

ФІЗИКО-МАТЕМАТИЧНІ НАУКИ

Szymon Świontek

*AGH University of Science and Technology,
Faculty of Materials Science and Ceramics*

THERMOLUMINESCENCE PROPERTIES OF CERIUM- DOPED BOROSILICATE GLASS AND GLASS-CERAMICS

The cerium-doped borosilicate glass and glass-ceramics from the CeO_2 - B_2O_3 - SiO_2 system are developed. The effect of SiO_2 admixture on the thermal stability of the glass and the thermoluminescence (TL) properties such as glow curves shape is studied. In this research, the thermal and optical properties of cerium-doped borosilicate glasses are improved by process of heat treatment. The results show that obtained glass-ceramics could be used as an active material in the TL detectors.

Modified glass can play a role of the radiation detector material in many applications nowadays. The commercially available thermoluminescent (TL) dosimetric detectors used in industry or research centers are in the form of crystalline material. Unfortunately, the vast majority of currently using crystalline materials are not biodegradable and toxic to human health. In some cases these features disqualify them from usage, especially in brachytherapy or food preservation. For this reason the special detectors measuring ionizing radiation inside biologic tissues are required. Therefore, glass or glass-ceramics are very encouraging materials in this kind of applications. What is more, the benefits of using glass as a radiation detector would be simplicity of manufacturing and the equivalent absorption coefficient similar to human tissue. It turns out that it is possible to form glass and obtain the effective atomic number (Z_{eff}) similar to human tissue for borate glass.

Some glasses doped with rare-earth elements or transition metal ions have been found to be very powerful as indicators of high-energy radiation. Thermoluminescence studies of borate glasses are of great interest due to their near tissue equivalent absorption coefficient which is equal to 1.8 cm^{-1} , good matrix for hosting rare-earth ions, very low cost of fabrication and ease of handling the process. However, their sensitivity and thermal stability depend strongly on the chemical composition. Moreover, borate glasses modified by

doping can exhibit superlinear dose response of thermoluminescence. Such material was successfully obtained for lithium borate glasses doped with Eu^{3+} , doped with Dy^{3+} or co-doped with activated zinc. However, elemental composition of the batch has the significant influence on the final thermoluminescence properties. The presence of SiO_2 in borate glass increases its mechanical strength and made the glass more chemical resistant especially for dissolution. Unfortunately, the incorporation of modifiers like rare earth elements into borosilicate structure breaks oxygen linkages which decreases its thermal stability. As a result the proper estimation of SiO_2 amount in borate glass is of great importance. Additionally, other effects, such as i.e. boron anomaly, have also significant impact on the final properties of the glass. On the other hand, the phase separation may appear in borosilicate glass due to immiscible phenomena in the system. Nevertheless, the chemical resistance for environmental factors is the key advantage of glass dosimeters over crystalline ones.

Experimental. All obtained glasses were good quality, homogeneous and without bubbles. Due to the CeO_2 admixture, the yellow-brown color appears in all glasses and remains unchanged regardless the $\text{SiO}_2/\text{B}_2\text{O}_3$ ratio. The studies revealed that up to 20 mol% SiO_2 no phase separation appears due to the high content of modifiers.

XRD analysis proved the formation only one phase $\text{BaCeB}_9\text{O}_{16}$ for all samples (Figure 1). The crystallization of $\text{BaCeB}_9\text{O}_{16}$ vanishes for sample with 20 mol% of SiO_2 what is in line with DSC analysis. The increase of SiO_2 content in the cerium-doped borosilicate glass causes contribution reduction of optically active phase. However, it enhances the thermal stability and reduces ΔH of crystallization.

The Hruby coefficient (k_{gl}), which is an indicator of thermal stability of glass, increases with $\text{SiO}_2/\text{B}_2\text{O}_3$ ratio and varies from 0.71 to 1.35. It is assumed that glasses with $k_{\text{gl}} > 1$ are believed to have high thermal stability. It shows that even small amount of SiO_2 (5 mol%) significantly increases the thermal stability.

However, the admixture of SiO_2 has an adverse impact on thermoluminescence efficiency and its content in the glass composition should be carefully balanced between thermal and luminescence properties. The process of thermal treatment leads to $\text{BaCeB}_9\text{O}_{16}$ formation what enhances the thermoluminescence signal (Figure 2). As a result, glass-ceramics has been obtained which TL efficiency is comparable with commercial crystalline materials but with the lower maximum temperature of the dose response.

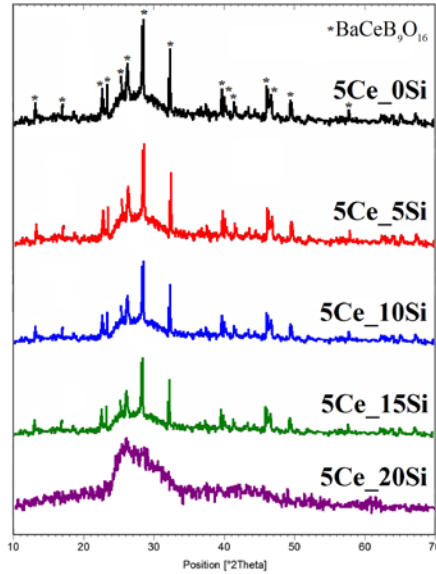


Figure 1. XRD patterns of cerium-doped borosilicate glasses heat treated in the range from 750°C to 800°C for 1 h. The asterisks indicate BaCeB₉O₁₆ phase.

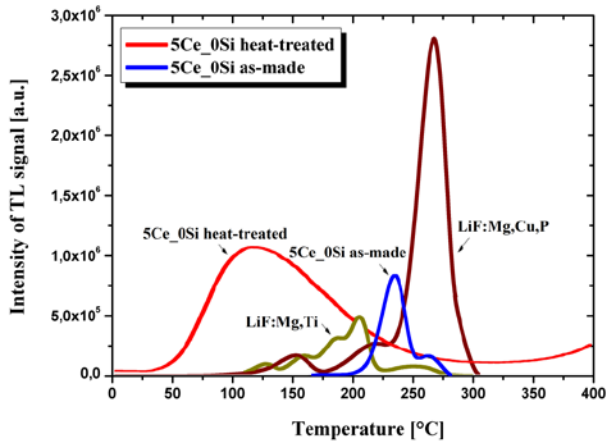


Figure 2. The comparison of thermoluminescence results for obtained glass-ceramics and as-made glass with data for commercially used TL materials: LiF:Mg,Ti and LiF:Mg,Cu,P.

All figures made by Author