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Influence of lead and cadmium fluoride variation on white light emission characteristics in oxyfluoride glasses and glass–ceramics

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ABSTRACT

The radiative properties of Dy-doped glasses and glass–ceramic phosphors with varying lead and cadmium fluoride content are investigated in the present study for white light emitting applications. The precipitation of cubic lead fluoride phase of 10–18 nm crystallites was determined with the help of x-ray diffraction studies and the nanocrystalline nature was confirmed with scanning electron microscopy studies. The small size of the nanocrystallites enables the fabrication of transparent glass–ceramics which is verified by UV–vis spectroscopic study. The photoluminescence and lifetime measurements indicate towards progressive changes in the Dy^{3+} ion surroundings and propose enhanced energy transfers taking place post-heat treatments. Finally, CIE chromaticity coordinates are found to lie in the white region proposing the suitability of the present studied materials for color display devices.

1. Introduction

Oxyfluoride glass–ceramics (GCs) have been considered as the most attractive rare earth (RE) ion hosts due to their two fold advantages which comprise low phonon energy of fluoride crystallites (300–400 cm^{-1}) along with superior mechanical and chemical stability of oxide base matrix [1,2]. The low vibrational phases formed after thermal treatment near crystallization peak are capable of accommodating the trivalent rare earth (RE^{3+}) ions on account of nearly similar ionic radii. This phenomenon promoted these glass composites in the field of high quality optically active devices [3]. Moreover they can be fabricated and manipulated in air and the process of thermal treatment improves the mechanical, chemical and optical properties of the materials. It is on account of the ease of formability and the mixed nature of fluoride, oxide environments that the oxyfluoride GCs have given potential replacements to individual existence of glasses and crystals [4,5].

The first RE-doped oxyfluoride GC composition proposed by Wang [6] gained enormous interest from researchers of glass fraternity. The composition was further explored with variations in components and presented interesting optical applications. Among the studied compositions lead and cadmium fluoride based compositions were most widely exploited in terms of the study of upconversion emission efficiency [7,8] and the effect of the variations in the RE content [9] on emissive properties. These compositions mostly precipitated cubic lead fluoride or $Pb_xCd_{1-x}F_2$ phases which could easily accommodate RE^{3+} ions and intensified emission efficiencies in comparison to the precursor glass. "*The PbF_2/CdF_2 are designated as toxic substance by RoHS in 2006 but at the same time*" cadmium fluoride was established to play important role in glass formation and further strengthening of glass network [10–12]. "*The energy difference in the levels of Dy^{3+} ion are very close and thus results in easy cross relaxation, the luminescence of Dy^{3+} is not strong as compared with Ce^{3+}, Tb^{3+}, Eu^{2+} in glasses*". It may be noted that relatively very few reports exist on Dy^{3+} ions in glass ceramics [13–18]. Martin et al. [13] found that optical amplification observed at 575 nm is due to emission of Dy^{3+} ions into $Ba_2TiSi_2O_8$ nanocrystals. Babu et al. [14] studied the lead and cadmium based composition doped with varying Dy^{3+} ion content for white light emitting application.

Specifically, Dy^{3+} ion is a capable emitter of two intense transitions in blue (470–500 nm) and yellow (560–600 nm) regions by transitions between its intra 4f levels. A combination of these two emissions, adjusted in a suitable ratio induces the capability of white light emission [15]. Also the research and development of white light emitting diodes (WLEDs) has witnessed an enormous upsurge

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[16–18]. In this regard compared to conventional phosphors, glasses and GCs doped with RE^{3+} ions offer an alternative approach with low cost production, simple manufacturing procedure, free from halo effect and environment friendly characteristics [19].

Thus, the present study chooses a sister composition of [14] with varying lead and cadmium fluoride content and constant (0.7 mol%) Dy^{3+} ion content for further exploration. It would be interesting to observe the change in thermal, structural, optical properties and consequently the white light emission characteristics due to increase in lead fluoride at the cost of cadmium fluoride. The characterizations or thermal properties are carried out with the help of differential thermal analysis (DTA) which enables determination of thermal treatment window for conversion into GCs. The post-heat treatment glasses i.e. GCs are qualitatively characterized by x-ray diffraction spectroscopy (XRD). The transparency of the samples is analyzed by UV–vis spectroscopy while Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy determines the structure of the formed glasses and GCs. Finally, photoluminescence studies have been carried out to compare the spectroscopic efficiency of the Dy^{3+} ions before and after heat treatment. The photoluminescence spectra was further used to determine the quality of white light emitted on CIE 1931 chromaticity scale and to determine the role of lead and cadmium fluoride for efficient white light emission. In this manner this work tries to fill in the interstices in the ongoing research of GCs as white light emitting phosphors.

2. Experimental

2.1. Glass preparation

The glass samples were prepared by mixing appropriate amounts of chemically pure SiO_2, Al_2O_3, PbF_2, CdF_2, YF_3 (Aldrich Chemical Company; purity 99.9%) and DyF_3 (Alfa Aesar, USA; purity 99.9%) in platinum crucible. Homogeneous mixtures of 50 g batches were obtained by ball milling and then placed in an electric furnace capable of reaching a temperature of 1600 °C and were heated at a temperature of 1100 °C for 1 h under normal atmospheric conditions. Glasses were obtained in bulk form by pouring the melts on preheated bronze molds and were subsequently annealed in a separate annealing furnace in order to release inner stresses. The bulk samples D1G and D2G were grounded with the help of an electric machine using different grades of SiC abrasives and aluminium oxide with machine oil by setting the sample in a specially designed holder to maintain the two faces parallel. The polishing was done with cerium oxide to obtain flatness and thickness was measured with the help of digital micrometer. Table 1 summarizes the nominal composition and thickness of two Dy-doped matrices briefly labeled as D1G and D2G.

2.2. Differential thermal analysis

The thermal properties of the studied glass systems D1G and D2G were measured using an STA449*F1* Jupiter (NETZSCH, Germany) DTA equipment. Samples were held in an alumina crucible and analyzed by taking air as reference at a heating rate of 10 °C min^{-1} under flowing dry argon [20].

Table 1
Mol% batch compositions of glasses D1G and D2G.

Matrix	Composition (mol%)						Thickness (mm)
	SiO_2	Al_2O_3	CdF_2	PbF_2	YF_3	DyF_3	
D1G	34	14	27	23	2	0.7	3.2
D2G	34	14	23	27	2	0.7	2.5

2.3. Heat treatment

Heat treatments were carried out on bulk glass samples with the help of Carbolite RWF 1100 furnace in accordance with the characteristic temperatures obtained from DTA data. Powders were obtained post-heat treatment by grinding part of the heat treated bulk glass for morphological and structural analysis. Both the Dy-doped glasses D1G and D2G were annealed at 450 °C for varying time 12, 24 and 36 h.

2.4. Structural and morphological analysis

Scanning electron microscopy (SEM) images were obtained by using a Zeiss Ultra 55 FESEM, with 3 kV accelerating voltage at 50k × magnification. The X-ray Diffraction (XRD) measurements were carried out with a Panalytical Xpertpro MPD diffractometer equipped with Xcelerator RTMS (Real Time Multiple Strip) diffracted beam monochromator, using the Cu Kα radiation ($\lambda = 1.5405$ Å). The size of the nanocrystallites was calculated by using the Scherrer formula [21] given by

$$D = 0.9\lambda_{inc}/\beta \cos \theta \quad (1)$$

where D is the crystallite size, λ_{inc} is the incident wavelength, β is the full width at half maximum of the diffraction line and θ is the position of the maximum of the peak. The amount of the crystalline phase was estimated from XRD measurements by calculation of the ratio R defined [22] by

$$R = A_1/A_2 \quad (2)$$

where A_1 is the total area of the crystalline peaks and A_2 is the total area of the XRD diagram obtained by integration in the range $2\theta = 20°–55°$.

Fourier transform infrared spectroscopy of studied glass and GC systems in the range from 400 to 4000 cm^{-1} was carried out using an IR Affinity-1 (Shimazdu Co., Japan) instrument equipped with powder sample analysis accessory (DRS-8000A Diffuse Reflectance Spectroscopy) [20]. Raman spectra were collected using a home-built micro-Raman setup equipped with a notch filter for rejection of elastically scattered light, and with a 550 mm triple grating monochromator. Excitation light provided by a 532 nm laser was delivered to the sample by a 20 × microscope objective and the scattered light was collected by the same optics in a backscattering geometry. The grating commonly used had 1200 g/mm and the center position of the monochromator was 700 cm^{-1}. Light was detected by a liquid-nitrogen cooled CCD. The spectral acquisition time was varied from 1 s to 10 s to achieve a good signal to noise ratio [15].

2.5. UV–vis spectroscopy

The transparency of the bulk glasses D1G and D2G and their corresponding GCs were measured using a UV–vis spectrophotometer (UV-2600, Shimadzu Co., Japan). The spectra were recorded in the wavelength range of 200–1100 nm with spectral resolution of 0.1 nm.

2.6. Photoluminescence spectroscopy

Luminescence emission and excitation spectra of bulk glasses and GCs were recorded on a spectrofluorimeter (Horiba Jobin Yvon Fluorolog 3-22) equipped with a 450 W continuous wave xenon lamp and double monochromators for excitation and emission. The detector was a Hamamatsu R2658 photomultiplier operating