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Magnetic resonance study of the crystallization behavior of InF_3-based glasses doped with Cu^{2+}, Mn^{2+} and Gd^{3+}

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Abstract

The crystallization of fluoroindate glasses doped with Gd^{3+}, Mn^{2+} and Cu^{2+} heat treated at different temperatures, ranging from the glass transition temperature (T_g) to the crystallization temperature (T_c), are investigated by electron paramagnetic resonance (EPR) and ^{19}F nuclear magnetic resonance (NMR). The EPR spectra indicate that the Cu^{2+} ions in the glass are located in axially distorted octahedral sites. In the crystallized glass, the *g*-values agreed with those reported for Ba_2ZnF_6, which correspond to Cu^{2+} in a tetragonal compressed F^- octahedron and to Cu^{2+} on interstitial sites with a square-planar F^- co-ordination. The EPR spectra of the Mn^{2+} doped glasses exhibit a sextet structure due to the Mn^{2+} hyperfine interaction. These spectra suggest a highly ordered environment for the Mn^{2+} ions (close to octahedral symmetry) in the glass. The EPR spectra of the recrystallized sample exhibit resonances at the same position, suggesting that the Mn^{2+} ions are located in sites of highly symmetric crystalline field. The increase of the line intensity of the sextet and the decrease of the background line in the thermal treated samples suggest that the Mn^{2+} ions move to the highly ordered sites which contribute to the sextet structure. The EPR spectra of the Gd^{3+} doped glasses exhibit the typical *U-spectrum* of a s-state ion in a low symmetry site in disordered systems. The EPR of the crystallized glasses, in contrast, have shown a strong resonance in $g \approx 2.0$, suggesting Gd^{3+} ions in environment close to cubic symmetry. The ^{19}F NMR spin–lattice relaxation rates were also strongly influenced by the crystallization process that takes over in samples annealed above T_c. For the glass samples (doped or undoped) the ^{19}F magnetization recoveries were found to be adjusted by an exponential function and the spin–lattice relaxation was characterized by a single relaxation time. In contrast, for the samples treated above T_c, the ^{19}F magnetization-recovery becomes non-exponential. A remarkable feature of our results is that the changes in the Cu^{2+}, Mn^{2+}, Gd^{3+} EPR spectra and NMR relaxation, are always observed for the samples annealed above T_c.

Keywords: Glass ceramics; Fluorides; Nuclear magnetic (and quadrupole) resonance; Rare-earths in glasses; Electron spin resonance; NMR, MAS-NMR and NQR; Nuclear spin relaxation

1. Introduction

Rare-earth doped fluoride glasses have been the subject of intense investigations during the last decade, partly because of their potential importance in the development of optical devices based on active glass materials, such as solid state lasers and optical fiber amplifiers [1–5]. Since the optical and spectroscopic properties of active glass materials are strongly affected by devitrification, the study of the crystallization phenomena of these materials is of scientific and technological importance. A considerable number of studies have addressed the problem of crystallization and devitrification in fluoride glasses, using several experimental techniques such as X-ray diffraction (XRD), differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), scanning electron microscopy, fluorescence spectroscopy, and so on [6–11].

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EPR is a sensitive spectroscopic technique for the characterization of local order in a variety of solid-state systems. It has proven to be extremely useful to investigate the coordination environment of even very small concentration of paramagnetic centers, such as transition metals ions, rare earth ions and radiation-induced color centers, in glasses. Reported studies have been reviewed by [12–14]. Recently, Muralli et al., reviewed the EPR studies of Gd^{3+} in vitreous and polycrystalline materials [15]. Although there are a considerable number of EPR studies concerned with the interpretation of the paramagnetic doping spectra, few studies have been dedicated to elucidate their relation with the devitrification process, which takes place in the glass [13,16,17]. Scholz et al. [16] reported the X-band EPR spectrum of a recrystallized copper doped ZBLAN fluoride glass sample. Legein and coworkers [18] studied EPR spectra and temperature and concentration dependence of PZG fluoride glasses and amorphous GaF_3, as a function of the heating time, using Cr^{3+} and Fe^{3+} as paramagnetic probes. Edgar et al. reported the EPR spectrum of ZBLAN glass doped with Eu^{3+} ions. They interpreted the EPR line observed at $g \approx 2$ in the annealed samples as an indication of the formation of europium-doped crystals within the glass [19].

NMR has proven to be a powerful tool for the structural characterization of solids. As an element-selective method, sensitive to local interactions, as homo- and hetero-dipolar interactions and nuclear electric quadrupolar couplings, NMR line shapes and relaxation times studies can provide valuable information on the microscopic nature of glass materials and their crystallization phenomena [20–24].

In the present paper, the crystallization process of the fluoroindate glass $45.21InF_3$–$18.26ZnF_2$–$14.6BaF_2$–$18.26SrF_2$–$1.82GaF_3$–$1.82NaF$ is investigated by using both, NMR and EPR resonance techniques. Fluoroindate glasses are promising materials with potential applications as infrared optical materials. Since the development of these applications requires reduced intrinsic nucleation and crystal growth, the crystallization kinetics of the InF_3-based glasses have been extensively studied in the last decade by isothermal and non-isothermal methods [25–30,11]. In a previous paper we reported a DSC, XRD and ^{19}F nuclear magnetic resonance (NMR) investigation of the crystallization and nucleation processes occurring in the fluoroindate glass $40InF_3$–$20ZnF_2$–$20SrF_2$–$20BaF_2$. Samples were treated at different temperatures, ranging from glass transition temperature (T_g) to crystallization temperature (T_c), and several crystalline phases were identified in the annealed samples [23]. In this work, glass samples doped with very small concentration ($\approx$100 ppm) of paramagnetic ions, such as Cu^{2+}, Mn^{2+} and Gd^{3+} were studied by EPR and ^{19}F NMR relaxation. The measurements were performed as a function of thermal treatments made in the range between glass transition and above crystallization temperatures. The isothermal heat treatment of the samples were carried out at a given temperature during a period of 1 h and then quenched to room temperature.

2. Experimental

Fluoroindate glasses, of composition (in mol%) $45.21InF_3$–$18.26ZnF_2$–$14.6BaF_2$–$18.26SrF_2$–$1.82GaF_3$–$1.82NaF$ (IZBSGN), doped with paramagnetic ions, were prepared. The raw material (In_2O_3, ZnF_2, SrF_2, NaF and BaF_2) was mixed with 100 ppm of the appropriate paramagnetic ion (0.018 mol% of Gd^{3+}, 0.022 mol% of Cu^{2+} and 0.013 mol% of Mn^{2+}), and then melted at 800 °C for 1 h. The melt was then poured into a pre-heated form, for annealing at 265 °C for 2 h to remove any internal stress and allowed to cool slowly. For each doping element, all samples used in the experiments were cut and powdered from the same glass rod. The glass transition temperature (T_g), the onset of crystallization temperature (T_x) and the exothermic crystallization temperatures (T_c), as determined by differential scanning calorimetry (DSC) for the pure glass, are: $T_g = 553$ K, $T_x = 632$ K, $T_c = 658$, 669 K. Within the experimental error (± 3 K), the same values were obtained for the doped glasses. Isothermal heat treatment of the samples was carried out in a pre-heated furnace at a given temperature, ranging from room temperature to 723 K, during a period of 1 h and then quenched to room temperature. For the first group of samples, the procedure just described was realized under atmospheric air. In the case of copper samples, a second batch was prepared under N_2 atmosphere, using a low humidity dry box (0.15% r.h.).

EPR experiments were carried out at X-band frequency (9.6 GHz), using 100 mg of the samples inserted in 3 mm quartz sample tubes. Most of the EPR measurements were performed using a home-built spectrometer and some were taken with a commercial spectrometer Varian E-109. ^{19}F NMR relaxation times measurements were carried out at room temperature, at the frequency of 36 MHz with a home build pulsed NMR spectrometer equipped with a TECMAG NMR-kit. Spin–lattice relaxation times were determined using the saturation-recovery method. For these experiments, glass samples were cut into small pieces to fill the 4 mm diameter sample tubes. To monitor the emerging crystalline phases, X-ray powder patterns were taken at room temperature. Well defined diffraction peaks, assigned to crystalline structures such as InF_3, ZnF_2, BaF_2 and Ba_2ZnF_6, were observed only for samples treated above T_x. The absorption spectra in the 200–1000 nm wavelength region were measured at room temperature using a Cary 17 double beam spectrophotometer.

3. Results and discussion

3.1. Electron paramagnetic resonance

The EPR spectrum of the non-doped IZBSGN glass exhibit two weak and broad lines, with effective g-values, $g \approx 2.0$ and $g \approx 4.3$. The broad line with $g \approx 2.0$ has been attributed to clusters of more than one Fe^{3+} ion, whereas the line with $g \approx 4.3$ is assigned to an isolated Fe^{3+} ($3d^5$) ion in a rhombic distorted tetrahedron site symmetry