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Preparation and spectral properties of Nd^{3+}-doped transparent glass ceramic containing $Ca_5(PO_4)_3F$ nanocrystals

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ABSTRACT

A Nd^{3+}-doped transparent oxyfluoride glass ceramic containing $Ca_5(PO_4)_3F$ nanocrystals was prepared by thermal treatment at the crystallization temperature for the precursor glass. The transmittances of the precursor glass and the glass ceramic with a thickness of about 2 mm are up to 84.7% and 77.4% in the visible range. The volume fraction of $Ca_5(PO_4)_3F$ nanocrystals in the glass ceramic is about 19% and the ingress fraction of Nd^{3+} ions into the $Ca_5(PO_4)_3F$ nanocrystals is about 32%. The peak absorption cross-section increases to 224% at 807 nm and the full width at half maximum for the 807 nm band decreases from 17.5 to 3.5 nm after the crystallization process. The peak stimulated emission cross-section increases from 1.89×10^{-20} to 2.42×10^{-20} cm^2 at 1062 nm and the effective width of the emission line for the 1062 nm band decreases from 34 to 29 nm after the crystallization process. The improvement of spectroscopic properties indicates that the glass ceramic is potentially applicable as the 1.06 μm laser material.

1. Introduction

Nd^{3+} is the most widely studied active ion in solid state laser. Laser with low threshold and high slope efficiency has been realized in Nd^{3+}:$Ca_5(PO_4)_3F$ (Nd^{3+}:FAP) crystal [1,2]. However, the poor thermomechanical properties and inadequate crystal quality of the FAP crystal [3] make it hard to be applied for high power laser. Furthermore, the growth of the single crystal is difficult and costly.

Transparent glass ceramics are obtained from precursor glasses by thermal treatment close to the crystallization temperature [4]. This kind of materials may combine the luminescence characteristics of rare earth ions in crystalline environment with the easy fabrication, high mechanical, chemical and thermal stabilities of the glass [5,6]. The key factors for this combination are the ingress of the rare earth ions into the precipitated nanocrystals and the maintenance of the transparency [7,8].

Laser operations have been successfully performed in some Nd^{3+}-doped lithium aluminosilicate (LAS) glass ceramic [9,10]. The upconversion luminescence of Er^{3+} ions has been reported for the oxyfluoride glass ceramic containing FAP nanocrystals [11]. The luminescence of Nd^{3+} ions has been observed for the oxyfluoride glass ceramic containing CaF_2, LaF_3 and PbF_2 nanocrystals, respectively [12–14]. To our knowledge, the spectroscopic properties of Nd^{3+}-doped oxyfluoride glass ceramic containing FAP nanocrystals have not been reported detailedly. In this work, a Nd^{3+}-doped transparent oxyfluoride glass ceramic containing FAP nanocrystals is prepared and the spectroscopic properties of Nd^{3+} ions in the glass ceramics are studied.

2. Experimental

The $29.4SiO_2$–$18.0Al_2O_3$–$12.0P_2O_3$–$20.0CaCO_3$–$18.0CaF_2$–$0.3La_2O_3$–$0.5Li_2CO_3$–$0.3B_2O_3$–$0.5ZrO_2$:$1.0Nd_2O_3$ (mol%) precursor glass (denoted as Nd^{3+}:PG) was prepared by melting a mixture of reagent grade chemical composition in an alumina crucible at 1450 °C for 2 h under air atmosphere. The melt was poured into a 280 °C preheated copper mold and then cooled down to room temperature naturally. The transparent glass ceramic (denoted as Nd^{3+}:GC) was obtained through crystallization after heating Nd^{3+}:PG at 790 °C for 24 h. The Nd^{3+} concentrations in Nd^{3+}:PG and Nd^{3+}:GC were estimated to be about 3.54×10^{20} and 3.66×10^{20} ions/cm^3, respectively. Two samples with thicknesses of 1.96 and 1.98 mm were cut from Nd^{3+}:PG and Nd^{3+}:GC, respectively. All the surfaces of these samples were polished for spectral experiments.

Differential scanning calorimetry (DSC) experiments were carried out with a DSC apparatus (STA449C, Netzsch) at a heating rate of 10 °C min^{-1}. To identify the crystallization phase, X-ray diffraction (XRD) analysis was carried out with a powder diffractometer (DMAX2500, Rigaku). Sizes and morphologies of the Nd^{3+}:GC sample were measured by a transmission electron microscope (TEM) (JEM-2010, JEOL). TEM specimen was prepared by dispersing the fine powder grinded from the bulk sample in ethanol, followed by ultrasonic agitation, and then depositing onto a carbon copper grid. Room temperature absorption and transmission spectra were recorded by a spectrophotometer (Lambda35, Perkin-Elmer). Room

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temperature emission spectra were recorded by a spectrometer (FL920, Edinburgh) using a Ti:sapphire laser (Model 3900s, Spectra-hysics) as the pump source. Transmission spectra at 3 K were recorded by a spectrophotometer (1000 M, SPEX). Emission spectra at 5 K were recorded by the spectrophotometer using the Ti:sapphire laser as the pump source. Room temperature fluorescence decay curves of the $^4F_{3/2}$ level for Nd^{3+} ions were recorded with a near infrared photomultiplier tuber (R5509, Hamamatsu) when the samples were excited at 807 nm by a microsecond flash lamp (μF900, Edinburgh).

Refractive indices of Nd^{3+}:PG and Nd^{3+}:GC at 473.0, 532.0, 632.8 and 1064.0 nm at room temperature were measured by the auto-collimation method [15]. The measured refractive indices of Nd^{3+}:PG and Nd^{3+}:GC, n_{pg} and n_{gc} respectively, are listed in Table 1. By fitting the data in Table 1, two rough Sellmeier equations of the refractive indices of Nd^{3+}:PG and Nd^{3+}:GC, respectively, were obtained

$$n_{pg}^2 = 2.4684 + \frac{23,200}{\lambda^2 + 56,400} \quad (1)$$

$$n_{gc}^2 = 2.4758 + \frac{26,500}{\lambda^2 + 70,000}. \quad (2)$$

3. Results and discussion

Fig. 1 shows the DSC curve of the Nd^{3+}:PG, where T_g (690 °C), T_{c1} (790 °C) and T_{c2} (905 °C) stand for the glass transition temperature, the crystallization temperatures for FAP and mullite, respectively [11,16]. For comparison, the DSC curve of the undoped PG is also shown in Fig. 1. It can be seen that the undoped PG has a similar glass transition temperature (687 °C), but the crystallization temperatures decreased to 761 °C and 878 °C, respectively. It reveals that the doped Nd_2O_3 can hinder the crystallization of FAP and mullite in the PG. Therefore, the Nd^{3+}:PG was heated at 790 °C for the crystallization of FAP. Fig. 2 displays the XRD pattern of the Nd^{3+}:GC. All diffraction peaks matched well with the standard data of hexagonal phase FAP (JCPDS 87-2462). The TEM image of the Nd^{3+}:GC shown in Fig. 3 exhibits that the FAP nanocrystals have a 10–45 nm size range among the glassy matrix.

The photographs of the Nd^{3+}:PG and Nd^{3+}:GC samples for spectral experiments are shown in the insets of Fig. 4, which display that the Nd^{3+}:PG and Nd^{3+}:GC are transparent in the visible range. As shown in Fig. 4 the transmittances of the Nd^{3+}:PG and Nd^{3+}:GC reach 84.7% and 77.4%, respectively, at 633 nm without the absorption of Nd^{3+} ions. The transmittance of glass ceramic would depend on the difference between the refractive indices of the crystal and glass, as well as the size and distribution of crystals in the glassy matrix [17]. The refractive indices n_a and n_c for *a* and *c* axes of FAP crystals, respectively, which are determined from the Sellmeier equations in Ref. [18], are also listed in Table 1. It can be seen from the table that the refractive indices of Nd^{3+}:GC are between those of Nd^{3+}:PG and FAP crystals. Similar result has also been found in the glass ceramic containing $LiNbO_3$ crystals [19]. Since the difference between the refractive indices of FAP crystal and Nd^{3+}:PG is only around 0.044, the size and distribution of FAP crystals in the glassy matrix would be the main factors affect the transparency of

Table 1
Refractive indices of Nd^{3+}:PG, Nd^{3+}:GC and FAP crystals.

λ (nm)	473.0	532.0	632.8	1064.0
n_{pg}	1.5974	1.5925	1.5874	1.5773
n_{gc}	1.6017	1.5975	1.5910	1.5805
n_a[a]	1.6415	1.6367	1.6314	1.6221
n_c[a]	1.6394	1.6347	1.6294	1.6201

[a] Data from Ref. [18].

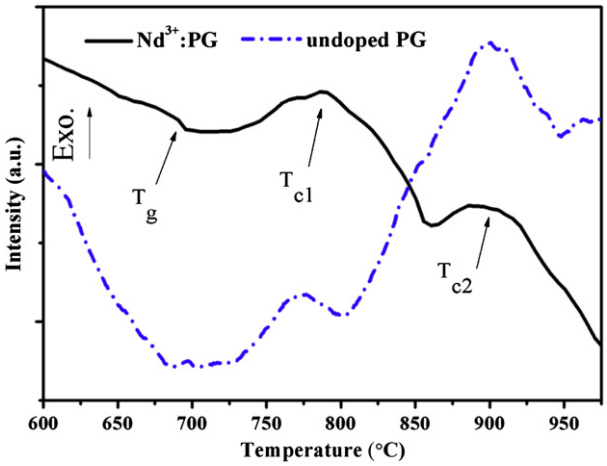

Fig. 1. DSC curves of Nd^{3+}:PG and undoped PG.

Nd^{3+}:GC. The transparency loss and the decline of the baseline at short wavelength for Nd^{3+}:GC imply that the sizes of some nanocrystals in the Nd^{3+}:GC are larger than the visible light wavelength [20]. The transmittance of Nd^{3+}:GC at wavelength λ, where there is not any absorption, can be evaluated by the equation: [21]

$$T = \exp\left\{-\frac{32\pi^4\varphi_c x r^3 n_{pg}^4}{\lambda^4}\left[\frac{\left(n_f/n_{pg}\right)^2-1}{\left(n_f/n_{pg}\right)^2+2}\right]^2\right\} \quad (3)$$

where ϕ_c is volume fraction of FAP nanocrystals, r is size of FAP nanocrystals and 27 ± 4 nm was adopted, x is the optical path length and was equivalent to the sample thickness, n_f is the average refractive index of FAP crystal and was calculated following $n_f = (2n_a + n_c)/3$. From the 77.4% transmittance of Nd^{3+}:GC at 633 nm, the volume fraction of FAP nanocrystals ϕ_c could be estimated to be about $19 \pm 6\%$.

The room temperature absorption spectra of Nd^{3+} ions for Nd^{3+}:PG and Nd^{3+}:GC are shown in Fig. 5. The absorption bands are corresponding to the transitions from the ground multiplet $^4I_{9/2}$ and the final multiplets marked in the figure. Compared to those of the Nd^{3+}:PG, the crystal-like absorption bands of the Nd^{3+}:GC reveal the incorporation of Nd^{3+} ions into the FAP nanocrystals. The peak absorption cross-section at 807 nm increases up to 224% after crystallization. The full width at half maximum (FWHM) of the absorption band around 807 nm is about 3.5 nm for Nd^{3+}:GC, which is much narrower than the 17.5 nm for Nd^{3+}:PG, but broader than the 2.5 nm for Nd^{3+}:FAP crystal [22].

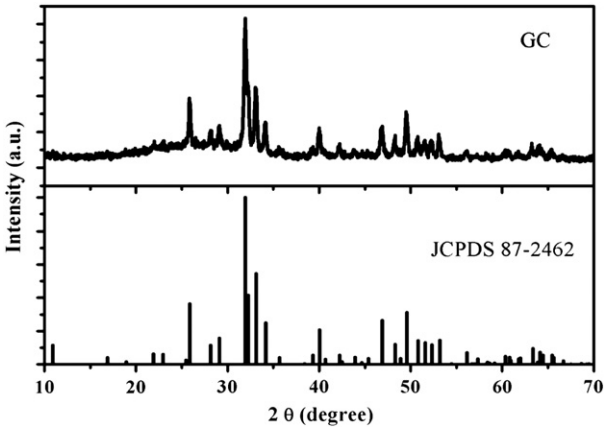

Fig. 2. XRD pattern of Nd^{3+}:GC, the bars represent the diffraction pattern of the standard hexagonal phase FAP.