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Local structure of gadolinium in oxyfluoride glass matrices containing SrF_2 and BaF_2 crystallites

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ABSTRACT

Gd^{3+} doped aluminosilicate oxyfluoride glasses and glass-ceramics containing SrF_2 and BaF_2 crystallites have been studied by differential thermal analysis (DTA), X-ray diffraction (XRD), transmission electron microscopy (TEM), photoluminescence (PL) and electron paramagnetic resonance (EPR) spectroscopy techniques. A pronounced EPR fine structure emerges after the heat treatment of the glass matrix. EPR spectra simulations indicate the formation of cubic, tetragonal and trigonal Gd^{3+} centres in the studied compositions.

1. Introduction

Oxyfluoride glass (OFG) matrices and ceramics are considered as suitable hosts for rare earth ions due to their high optical transparency and low phonon energy [1,2]. A particularly promising application for OFG ceramics is the white light-emitting diode (WLED), where the current commercial phosphors suffer from heating caused degradation resulting in lumen loss and chromatic shift of the illumination. The vitreous matrix of OFG ceramics, on the other hand, offers superior physical, thermal and chemical stability [3].

Luminescence properties of different phosphors can be enhanced by introducing Gd^{3+} impurities as sensitizers. Several studies have shown that coactivation with Eu and Gd ions results in increased luminous intensity and adjusts the colour coordinates of samples [4–6]. Properties of luminescence centres are influenced by the surrounding ligands, therefore, a detailed information is necessary about their local structure.

The paramagnetic nature of the Gd^{3+} ion is caused by the seven unpaired electrons in its outer electron shell. The resulting effective spin value $S = 7/2$ and distinct interaction with its surrounding environment allows Gd^{3+} impurities to be used as probes in magnetic resonance spectroscopy for various applications such as studying the temperature behaviour of materials with negative thermal expansion [7], measuring nanometer scale distances in biomolecules [8] and improving signal intensity in magnetic resonance imaging [9].

In the present study we use Gd^{3+} impurities as paramagnetic probes to investigate the local structure of trivalent rare earth ions via electron paramagnetic resonance (EPR) spectroscopy. Previously we have studied OFG ceramics containing CaF_2 nanocrystals and observed electron EPR spectra with a detailed fine structure characteristic to Gd^{3+} in a cubic point symmetry [10]. In this work, we investigate the symmetry of Gd^{3+} centres in OFG matrices containing SrF_2 and BaF_2 crystallites. Experimental EPR spectra measurements and spectral simulations show presence of cubic, tetragonal and trigonal Gd^{3+} centres in the studied matrices.

2. Experimental

OFG samples of nominal compositions $40SiO_2$-$25Al_2O_3$-$15Na_2CO_3$-$20SrF_2$-$0.1GdF_3$ (SANS) and $40SiO_2$-$25Al_2O_3$-$15Na_2CO_3$-$20BaF_2$-$0.1GdF_3$ (SANB) were prepared by the melt quenching technique. The corresponding high purity commercial chemicals (SiO_2, Al_2O_3, Na_2CO_3, GdF_3 and SrF_2 or BaF_2) were carefully weighed, mixed and melted in an alumina crucible at 1450 ± 10 °C for 45 min in an electric furnace with air atmosphere. Quenching was done by pouring the molten material onto a stainless steel plate at room temperature and pressing it with another stainless steel plate. The corresponding glass ceramics were prepared by the heat treatment method of the obtained colourless, transparent glass samples for 1 h in a furnace with temperature regulation precision of ±10 °C.

Differential thermal analysis (DTA) measurements were made for powdered samples with 10 °C/min heating rate using Shimadzu DTG-60 analyzer and alumina reference with ±3 °C accuracy.

Formation of the crystalline phases was studied by X-ray diffraction (XRD) measurements with PANalytical X'Pert Pro diffractometer using 1.54 Å Cu K_α radiation. The average crystallite size was calculated using the Rietveld spectral peak analysis.

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The nanostructure of glass ceramics was studied by transmission electron microscope (TEM) Tecnai GF20 operating at 200 kV. Sample preparation was done as mentioned in [11,12].

Photoluminescence (PL) was investigated with Andor Technology spectrometer SR-303i-B and Andor CCD camera DU401-BV using 273 nm excitation from Xe lamp Hamamatsu C2577.

The EPR measurements were made using a conventional X-band (≈9.10 GHz with 0.01 GHz accuracy) spectrometer RE 13-06 with 100 kHz field modulation at 77 K by submerging samples in a cold-finger dewar filled with liquid nitrogen. The magnetic field calibration was done using a polycrystalline DPPH standard with $g = 2.0036 \pm 0.0001$. Spectra parameters were calculated in EasySpin using the built-in least-squares fitting techniques [13].

3. Results

3.1. Structure characterization

DTA curves of the studied samples are presented in Fig. 1. Here T_g denotes the glass transition temperature, T_{C1} – the crystallization temperature of the corresponding fluorite structure phase (SrF_2 for SANS; BaF_2 for SANB), T_{C2} – the silicate crystallization temperature in the matrix. The temperature values are summarized in Table 1.

Both compositions have primary crystallization peaks around 600 °C, however the T_{C1} peak for SANB is broad and not as pronounced as for SANS glass. Previous study has shown that this "sluggish" crystallization is a consequence of high dissociation energies for Ba—O and Ba—F atomic bonds [14].

Formation of crystalline phases occurs after heat treatment above T_{C1} of the parent glass. The XRD data are presented in Fig. 2 and Table 2. Both glasses show presence of the corresponding fluoride phase after heat treatment at different temperatures. BaF_2 XRD lines in the SANB sample treated at 700 °C are broad and overlap with lines caused by other crystalline phases, therefore, crystallite size is not calculated. After heat treatment at 800 °C BaF_2 lines are not observed at all, thus we can conclude that crystallization of different silicate structures such as $BaAl_2Si_2O_8$ suppresses the formation of BaF_2. In SANS samples $NaAlSiO_4$ and Na_2SrAlO_4 crystalline phases are present after heat treatment at temperatures above 700 °C, however, SrF_2 lines are still dominant.

TEM measurements were made for samples heated at 650 °C in order to validate the results obtained with XRD. Crystallite size and distribution was uniform in SANS composition, a typical image of the sample is shown in Fig. 3a. SANB composition glass ceramics were less homogenous consisting of regions of sparsely distributed smaller crystallites, some larger agglomerates as well as regions with uniformly distributed crystallites. A selected image of SANB composition is shown in Fig. 3b.

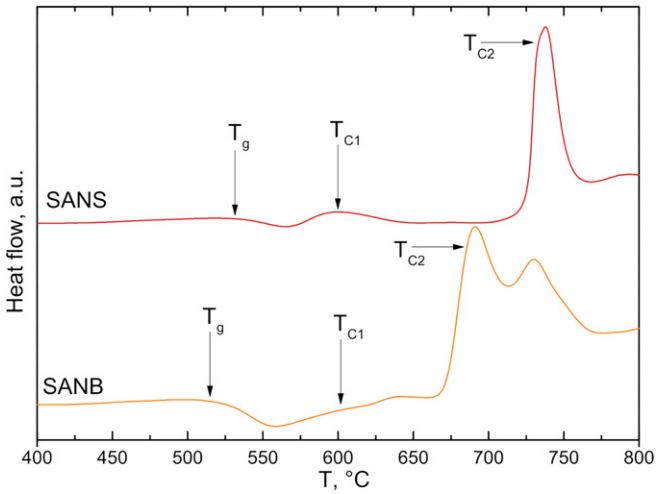

Fig. 1. DTA curves for the studied glass compositions.

Table 1
Temperature values determined from Fig. 1 with ±5 °C accuracy.

	SANS	SANB
T_g	520	507
T_{C1}	600	594
T_{C2}	735	691

3.2. PL investigations

Normalized PL spectra of the studied samples excited by 273 nm (shown in Fig. 4) have an intensive line peaking at 311.2 nm. This line is caused by the forced electric dipole transition $^6P_{7/2} \rightarrow {}^8S_{7/2}$ of Gd^{3+} ion [15–17]. The SANS composition glass ceramic samples heated at 600 and 650 °C have an additional peak at 310.5 nm. No change in the PL spectra was observed after the heat treatment of the initial glass samples of SANB composition.

3.3. EPR measurements

The EPR measurements of the glass samples (see Fig. 5) show features at g = 6.0, 2.8 and 2.0 characteristic to Gd^{3+} ions in disordered

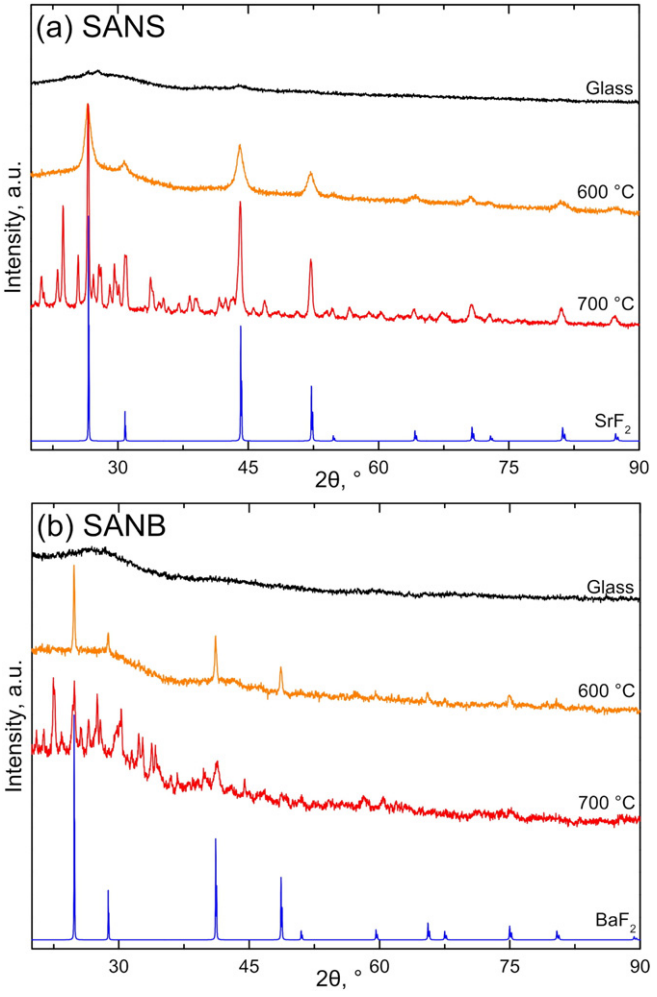

Fig. 2. XRD patterns of (a) SANS; (b) SANB glass and heat annealed samples with peak position calculation for the pure fluorite phase.