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Cross Relaxation in rare-earth-doped oxyfluoride glasses

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ABSTRACT

The excited-state relaxation dynamics of Tb^{3+}, Sm^{3+}, and Eu^{3+} doped into a $50SiO_2$–$20Al_2O_3$–$10Na_2O$–$20LaF_3$ (mol%) oxyfluoride glass are studied. Multiphonon relaxation of the primary emitting states in Tb^{3+} ($^5D_3$ and $^5D_4$), Sm^{3+} ($^4G_{5/2}$), and Eu^{3+} ($^5D_0$) was found to be negligible in the present host. The relaxation of Tb^{3+} ($^5D_4$) and Eu^{3+} ($^5D_0$) is dominated by radiative decay. For Tb^{3+} ($^5D_3$) and Sm^{3+} ($^4G_{5/2}$) in contrast, radiative relaxation is in competition with several non-radiative cross-relaxation processes. This competition was found to be particularly pronounced for the $^5D_3$ excited state in Tb^{3+}, where a 124-fold decrease of the ($^5D_3 \rightarrow {}^7F_5$)/($^5D_4 \rightarrow {}^7F_5$) emission intensity ratio and a ~10-fold shortening of the $^5D_3$ lifetime was observed upon increasing the Tb^{3+} concentration from 0.01% to 1%. The Tb^{3+} concentration dependence of $^5D_3$ also points to some degree of ion aggregation in the "as quenched" glasses. A Judd–Ofelt intensity analysis was performed for Sm^{3+} and used to estimate the relative magnitude of $^4G_{5/2}$ cross-relaxation processes. Four cross-relaxation processes in particular were identified to account for 92% of the total $^4G_{5/2}$ non-radiative decay, and a 11% quantum efficiency was estimated for the $^4G_{5/2}$ excited state. Non-exponentiality in the $^5D_0$ decay of Eu^{3+} is evidence for several Eu^{3+} coordination environments in the glass host that manifest in different $^5D_0$ decay constants because of the hypersensitivity of the $^5D_0 \rightarrow {}^7F_2$ transition.

1. Introduction

Oxyfluoride glasses have gained considerable attention over the past decade for applications in active and passive optical devices [1,2]. The addition of a metal fluoride – often in the form of LaF_3 – to an oxide melt affects several key properties of the resulting glass. First, the higher mass of F^- vs. O^{2-} lowers the average phonon energy as the fluoride content in an oxyfluoride glass is increased [3]. This reduces the multi-phonon relaxation rate of rare-earth ion (RE^{3+}) excited states [4], *i.e.* increases the quantum efficiency of the material. Second, the high rare-earth fluoride content achieved in some oxyfluoride glasses results in a relatively high refractive index [5] that enhances radiative relaxation rates and is desired for the design of waveguide devices. Third, at a given temperature, oxyfluoride glasses tend to have a higher crystallization rate than their fluoride-free counterparts [1]. As a result, metal fluoride crystalline phases tend to readily precipitate within the glassy matrix, which can lead to the formation of optically transparent glass ceramics [5]. The spectroscopic properties of such composite materials have been studied extensively [6], and RE^{3+}-doped glass ceramics show promise in a range of applications such as lasers, optical amplifiers, and upconversion materials.

The ease with which a fluoride crystalline phase can form within an oxyfluoride glass poses challenges when the preparation of a purely amorphous oxyfluoride glass is sought. Careful control of the melt-quenching and glass annealing conditions is required in order to suppress premature crystallization. This pre-ceramic glassy state is interesting because (1) it offers both oxygen and fluoride anions for coordination with RE^{3+} ions, and (2) it can contain compositional inhomogeneities that are the precursors for subsequent nucleation and growth of the crystalline phase. Both of these aspects can affect the relaxation dynamics of RE^{3+} ions. Goutaland et al. have performed excited-state lifetime measurements of Pr^{3+} and Er^{3+} doped into a SiO_2–Al_2O_3–Na_2O–AlF_3–LaF_3 oxyfluoride glass [7]. They found that some of these RE^{3+} ions occupy sites that are purely associated with oxygen while others are also coordinated by fluoride. This is evidence that some degree of separation into fluoride and oxide phases had already occurred in the glass [7]. Similarly, nano-sized phase separation droplets enriched in lanthanum and silicon have been found in SiO_2–Al_2O_3–Na_2O–LaF_3 glass by transmission electron microscopy [8].

In this paper, we focus on the nominally amorphous stage in SiO_2–Al_2O_3–Na_2O–LaF_3 oxyfluoride glass prior to the formation of

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a glass ceramic. We use Tb^{3+}, Sm^{3+}, and Eu^{3+} ions as local probes for ion-clustering and coordination geometry. Tb^{3+} (Section 3.2) and Sm^{3+} (Section 3.3) have excited states that can decay by two-ion cross relaxation, and they are used as sensitive probes for ion clustering. In contrast, the primary $^5D_0$ emitting state in Eu^{3+} cannot decay by cross relaxation and is used as a probe for the radiative decay in different coordination geometries (Section 3.4). Unlike in previous studies, a high 20 mol% nominal LaF_3 concentration was chosen here to enhance the ceramming tendency and the associated effects on RE^{3+} ions doped into the glass. The excited-state relaxation dynamics reveals competition between radiative decay, multi-phonon decay, and two-ion cross relaxation, depending on the nature of the excited state. From the concentration dependence of cross relaxation in Tb^{3+} we find that there is some degree of RE^{3+} ion aggregation in the "as quenched" glasses, which is reduced upon annealing at T_g-20 K. We also confirm the presence of several coordination geometries for RE^{3+} ions in the glass.

2. Experimental

2.1. Glass preparation

The starting materials were reagent grade SiO_2 (99.8%), Al_2O_3 (99.5%), Na_2CO_3 (99.5%), LaF_3 (99.99%), Tb_4O_7 (99.99%), Sm_2O_3 (99.99%), and Eu_2O_3 (99.99%). A melt-quench method was used to prepare Sm^{3+}, Eu^{3+}, and Tb^{3+} doped oxyfluoride glasses as well as an undoped reference (host) glass. The molar compositions are shown in Table 1. An excess of 1.0 mol% LaF_3 was added to each composition to compensate for possible fluorine evaporation losses during the melting of the glass. All the weighed chemicals were finely powdered and thoroughly mixed in an agate mortar before each batch (20 g) was melted in a covered alumina crucible at 1550 °C for 40 min in an argon gas atmosphere. Two types of quenching of the melt were used. The first method involved pouring of the melt onto a copper plate (10 cm diameter and 2 cm thickness) at room temperature and then quickly pressing with another identical copper plate. These "as-quenched" glass disks had a diameter of 3–4 cm, a thickness of ~0.3 cm, and good transparency. The second method involved pouring the melt directly into an insulated steel beaker filled with liquid nitrogen. This method of fast quenching yielded glass blobs suited for photoluminescence studies. Note that a nitrogen gas film formed around the hot glass melt blobs as they descended into liquid nitrogen, creating a rather complex thermal system that made it difficult to accurately estimate the actual cooling rate. However, the cooling rate in liquid nitrogen was clearly substantially larger than the rate achieved by quenching between copper plates. The internal stress induced in the glasses during melt quenching was released by annealing the samples at 575 °C for 10 h. Some glasses were cut to 20 mm × 20 mm × 2.0 mm size and mechanically polished to a mirror finish using a SiC/water polishing medium for the optical measurements.

Table 1
Molar composition of the eight oxyfluoride glasses prepared in this study. Also shown are the conditions of quenching (RT: room temperature between copper plates; LN2: into liquid nitrogen) and annealing (at 575 °C for 10 h).

No.	Composition (mol%)							Quench	Anneal
	SiO_2	Al_2O_3	Na_2O	LaF_3	Tb_4O_7	Sm_2O_3	Eu_2O_3		
H1	50	20	10	20				RT	Yes
H2	50	20	10	20				RT	No
Tb1	50	20	10	19	1.0			RT	Yes
Tb01a	50	20	10	19.99	0.01			RT	Yes
Tb01b	50	20	10	19.99	0.01			LN2	Yes
Tb01c	50	20	10	19.99	0.01			LN2	No
Sm1	50	20	10	19		1.0		RT	Yes
Eu1	50	20	10	19			1.0	RT	Yes

2.2. Sample characterization

The powder X-ray diffraction (XRD) profile was obtained on a Rigaku Ultima III diffractometer with CuKα ($\lambda=1.542$ Å) radiation using an applied voltage of 40 kV and 20 mA anode current, calibrated with Si at a rate of 2 deg/min. The surface morphology of the prepared oxyfluoride glasses was observed by scanning electron microscopy (Quanta 400 FEG- D 8055, FEI Company) and X-ray energy dispersive spectroscopy (EDS, equipped on Quanta 400 FEG-SEM). The thermal stability of the host glass was evaluated by differential scanning calorimetry (DSC; Netzsch DSC 404 F1). The measurement was carried out under dry air with a covered Pt–Rh crucible and using heating rates of 5, 10, 15, 20, and 25 K/min.

The UV–vis absorption spectra of all the studied glasses were measured on a Varian Cary 5000 double-beam and double-

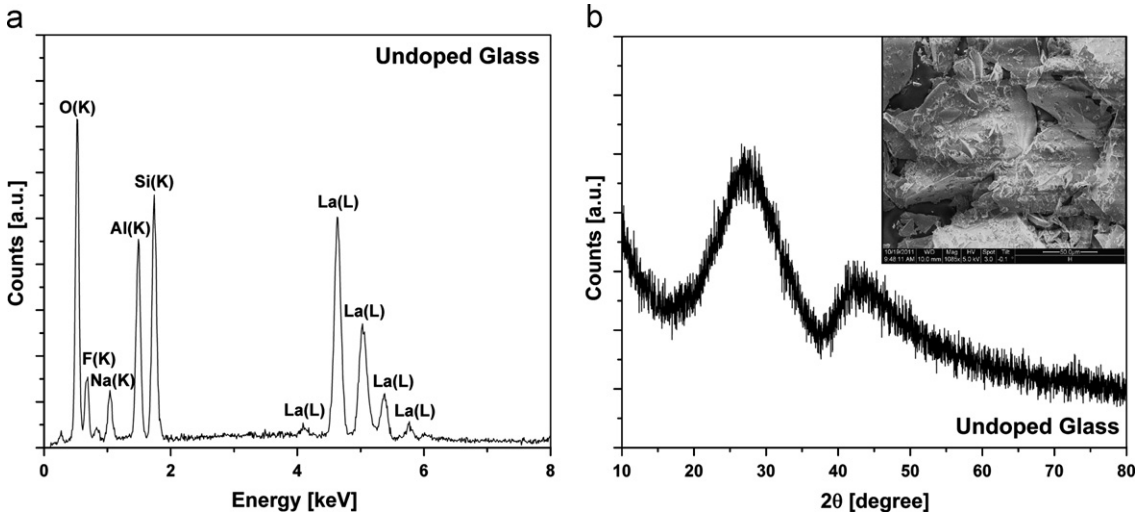

Fig. 1. (a) EDS spectrum of the undoped host glass (sample H1). All major glass constituents are identified and the respective X-ray line is indicated in parenthesis and (b) X-ray diffraction scan and SEM image (inset) of the undoped host glass (sample H1).