

Influence of the technological issues on spectroscopic properties of transparent glass-ceramic doped with europium ions

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Abstract—The production of transparent glass-ceramic materials often faces challenges, such as inhomogeneities, inclusions, uncontrolled crystallization and other defects that make glass ceramics unsuitable for fiber optics, for example. At the same time, the chosen chemical composition is valuable for its unique properties.

The present study investigated the effect of different methods of synthesizing glass-ceramic silica-germanium-antimony matrices on their transmittance optimization and luminescence properties where the conventional melt-quenching route is insufficient in terms of the transparency and homogeneity of the material obtained. The effect of heat treatment on the studied properties was also considered.

The manufacturing of transparent glass-ceramics (G-C) doped with lanthanide ions, especially for the cores of optical fibers, poses numerous challenges related to maintaining high transmission, which is significant in optical and fiber optic systems and luminescence properties. Loss of transmission is usually associated with the presence of inhomogeneities, the presence of inclusions, uncontrolled crystallization, and other optical defects, such as refractive index variations [1–3]. If the effects of thermal treatment are considered, problems related to uncontrolled crystallization, loss of transparency, and refractive index variations arise. Those imperfections are usually addressed by altering the chemical composition or the manufacturing conditions, such as temperature, pressure, and duration. However, if there is a requirement to maintain the chemical composition unchanged due to the unique luminescent properties it imparts, the only option left is to modify the manufacturing method [1, 4]. An example is a material that, depending on the cooling rate after being poured into a mold, can remain transparent and amorphous or crystallize to form an opaque G-C.

Various types of defects can occur in a multi-step procedure for producing a glass-ceramic material, resulting in a loss of transparency or luminescent properties. At the preparation stage of chemical components, some components' presence can reduce thermal stability, leading to uncontrolled crystallization [1, 2]; lack of proper homogenization by mixing and grinding of the components can lead to the formation of difficult-to-melt inclusions. Calcination and sintering can lead to the formation of porous structures with encapsulated inclusions and gas bubbles. Finally, every process of pouring molten glass mass of great lightness into a mold can result in the entrapment of air bubbles. Any imperfections in the technological process also cause local changes in chemical

composition, translating into RI fluctuations [1, 3]; inclusions and micro-bubbles can be nucleators that cause uncontrolled crystallization reactions.

In this experiment, the SGS (silica, germanite, antimony) matrices are used due (see Tab. 1) to their relatively low phonon energy and good thermal stability [5] in combination with EuPO_4 nanocrystals (diameter < 30 nm) grown in this structure. Typically, these crystals are characterized by high transparency, and light scattering is related to the difference in the refractive index of the crystal and the vitreous material in which the crystals are suspended. As a case in point, Xiaofeng Liu's research [6] can be used, where an increase in scattering in conjunction with an increase in crystallite size and an increase in the RI difference between the crystal and the host material was shown.

Europium ions were used to detect the level of crystallization by luminescence shape changes and asymmetry ratio (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$) changes [4, 7] where a ratio higher than 1 suggests a predominantly amorphous character of the sample.

Tab. 1. Properties of chosen SGS matrix.

SGS RI	EuPO ₄ RI	SGS T _g	SGS T _x	SGS ΔT
1.69	1.67-1.7	415 °C	559 °C	144 °C

The main goal of the experiment was to optimize the manufacturing method of SGS glasses in terms of transmission improvement. The selected SGS material was synthesized during the experiment using the classical melt-quenching method and other more elaborate fabrication methods. Simultaneously, changes in the luminescence spectrum were observed to determine the impact of fabrication technology alterations on the luminescence shape and indirectly on structural changes.

As a result, a method was developed to improve transmission by more than 330% without significant changes in luminescence shape for annealed samples.

An SGS glass with a molar composition of $35\text{SiO}_2 - 5\text{Al}_2\text{O}_3 - 30\text{GeO}_2 - 20\text{Sb}_2\text{O}_3 - 10\text{Na}_2\text{O}$ was prepared by different routes of melting and quenching technique (Fig. 2). In all cases, 0.5 mol.% of P_2O_5 was added to the SGS base and doped with 0.5 mol.% of Eu_2O_3 .

All raw compounds were homogenized in a gate mortar before drying. Calcination, heat treatment, and annealing temperatures were chosen based on DSC measurements (Tab. 1). Drying of the samples was carried out at 140 °C for 1h. Calcination was carried out at 525 °C for 2h. All

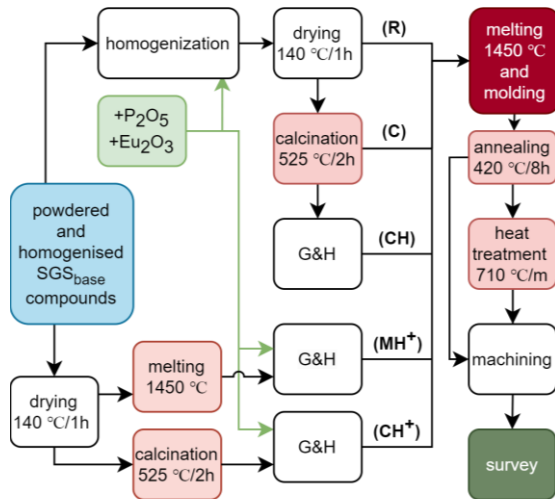


Fig. 1. Diagram of sample preparation and fabrication for optical and luminescence survey, G&H – grinding and homogenization process. Sample identification: R – reference sample, C – calcinated sample, CH – calcinated and homogenized, MH⁺ – melted, doped and homogenized, CH⁺ – calcinated, doped and homogenized.

grinding and homogenization processes were carried out manually using an a gate mortar.

Melting was carried out in an electric furnace at 1450 °C with a temperature increment of 10 °C/min. The melted liquid material was poured into a brass mold to form rods 10 mm in diameter. After that, samples were annealed at 420 °C for 8h to reduce internal stresses. All samples for microscopy and spectroscopic measurements were cut as 2.5mm disks from fabricated rods and polished.

The heat treatment process was carried out at 710 °C. The samples were placed in a preheated furnace for 3 minutes. After this time, they were removed from the furnace and allowed to cool naturally to room temperature (25 °C). A spectrometer (GREEN-Wave StellarNet Inc. USA) was used to record the spectrum. A tungsten halogen with a deuterium lamp (SL5 light source, StellarNet Inc. U.S.A) was used as a light source to measure transmittance. A semiconductor laser with a wavelength of 395 nm was used as the excitation source for europium ions. (MLL-III-395-100mW, 7,96mW/mm², CNI, China) with a 450nm filter to remove the pump signal before luminescence shape measurement (Fig. 2).



Fig. 2. Measurement system for studying the shape of the luminescence.

Due to the high independence of the intensity of the ${}^5D^0 \rightarrow {}^7F^1$ transition in relation to the ordering of the environment around the europium ions, it was chosen for the normalization of the emission spectra graphs [4, 7]. Figure 3 shows selected rods and samples after the annealing process; the reference sample (R) shows a loss of transparency (R_t) due to uncontrolled crystallization (R_o). This is the result of cooling too slowly, where the crystals had adequate temperature (higher than T_g) and

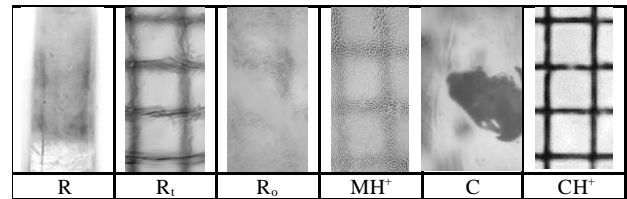


Fig. 3. Photos of: R) reference as melted rod, and samples after annealing process: R_t) reference sample transparent part of reference rod, R_o) part of rod with uncontrolled crystallization, C) sample after calcination with inclusion, MH⁺) sample with air bubbles, CH⁺) sample with doping after calcination.

time to grow [1, 8]. Also, samples visible in Fig. 3 (C, MH⁺) have a variety of imperfections, where most common being air bubbles and inclusions. These deficiencies have several sources. Air bubbles are caused by purring high-viscosity liquid into brass mold [3]. Inclusions are the effect of calcination without grinding and homogenization. The chemical reactions between the compounds during the calcination process led to hard-to-melt contaminants [9]. As an effect of both, bubbles and impurities can be considered as nucleation centers for the crystallization process [2, 3].

The defect-free rod (Fig. 3 CH⁺) was obtained in the process where the homogenized SGS base was calcined. This process resulted in a sinter with high porosity, which was then ground and homogenized. A fine powder was then produced, to which P₂O₅ and Eu₂O₃ were added, and the mixture was homogenized again.

Transmittance measurements showed a correlation between the loss of transparency of the samples and the measurement result. As expected, the reference sample (R) showed considerable variation in transmittance and, depending on whether the transparent (Fig. 4 R_t) or translucent part was tested (Fig. 4 R_o). The best results

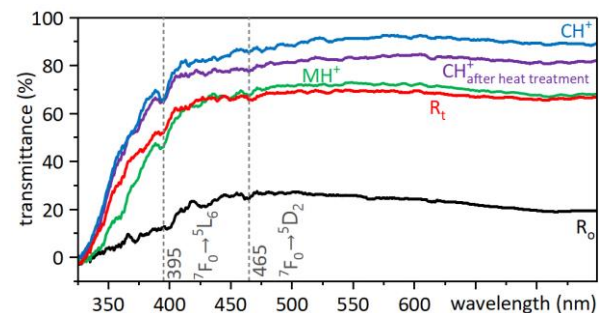


Fig. 4. Transmittance of chosen samples.

were obtained for CH⁺ samples. They are characterized by a transmittance of up to 93%. Which clearly decreases by about 10% after the heat treatment process.

Transmittance changes in conjunction with crystallization are a well-known phenomenon, mainly related to the difference in RI between the host material and the forming crystals [1, 3, 8]. The second-best transmittance result belongs to the MH⁺ sample and is up to 73%.

Luminescence measurements of melted samples show luminescence shape changes (Fig. 5) due to a change in how the material was manufactured. Samples, with the exception of R₀, show predominantly amorphous character (asymmetry ratio > 1) [7, 8]. The largest ratio (3.12:1) is for R_t sample. R₀ sample was crystallized as melted, so the ratio is about 1.12:1 and still unchanged after heat-treatment process. The lowest 1.61:1 asymmetry ratio is for the CH⁺ sample.

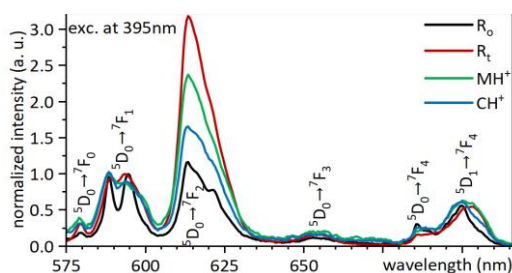


Fig. 5. Emission spectra of melted samples.

On the other hand, the changes in the shape of the spectrum of the ${}^5D_0 \rightarrow {}^7F_1$ transition are small (except for R₀). The luminescence effect of Stark's splitting is observable only to a small extent. This suggests subtle structural changes related to the low level of crystallization of the test sample [4, 7, 8].

After heat treatment, the samples have a luminescence shape (Figure 6) (${}^5D_0 \rightarrow {}^7F_1$), indicating crystallization (Stark's splitting), which is further confirmed by the asymmetry ratio reduced to about 1:1 [7, 8]. The exception is the R₀ sample, which crystallized as melted.

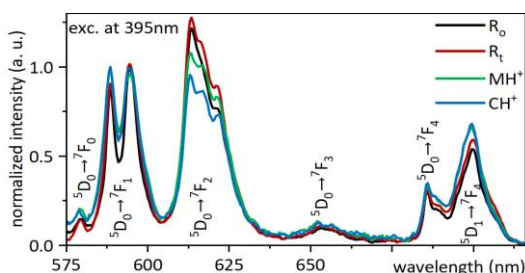


Fig. 6. Emission spectra of heat treatment samples.

Reference samples have the highest asymmetry ratio (1.25:1). For sample CH⁺ after heat treatment, the asymmetry ratio is the lowest (0.95:1), suggesting the highest level ordered environment around europium ions. From the changes in the asymmetry coefficient, as the transmittance of the samples increased, a lower asymmetry

coefficient was achieved. This suggests the possibility of achieving a higher level of crystallization [4, 7, 8] in a defect-free environment (inclusions, air bubbles, crystal clusters).

Experiments clearly show that the developed SGS material preparation process reduces inclusions and improves transmittance. The key seems to be to separate the process of creating the SGS base material from its subsequent enrichment with the chemical components necessary for crystal growth, thus preventing uncontrolled crystallization. The calcination process, in combination with multi-stage homogenization, also plays an important role. As the final effect, the chosen SGS material, without changing chemical composition, improves transmittance from about 20% up to above 90%. Moreover, it was possible to indirectly confirm the presence of crystals with built-in Eu³⁺ ions by changing the shape of the luminescence. At the same time, it was shown for heat-treated samples that it is possible to improve the transmittance without significantly changing the shape of the luminescence spectra.

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