Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 134 (2015) 631–637

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Spectroscopic properties of transparent Er-doped oxyfluoride glass–ceramics with GdF_3 ☆

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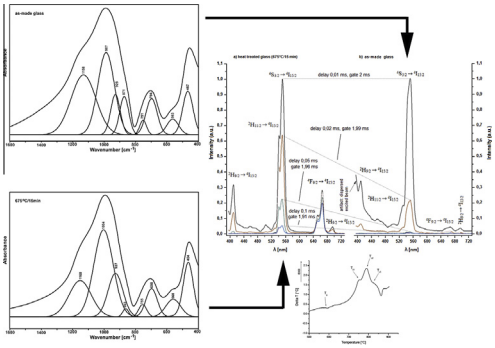
HIGHLIGHTS

- $NaGdF_4$ and $BaGdF_5$ fluorides doped with Er^{3+} was obtained in the glass–ceramics.
- Gd-containing fluorides can be a good host for incorporation of Er^{3+} ions.
- 3 and 8 times increase of luminescence lifetime from $^4S_{3/2}$ and $^4F_{9/2}$ was observed.
- The structural rigid of the framework influences the formation of fluorides.
- The formation of $Gd_{9.33}(SiO_4)_6O$ was confirmed at higher temperature.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 December 2013
Received in revised form 23 May 2014
Accepted 9 June 2014
Available online 28 June 2014

Keywords:
Oxyfluoride glass
GdF_3
Er
Transparent glass–ceramics
FTIR
Time-resolved spectroscopy

ABSTRACT

Optically active glass–ceramics (GC) with the low–phonon phases of fluorides, doped with Er^{3+} was studied. Glass based on SiO_2–Al_2O_3–Na_2F_2–Na_2O–GdF_3–BaO system was obtained. Dopant were introduced to the glass in an amount of 0.01 mol Er_2O_3 per 1 mol of glass. DTA/DSC study shows multi–stage crystallization. XRD identification of obtained phases did not confirm the presence of pure GdF_3 phase. Instead of that ceramization process led to formation of $NaGdF_4$ and $BaGdF_5$. The structural changes were studied using FT-IR spectroscopic method. The study of luminescence of the samples confirmed that optical properties of the obtained GC depend on crystallizing phases during ceramization. Time resolved spectroscopy of Er-doped glass showed the 3 and 8 times increase of lifetime of emission from $^4S_{3/2}$ and $^4F_{9/2}$ states, respectively. It confirms the erbium ions have ability to locate in the low phonon gadolinium-based crystallites. The results give possibility to obtain a new material for optoelectronic application.

Introduction

Optically active materials for optoelectronic application should give intensive fluorescence, which is highly dependent on efficiency of radiative decay from excitation states of the rare earth ions. Transparent oxyfluoride nano-glass–ceramics (GC) doping with rare earth (RE) ions have been shown recently to be promising materials for new optical devices such as bulk laser media and amplifying laser fibers for optical communications [1–3]. Oxyfluoride GC can be obtained by the process of the heat treatment of glass close to the glass transition temperature, in which fluoride crystallites are formed without clustering in the oxide glass matrix [4–8]. For the transparent oxyfluoride GC a combination of attractive optical properties with RE ion solubility in the fluoride compounds and high durability and easiness of oxide glasses

☆ Selected paper presented at XIIth International Conference on Molecular spectroscopy, Kraków – Bialka Tatrzanska, Poland, September 8-12, 2013.

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http://dx.doi.org/10.1016/j.saa.2014.06.066
1386-1425/

fabrication can be achieved. A problem arises to get glass in which low phonon fluoride nanocrystalites could be controllably formed without clustering by the thermal treatment and RE ions could be incorporated into them, simultaneously. The incorporation of RE ions into fluoride phase is distinct. Thus, new materials are searched to obtain low phonon hosts for the various optical active ions [9–12]. In last few years, most research on oxyfluoride GC was focused on inducing crystallization of $Pb_xCd_{1-x}F_2$ and LaF_3 nanocrystals [5–7,13–17] as well as Ba_2LaF_7, Sr_2LaF_7 [18,19].

In recent time, a few papers present a possibility of Gd-based fluorides to be obtained as low phonon phases [e.g. 18–21]. Most of them are focused on crystallite form of gadolinium fluoride as a host for optical active ions. It is likely to the low tendency to crystallization of gadolinium fluoride from the glass. In this work, the new gadolinium oxyfluoride alumino-silicate glass with barium modifier has been studied due to the spectroscopic properties of Gd-fluorides doped with Er^{3+}. The effect of glass structure on the process of Gd-based fluoride formation was analyzed.

Experiment

The SiO_2–Al_2O_3–NaF–Na_2O–GdF_3–BaO system was studied to obtain a chemical composition of glass which the batch could be melted at temperature below 1500 °C and the fluoride low phonon phase would appear after the heat treatment.

The following raw materials of analytical purity were used to prepare the batches: silica oxide (SiO_2), alumina oxide (Al_2O_3), gadolinium fluoride (GdF_3), sodium carbonate (Na_2CO_3), sodium fluoride (NaF) and barium oxide (BaO). RE-dopant of high purity was introduced to the glass in an amount of 0.01 mol Er_2O_3 per 1 mol of glass The composition of the investigated glass was following (mole%): $55SiO_2$–$17Al_2O_3$–$5Na_2F_2$–$8Na_2O$–$10GdF_3$–5BaO. It was calculated for the glass that the number of Er^{3+} ions per unit volume averages $5 \cdot 10^{19}$ ions/cm^3. All the chemicals were mixed properly using 5 min mechanical mixing to ensure the homogeneity. Oxyfluoride glass was obtained by melting 25 g batch in platinum crucibles in an electric furnace at temperature of 1450 °C in air atmosphere for 3 h. The crucible was covered with a platinum plate to reduce vaporization losses. The melt after holding at the melting temperature for 0.5 h was poured out onto a steel forming a layer thickness of 2–5 mm, than annealed at a temperature near the T_g and subsequently polished. The samples could have been obtained with good transparency.

The XRD analysis (Philiphs X'Pert Diffractometer with Cu Kα radiation) was used to confirm the amorphous nature of glass and products of the thermal treatment. The ability of the glass to crystallization was determined by DTA/DSC measurements conducted on the Perkin Elmer DTA-7 System operating in heat flux DSC mode for obtaining Δc_p and ΔH parameters. The samples of 60 mg in weight were heated in a platinum crucible at a rate 10 °C min^{-1} in dry nitrogen atmosphere to the temperature 920 °C.

FTIR spectra were recorded with a Bruker Company Vertex 70v spectrometer. Spectra were collected in the middle infrared regions (MIR) 4000–400 cm^{-1} after 128 scans at 4 cm^{-1} resolution. Samples were prepared by the standard KBr pellets methods. Spectra deconvolution has been carried out according to the method proposed by Handke et al. [22].

The time resolved emission spectra were obtained using Luminescence LS50B Spectrometer by Perkin–Elmer. The fluorescence decay measurements were carried out with a pulsed tunable dye laser as an excitation source, working at 379 nm line. The fluorescence was dispersed by 0.4 m monochromator, detected by photomultiplier working in photon counting regime and recorded by a digital boxcar integrator system or the SR400 Dual-Channel Gated Photon Counter.

Results

DTA/DSC and X-ray characterization

DTA/DSC study of the glass shows multi-stage crystallization (Fig. 1). XRD identification of the obtained phases did not confirm the presence of pure GdF_3 phase. Instead of that ceramization process led to formation of $NaGdF_4$ and $BaGdF_5$ phases on the first stage of crystallization. The phase of $Ba_{0.625}Er_{0.375}F_{2.375}$ could be fitted in a pattern of the X-ray diagram, simultaneously (Fig. 2). The size of crystallites was calculated from the Scherrer formula. The fluoride phase was estimated to be 41 nm in size. Our study of the glass system confirmed that when Na displaces Ba ions in the glass composition $NaGdF_4$ is preferable to crystallize from the glass. Gadolinium ions show also adverse ability to form gadolinium silicate ($Gd_{9,33}(SiO_4)_6O_2$) at the next stage of glass crystallization. The $NaAl_3Si_3O_{11}$ crystals form as a third phase at higher temperature what makes the sample viewless (Fot. 1). All these phases crystallize without significant temperature separation at a range from 650 to 860 °C. The thermal properties are shown in Table 1 for DTA/DSC analysis.

FTIR study

Fig. 3 shows FTIR spectra of the as-made glass and the glass after thermal treatment in comparison with spectrum of the pure GdF_3 phase. GdF_3 shows intensive bands in the region 600–400 cm^{-1}. For spectra of the glass three broad bands in the middle infrared region (1600–400 cm^{-1}) are visible. The most intense absorption bands are observed in the 1300–850 cm^{-1} and 500–400 cm^{-1} regions. The less intensive bands is in the 800–650 cm^{-1} region.

The absorption band 1300–850 cm^{-1} is assigned to antisymmetric stretching vibrations of the bridging Si—O—Si bonds within [SiO_4] tetrahedral [23]. Its width is the result of the occurrence in the glass structure of Q^n units, where Q refers to a silicate tetrahedron with n non-bridging oxygen (NBO). When the value n increases from 0 to 4 the absorption bands shift to lower wavenumbers. Similar effect is observed when Si^{4+} is substituted by Al^{3+} in aluminosilicate which is due to weaker bonding Al—O [24]. The band 800–650 cm^{-1} is connected with Si—O—(Si, Al) symmetric stretching vibrations between the tetrahedra. In the nepheline glass the [SiO_4] tetrahedral are combined with four [AlO_4] tetrahedra in the structure and the maximum of this line

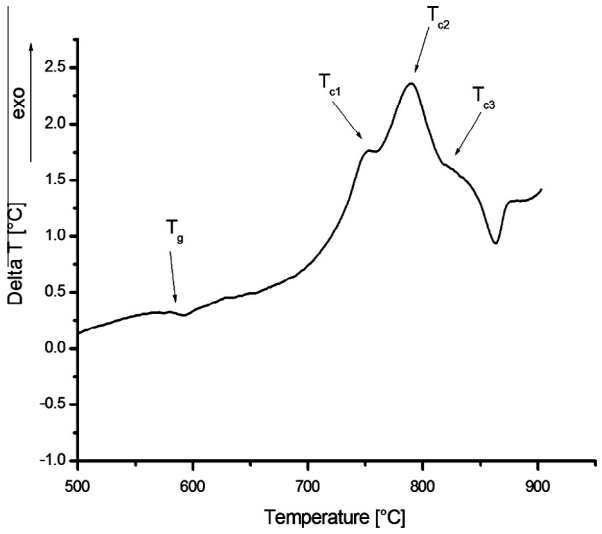

Fig. 1. DTA curve of gadolinium oxyfluoride aluminosilicate glasses.