* **263–264** (2000) 318–341.

(5) Boetti, N., Pugliese D., Ceci-Ginistrelli E., Lousteau J., Janner D., Milanese D., *Applied Sciences* **7** (2017) 1295–1312.

(6) Hu, Z., Huang X., Yang Z., Qiu J., Song Z., Zhang J., Dong G., *Light: Science & Applications* **10**(1) (2021) 140.

(7) Day, D.E., Wu Z., Ray C.S., Hrma P., *Journal of Non-Crystalline Solids* **241**(1) (1998) 1-12.

(8) Jiménez, J.A., *Applied Physics A* **114**(4) (2014) 1369-1376.

(9) Tanaka, K., Yano T., Shibata S., Yamane M., Inoue S., *Journal of Non-Crystalline Solids* **178** (1994) 9-14.

(10) Jiménez, J.A., *Journal of Materials Science* **49**(12) (2014) 4387-4393.

(11) Smolík, J., Černošková E., Knotek P., Zmrhalová Z., Schwarz J., Černošek Z., Plecháček T., *Journal of Non-Crystalline Solids* **594** (2022) 121790.

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