



# Rare earth ions feel the electric: A novel strategy to obtain efficient near-infrared photoluminescence

Yangjian Cai, Gongxun Bai, Shiqing Xu, Junjie Zhang\*

College of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, PR China



## ARTICLE INFO

### Article history:

Received 29 May 2018

Received in revised form

21 July 2018

Accepted 24 July 2018

Available online 25 July 2018

### Keywords:

Photoluminescence

Near infrared

Ferroelectric

Polarization

Optoelectronic

## ABSTRACT

Ferroelectrics doped with active luminescent ions have gradually paved the path of optoelectronic industry due to their multifunctionality and the dynamic modulation of luminescent properties through electric method widely broadens their application prospect in future devices. In this work, a novel strategy without compositional change is employed on the  $\text{Er}^{3+}$  doped transparent hybrid enriched with nano-sized ferroelectric  $\text{LiNbO}_3$  crystals to investigate the tunable photoluminescence performance. The results demonstrate that the photoluminescence acquires a tremendous boost after polarization engineering, that is, a six times enlargement. This notably light amplification effect is propelled by the reduction of environmental symmetry around luminescent  $\text{Er}^{3+}$  ions that is originated from electric polarization. Additionally, the prepared samples are proved to possess optical and electric properties simultaneously. Therefore, this multifunctional material with tunable luminescent properties is beneficial for regulating the physical couplings of electric and optics, which highlights the prospect in future optoelectronic industry.

© 2018 Published by Elsevier B.V.

## 1. Introduction

Ferroelectric materials including crystals, ceramics, polymer-based dielectrics and glass ceramics are playing more and more vital roles in 3D display [1–3], non-volatile memory devices, energy storage industries [4–7] and some non-linear domains such as hologram storage, phase conjugation, optical resonator [8–13] due to their excellent dielectric properties. Among them, the glass ceramics containing ferroelectric crystallites are becoming researching hotspot because they possess lots of merits over other matrixes. Normally, through secondary annealing process in the glassy phases, the homogeneous distribution of crystallites inside the glass matrix with controllable size can be realized. Meanwhile, depending on the feature of crystallites, the obtained crystal-in-glass composite which is the so-called glass ceramic (GC) presents new kinds of functionalities such as ferroelectric properties. Additionally, highly compositional flexibility enables the transparency of GC materials, which broadens their application in optical industry [14,15]. And as for being the matrix of ferroelectric materials, excellent thermal stability originated from the high

transition temperature of glass provides a better thermal performance and the dense structure of glass matrix would increase their breakdown strength (BDS), which is beneficial when applied in elevated temperatures and electric fields. Therefore, ferroelectric glass ceramics are potential candidates for energy storage devices or applications carried out at elevated temperatures [16].

With the increasing need for the ferroelectric materials to be multifunctional [17–20], such as owning luminescent properties as the benefits of luminescent materials permeate almost every facet of our lives [21–24], rare earth ion doped ferroelectric glass ceramics are emerging [25]. The investigations nowadays are mainly focused on the visible region (0.3–0.8  $\mu\text{m}$ ) [26–31] and fewer on infrared wavelength [32,33], which means their applications in the infrared wavelength region (NIR and MIR) are still limited and worth of intense research while the light sources operating in this special band are of vast researching value due to their potential in fields of soft-tissue medicine, military defend and environmental detection [34,35]. Among different kinds of rare earth elements,  $\text{Er}^{3+}$  ions are widely applied to generate  $\sim 1.5 \mu\text{m}$  emission because of  $\text{Er}^{3+}$ :  $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$  transition [36], at which the materials possess a vast prospect in biomedicine, optical communication and so on [37–40]. Therefore, ferroelectric glass ceramics doped with  $\text{Er}^{3+}$  ion are of researching prospect as they have the potential to fabricate devices acting in double modes like optical source and

\* Corresponding author.

E-mail address: [jjzhang@cju.edu.cn](mailto:jjzhang@cju.edu.cn) (J. Zhang).

capacitors at the same time [30,41,42]. In this case, the ferroelectric lithium niobate ( $\text{LiNbO}_3$ ) is chosen as the doping matrix because it has been widely used in memory devices, optical phase modulators, Q-switches, filters, second-harmonic generators and so on [3,43] due to the outstanding ferroelectric properties such as the large pyroelectric, piezoelectric, electro-optic, and photo-elastic coefficients because of its oxygen octahedral structure [44]. The  $\text{LiNbO}_3$  crystal belongs to the hexagonal system under its Curie temperature around 1210 °C, thus it can be applied at elevated temperatures to meet the requirements for some specific applications [30].

The photoluminescence (PL) spectroscopic property has been the key parameter to evaluate the prospect of optoelectronic materials doped with active luminescent center, therefore the enhancement of NIR PL is urgent in this rare earth ions doped ferroelectric glass ceramic system. Up to now, prior investigations have implemented diverse approaches to the modification of PL by compositional change such as changing the composition of host materials or doping ions [45–48], which hinders the further understanding of kinetic process between luminescence and the symmetry of ligand field because the chemical way is irreversible. Therefore, from this point of view, the investigation of rare earth ions doped ferroelectric glass ceramic is definitely imperative due to the unique oxygen octahedron of ferroelectric phase that is sensitively tunable towards external electric field, which promotes the analysis of the dynamic relationship between photoluminescence and environmental symmetry. Meanwhile, the enhancement of luminescent performance without compositional change in this material is also of great value from the energy saving point of view.

Therefore, in this work, the transparent  $\text{Er}^{3+}$  doped ferroelectric glass ceramic with high crystallinity are synthesized to satisfy the need of being multifunctional, and a novel approach to realize the enhancement of NIR PL due to the special oxygen octahedral structure of ferroelectric  $\text{LiNbO}_3$  phase is performed.

## 2. Experimental

### 2.1. Samples fabrication

The glasses of the following composition:  $x\text{Li}_2\text{O}-x\text{Nb}_2\text{O}_5-(100-2x)\text{SiO}_2-1\text{Er}_2\text{O}_3$  were prepared by the traditional melting method with all the raw materials of high purity. The raw materials were well mixed and then placed to the alumina crucible to melt at 1500 °C for 45 min. And then the transparent glasses were obtained by cold-press method after pouring the melt to the cold stainless steel plate. After that, the samples were annealed at 450 °C for 2 h to release the residual stress. The as-quenched glasses were firstly heat treated at 580 °C for 2 h for nucleation process and then at 640 °C for 0.3, 0.75, 1, 3, 5 h respectively for growth process to obtain glass ceramics enriched with  $\text{LiNbO}_3$  crystallites, and the samples were named as LNO-0 (precursor glass), LNO-0.3, LNO-0.75, LNO-1, LNO-3, LNO-5 hereafter for convenience. Then they were cut into desired dimension to make optical measurements. The samples were painted with silver paste on both sides to be electrodes for ferroelectric test.

### 2.2. Measurements

The density of the sample was tested by the Archimedes method using distilled water as an immersion liquid with the error limit within 0.001  $\text{g}/\text{cm}^3$ . The characteristic temperatures ( $T_g$ ,  $T_x$  and  $T_p$ ) were obtained via NETZSCH DTA 404 PC differential scanning calorimeter, which was measured to 1000 °C at a heating of 10 °C/min. The crystal phase of the glass ceramics were investigated by X-

ray powder Diffract (XRD, D2 PHASER, BRUKER) using  $\text{Cu K}\alpha$  radiation. Absorption spectra were measured using a Perkin Elmer Lambda 900 UV-VIS-NIR spectrophotometer in the range of 1400–1700 nm. The fluorescence spectra was tested using a Triax 320 type spectrometer by pumping the sample with 980 nm laser diode (LD). Polarization–electric field (P–E) curves were measured under the frequency of 10 Hz by means of a ferroelectric testing system (Radiant Precision Premier II Technology) in a silicon oil bath to avoid electrical discharges. All the measurements were carried out at room temperature.

## 3. Results and discussion

### 3.1. Phase and structure analysis

According to the preparation technics, the LNO samples are successfully prepared and their phase characters are analyzed. Fig. 1(a) presents the XRD patterns of the LNO samples. As is clearly shown, all the peaks from 10° to 70° match well with the JCPDS file card: 20-0631 ( $\text{LiNbO}_3$ ) except for one unknown peak centered at the angle of 31.8°. It's worth noting that the position of LNO peaks shift gradually towards smaller angle with the increment of crystallization time and their magnified drawing is shown in Fig. 1(b), which indicates the increasing of the crystallite volume resulted from the incorporation of  $\text{Er}^{3+}$  ions into the  $\text{LiNbO}_3$  structure. Moreover, in terms of the larger diameter of  $\text{Er}^{3+}$  (0.89 Å) than  $\text{Li}^+$  (0.76 Å) and  $\text{Nb}^{5+}$  (0.64 Å), the embed mode can be the substitution of  $\text{Er}^{3+}$  for  $\text{Li}^+$  or  $\text{Nb}^{5+}$ . The Scherrer formula [49] can be applied to calculate the average diameter of crystals:

$$d = \frac{0.89\lambda}{\beta \cos \theta}$$

where  $\lambda$  is the wavelength of the X-ray radiation,  $\beta$  is the full width at half maximum (FWHM) of the most intense peak. The calculated average diameters is shown inside Fig. 1(a). The TEM micrograph of LNO-5 sample, as shown in Fig. 1(c), demonstrates the distribution of  $\text{LiNbO}_3$  crystallites in the glass matrix and the crystal size is approximately ~10 nm, which is in line with the XRD result. A high resolution transmission electron microscope (HRTEM) image with the d-spacing structure is shown in Fig. 1(d). The calculated d-spacing value is 3.75 Å, which is consistent with the (012) plane of hexagonal  $\text{LiNbO}_3$  crystals ( $d_{(012)} = 3.75 \text{ \AA}$ ).

The transmittance spectrum at 1350–1650 nm is shown in Fig. 2(a). The loss includes the Fresnel reflections, dispersion and the absorption of the glass [50]. As it can be seen, the measured transmittance curves have a slight decline at 1.5  $\mu\text{m}$  because of the absorption of  $\text{Er}^{3+}$  ions and the transparency is decreasing which is owing to the increasing amount of LNO crystallites that have formed in the glass matrix. Meanwhile, the samples are visible transparent according to the inset photograph. To better evaluate the structure of  $\text{LiNbO}_3$ , the 3D unit cell model of crystal is depicted in Fig. 2(b) and the oxygen octahedrons are also labeled inside, which contains  $[\text{LiO}_6]$  and  $[\text{NbO}_6]$ . The structure of LNO below Curie temperature (1210 °C) is hexagonal and the oxygen octahedrons formed in this structure are filled by lithium atoms, niobium atoms and vacancies orderly in the +c direction, each of which are one third filled, which is in line with the former investigation [44]. The scheme diagrams of the substitution process are presented in Fig. 2(c), which is obtained from the 3D model of LNO unit cell (Fig. 2(b)). In order to better analyze the substitution process, it's reasonable to assume that  $\text{Er}^{3+}$  ions substitute both  $\text{Li}^+$  and  $\text{Nb}^{5+}$  as illustrated. And in terms of its ferroelectric structure below Curie temperature, the position of each cations would exhibit slight shift away from oxygen layer ( $\text{Li}^+$ ) or middle of oxygen layers ( $\text{Nb}^{5+}$ )

Download English Version:

<https://daneshyari.com/en/article/7990160>

Download Persian Version:

<https://daneshyari.com/article/7990160>

[Daneshyari.com](https://daneshyari.com)