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INVESTIGATION OF PROPERTIES OF ALKALINE-FREE GLASSES FOR SINTERING DIELECTRIC CERAMIC MATERIALS

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Abstract: *The article presents the basic physical and technical properties of alkaline-free glasses for sintering dielectric ceramic materials. The effect of chemical composition on the density, volumetric electrical resistance and thermal coefficient of linear expansion of alkaline-free glasses is determined. The tendency of glasses to crystallize is determined by the method of differential thermal analysis. The main crystalline phases formed as a result of the crystallization of the experimental glasses were determined by X-ray phase analysis.*

Keywords: *Alkaline-free glasses, Strontium anorthite, X-ray phase analysis*

INTRODUCTION

Advancements in knowledge-intensive technologies necessitate the development of new materials that can serve as dielectric elements in structural units for various functional purposes, such as substrates of integrated circuits, elements of phased antenna arrays, and aircraft fairings. Traditionally, these materials are made from aluminosilicate ceramics of varying chemical compositions, ranging from eucryptite to Celsian, each with its own set of advantages and disadvantages. However, ceramics based on strontium anorthite have emerged as the most promising due to their superior properties.

The production of densely sintered ceramics for dielectric products typically requires high sintering temperatures or the application of hot pressing techniques, significantly increasing the final products' cost. Introducing glass binders into the manufacturing process can promote the formation of a liquid phase at lower temperatures, thereby accelerating the sintering process of ceramics.

Previous studies (Zaichuk et al., 2020) have investigated the influence of lithium-aluminosilicate glass on the sintering temperature and properties of strontium anorthite ceramics. The main drawbacks of these ceramics are their low refractoriness and suboptimal dielectric properties. To address these issues, the use of alkali-free glasses for sintering ceramic materials based on strontium anorthite can enhance fire resistance and provide the necessary dielectric properties, thus expanding the potential applications of these products.

Recent research has focused on alkali-free glasses and their properties. For instance, Hordieiev and Amelina (2021) determined the glass formation region and structural features of glasses in the $SrO–B_2O_3–SiO_2–xAl_2O_3$ system, where x = 0 or 10 mol%. Additionally, Sung and Kim (2000) demonstrated the positive influence of strontium oxide on the crystallization of monoclinic Celsian and investigated the sintering ability of glass powders.

In another study, Tong et al. (2019) produced glass ceramics by solid-phase sintering of eutectic glass within the $BaO–Al_2O_3–SiO_2$ system using $BaAl_2O_4$ and $SrAl_2O_4$ powders, resulting in a monoclinic form of strontium anorthite. However, high synthesis temperatures remain a limitation for this glass ceramic.

While substantial research has focused on developing alkali-free glasses for sintering ceramics, achieving a balance of required properties – especially high refractoriness and stable dielectric performance at low sintering temperatures – remains challenging.

Thus, this study aims to investigate the structural characteristics and properties of glasses within the $SrO–xBaO–Al_2O_3–B_2O_3–SiO_2$ (x = 0–20 mol.%) (SBABS) system to assess their effectiveness as glass binders for dielectric ceramic materials.

EXPOSITION

The following components were used for glass making: strontium carbonate of grade chemically pure, barium carbonate of grade chemically pure, alumina of grade G-0, silicon(IV) oxide of grade A, and boric acid of grade chemically pure. The glasses were synthesized in an electric furnace with silicon carbide heaters at a temperature of 1350°C for 1 hour. Corundum crucibles were used for synthesis.

Standard methods were used to determine the properties of the glasses. Density (ρ) was measured by hydrostatic weighing in distilled water. Specific volume resistivity was determined over the temperature range of 100–400°C on plane-parallel plates placed in a cell with graphite electrodes using a teraohmmeter E6-13A. The relative elongation (Δl) as a function of temperature was measured on samples with dimensions of 5×5×50 mm, allowing the calculation of the average coefficient of thermal expansion (CTE) between 20°C and 400°C.

The softening and crystallization temperatures of the SBABS glass were determined using a synchronous thermal analyzer (STA PT 1600, Linseis GmbH) operating from 20°C to 1000°C at a heating rate of 10°C/min.

Previous studies (Zaichuk, O.V., Sukhyy, K.M., Amelina, O.A., et al., 2023) showed, through thermodynamic analysis, that strontium anorthite could form through a reaction between eutectic glass compositions and additional components. The base glass composition, labeled S-1, corresponded to the eutectic point on the $SrO–Al_2O_3–SiO_2$ system diagram. Additional fusibility was introduced by adding 10 wt.% B_2O_3, surpassing 100 wt.% of the primary components. To assess the influence of barium oxide on glass properties, SrO was progressively replaced with BaO in 5 mol% increments, up to 20 mol%. The compositions were labeled as follows: S-1 contained no BaO, S-2 included 5 mol% BaO, S-3 had 10 mol% BaO, S-4 contained 15 mol% BaO, and S-5 had 20 mol% BaO.

Density, specific volume resistivity, and coefficient of thermal expansion were measured for each glass sample, and the results are shown in Figure 1.

Analysis revealed that the CTE of the samples, which was in the range of $(71–78)\times10^{-7}$ °C^{-1}, decreased with increasing barium oxide content. The specific volume resistivity at 300°C was in the range $\lg\rho_{300}$ = (10.7–11.6) Ohm·cm, indicating that the samples belong to the dielectric class. The volume resistivity logarithm values decreased as the amount of the second alkaline earth oxide increased. Density values ranged from 3.20 to 3.34 g/cm^3 and increased from S-1 to S-5 as the content of heavier barium oxide increased.

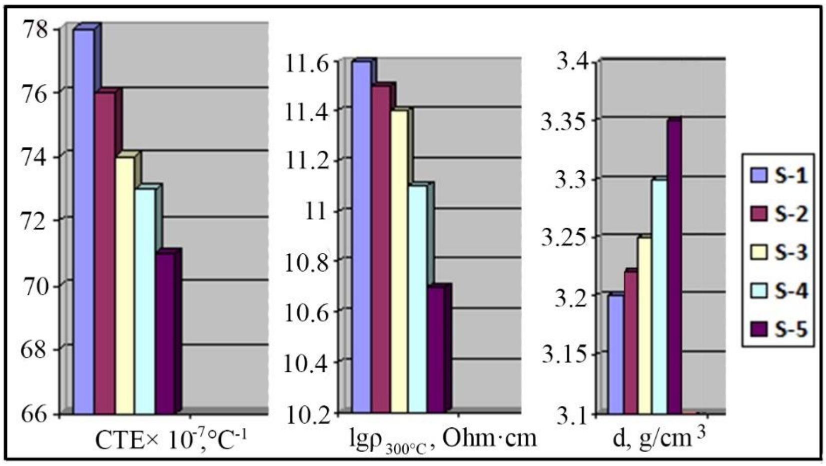
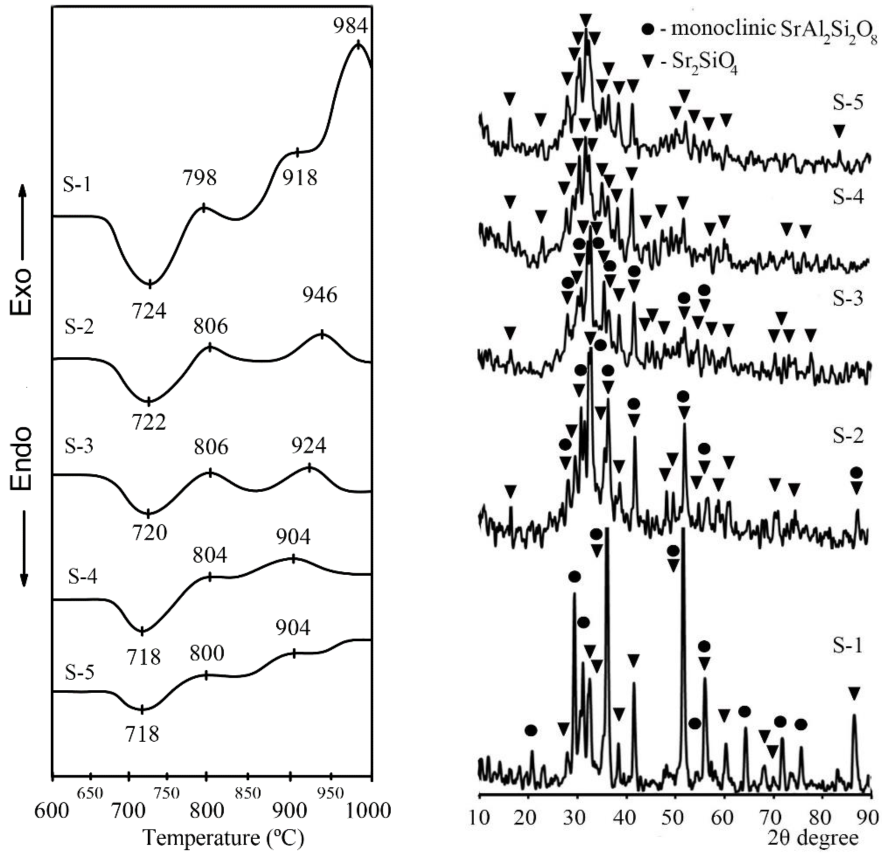


Fig. 1. Physical properties of SBABS glasses

In order to assess the crystallization tendency of the glass, differential thermal analysis was performed on powdered glass samples over a temperature range of 20–1000°C (see Fig. 2a). Up to 600°C, the DTA curves showed no significant changes. The first endothermic effect, associated with glass softening, occurred between 650°C and 750°C, with minima at 718–724°C. This endothermic effect shifted to lower temperatures with increasing BaO content from S-1 to S-5. A second, less pronounced endothermic effect was observed between 800°C and 918°C; the area under this effect decreased with higher BaO content. A distinct exothermic crystallization peak at 984°C was observed only for the initial glass composition S-1, which lacked BaO. Generally, increasing BaO content in SBABS glasses lowered their crystallization tendency, with the crystallization peak shifting progressively to lower temperatures (from 984°C to 904°C).



a) b)

Fig. 2. DTA (a) and XRD (b) of SBABS glasses

In order to determine the crystalline phase composition, the glasses were thermally treated based on DTA results. X-ray diffraction analysis (Fig. 2b) of the crystallized SBABS glasses identified strontium metasilicate as the primary crystalline phase, with notable peaks at 3.55, 3.34, 2.90, 2.52, 2.05, and 1.90 Å. Monoclinic strontium anorthite (with peaks at 3.72, 3.40, 3.24, 3.21, 2.90, and 2.52 Å) was also detected, forming a solid substitution solution with Celsian due to the similarity in ionic radii of Sr^{2+} and Ba^{2+}. Overall, X-ray diffraction patterns showed a marked decrease in diffraction peak intensity with increasing BaO content in the base strontium-aluminum borosilicate glass S-1, indicating reduced crystallization potential in these modified glasses.

CONCLUSION

This study examined the properties of glasses within the $SrO–xBaO–Al_2O_3–B_2O_3–SiO_2$ system (x = 0–20 mol%). Replacing SrO with up to 20 mol% BaO positively influenced the glass-forming ability and facilitated the formation of a monoclinic form of strontium anorthite during crystallization. The formation of a solid substitution solution with Celsian is attributed to the similar ionic radii of Sr^{2+} and Ba^{2+}. Incorporating these alkali-free experimental glasses into composite materials as a glass binder could reduce sintering temperatures and enhance dielectric properties.

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