

Optical study of the effect of the impurity content on the ferroelectric properties of Er³⁺ doped SBN glass-ceramic samples

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Photoluminescence measurements have been performed on glass ceramic samples of strontium barium niobate doped with Er³⁺. The glass-ceramic samples were obtained from the precursor glass by thermal treatment and were doped with different contents of Er³⁺ ions. The average size of the nanocrystals in the samples was about 50 nm. The optical properties of the Er³⁺ ions were studied upon 532 nm excitation and the luminescence changes were measured as a function of temperature. The study of the luminescence spectra with increasing temperature has allowed us to ascertain the occurrence of the ferroelectric-paraelectric phase transition in the strontium barium niobate nanocrystals embedded in the glass matrix. We have particularly focused on the temperature range around the Curie temperature, when the system undergoes the transition from the ferroelectric phase to the paraelectric phase. Doping of the strontium barium niobate samples results in a change in the measured value of the Curie temperature which induces a change in the ferroelectric properties. It is interesting to note that this phase transition in the nanocrystals immersed in the glass matrix had previously not been detected. © 2011 American Institute of Physics. [doi:10.1063/1.3651476]

I. INTRODUCTION

Strontium barium niobate (SBN) belongs to a family of ferroelectric crystals with a large number of applications due to their piezoelectric, pyroelectric, electro-optic, and non-linear properties,^{3,4} such as pyroelectric detection,⁵ construction of surface acoustic wave devices,⁶ electro-optic modulation,⁷ and others. Because of its highly disordered tungsten-bronze type structure, SBN shows typical ferroelectric relaxor behaviour.^{8,9} The ferroelectric to paraelectric phase transition of the SBN crystal has been extensively studied in the last years^{10,11} and a variety of experimental techniques have been used to monitor the phase transition, including electrical and optical measurements.^{3,11–14} Of particular interest is the relatively low value of the Curie temperature (T_C) displayed by SBN crystals and the possibility of modifying it by means of compositional changes ($0.25 \leq x \leq 0.75$) or by doping.^{5,15,16} In a previous work by Feofilov *et al.*,¹ this ferroelectric transition was reported in BaTiO₃ nanocrystals, whereas no evidence of the transition was found when the nanocrystals were embedded within a glassy matrix, which the authors of Ref. 2 consider possibly related to the suppression of the process of spontaneous ordering of polarization in the system of nanocrystals when clamped inside the dense medium.

In the present work, glass-ceramics SBN samples doped with Er³⁺ ions have been obtained by thermal treatment from a precursor glass. These samples have SBN nanocrystals with an average size of 50 nm immersed within a glassy

phase.^{18,19} The luminescence associated to the Er³⁺ ions is highly sensitive to the change of environment of the site in which the dopant enters. Luminescence measurements can thus be advantageously used to evidence the occurrence of the phase transition in this material. By means of optical measurements, we have been able to detect the ferroelectric to paraelectric phase transition undergone by the SBN nanocrystals in the glassy matrix. We have further studied the change in Curie temperature as a function of Er³⁺ concentration.

II. EXPERIMENTAL DETAILS

The Er₂O₃-SrO-BaO-Nb₂O₅-B₂O₃ glasses were prepared using the melt-quenching method, doping respectively with 1, 2.5, and 5 mol. % of Er₂O₃. Commercial powders of reagent grade were mixed and melted in a platinum crucible during 1 h inside electric furnace at 1400 °C. The melted component was placed between two flat iron plates with 1.6 mm distance. The glass samples were polished to obtain a smooth and flat surface so as to avoid laser light divergence during irradiation. The glass ceramics were obtained by thermal treatment of the primary glass samples at 620 °C during 2 h in an electric furnace. The final glass-ceramic samples consist of a glassy phase and a crystalline phase of embedded SBN nanocrystals.^{18,19}

The SBN glass ceramic samples were excited under cw 532 nm diode laser and the Er³⁺: ⁴S_{3/2} (²H_{11/2}) → ⁴I_{13/2} (850 nm), ⁴F_{9/2} → ⁴I_{15/2} (650 nm), and ⁴I_{11/2} → ⁴I_{15/2} (975 nm) transitions were measured using an ANDOR NEWTON CCD monochromator.

High temperature measurements were performed by placing the sample inside an electric furnace to increase the

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temperature from 295 K (room temperature) to 355 K at a rate of 0.5 K/min.

III. RESULTS AND DISCUSSION

The emission spectra for the Er^{3+} doped SBN glass-ceramic samples obtained upon 532 nm excitation were systematically investigated as a function of temperature. We observed a significant change in the emission spectra as the temperature was increased, which is consistent with structural changes undergone by the nanocrystals in this material at the ferroelectric to paraelectric phase transition (see below). In Figures 1, 2, and 3, we show the emission spectra of the Er^{3+} ions corresponding to the different optical transitions, at two reference temperatures both above (295 K) and below (355 K) the estimated Curie temperature for the transition. From Figures 1–3, one can see that the intensity of the emission spectra change abruptly as temperature increases. This is indicative of the occurrence of a transition where luminescence emission in each of the phases is sensitive to the change in the Er environment during the phase transition. The intensity of the emission bands is greatly reduced in the high-temperature paraelectric phase, although it does not become zero. In the insets to each figure, we show the integer area of these emission spectra as a function of the temperature which clearly shows the changes across the Curie temperature. To the best of our knowledge, this is the first time that the ferroelectric phase transition in doped SBN glass-ceramics has been reported.

The glass-ceramics samples are formed by both a glassy phase and an embedded crystalline phase of SBN nanocrystals.^{18,19} Thus, in principle, the Er^{3+} ions in both phases can produce light. In a previous work, Kowalska *et al.*¹⁹ have used time-resolved laser spectroscopy to estimate the percentage contribution from the nanocrystalline phase in glass ceramic samples (75%, 75%, and 65% for 1, 2.5, and 5 mol. % of Er^{3+} -ion concentration, respectively). Additionally, due to the differences between the phonon energy in each environment, some of the Er^{3+} emission bands are

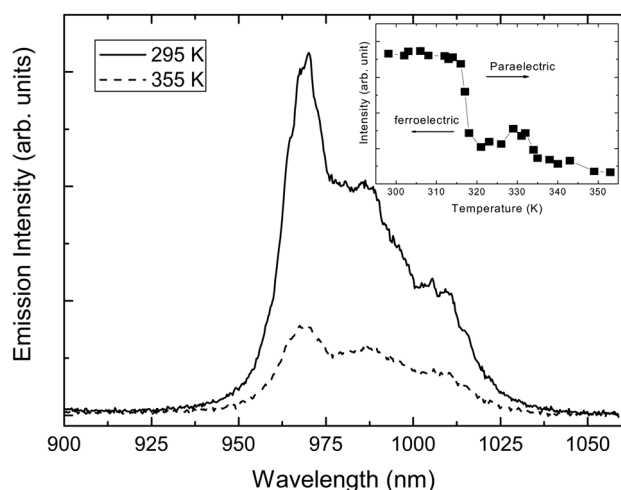


FIG. 1. Emission spectra of the Er^{3+} : ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$ (975 nm) transition at temperature above (295 K) and below (355 K) the phase transition. The inset shows the integer area of this emission as a function of the temperature.

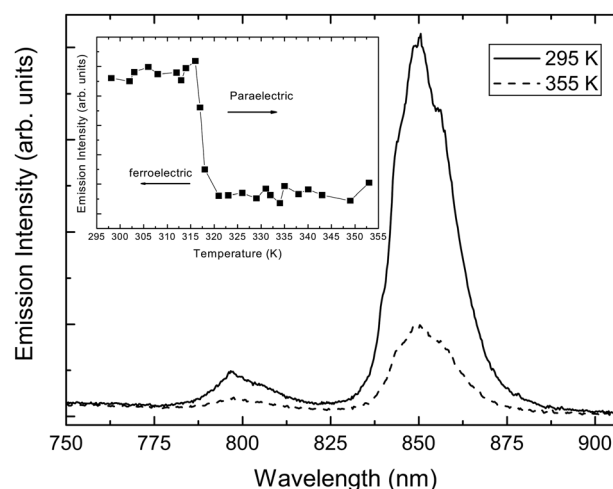


FIG. 2. Emission spectra of the Er^{3+} : ${}^4S_{3/2} ({}^2H_{11/2}) \rightarrow {}^4I_{13/2}$ (850 nm) transitions at temperature above (295 K) and below (355 K) the phase transition. The inset shows the integer area of these emissions as a function of the temperature.

more difficult to obtain.¹⁸ The emission bands corresponding to the ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ and ${}^4I_{9/2} \rightarrow {}^4I_{15/2}$ transitions of the Er^{3+} ions are practically negligible by comparing them with the same transitions in the crystalline environment. Taking these observations into consideration, it has been argued that the luminescence is mainly due to the Er^{3+} ions which are present in the crystalline phase of SBN nanocrystals, whereas the contribution from the Er^{3+} ions within the glassy phase is rather small.

In the ferroelectric phase, the SBN host crystals have a tetragonal tungsten bronze-type structure with space group $P4bm$ No. 100.²⁰ The general structural formula can be written as $(A_1)_4(A_2)_2(B_1)_2(B_2)_8O_{30}$, with the cations occupying the A and B sites. The A_1 sites have C_4 symmetry and are partially filled by Sr^{2+} ions; the A_2 sites have C_s symmetry and are partially occupied (in a random way) by both Sr^{2+} and Ba^{2+} ions, while the Nb^{5+} ions completely fill both the B_1 sites (C_{2v} symmetry) and the B_2 sites (C_1 symmetry). Thus, four different cationic sites of the host crystal, each

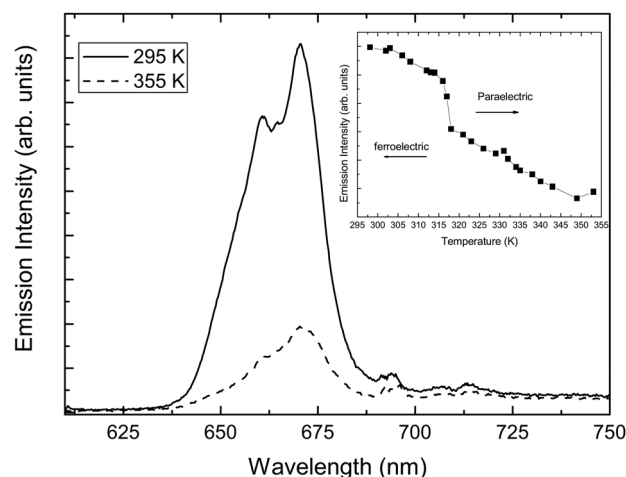


FIG. 3. Emission spectra of the Er^{3+} : ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ (650 nm) transitions at temperature above (295 K) and below (355 K) the phase transition. The inset shows the integer area of this emission as a function of the temperature.

with a different local symmetry, can in principle be occupied by the Er^{3+} ions in the ferroelectric phase.

The local environment around the constituting Ba^{2+} , Sr^{2+} , and Nb^{5+} cations is strongly modified when the crystal undergoes the ferroelectric to paraelectric phase transition, with the modification being different for the different crystallographic sites. In the paraelectric phase, the space group is $P4b2$ No. 117, which is a non-centrosymmetric group, although the crystal is non-polar. According to one of the models used to describe the non-polar phase,^{20–23} after the transition, the A_1 , A_2 , and B_1 sites adopt C_{4h} , C_{2v} , and D_{2h} symmetries, respectively, while the B_2 sites keep their original C_1 symmetry. The point groups C_{4h} and D_{2h} are centrosymmetric and thus the Er^{3+} ions located in the A_1 and B_1 sites become dead sites after the transition and their emission is quenched. The quenching of the luminescence of the Er^{3+} (A_1) and the Er^{3+} (B_1) ions in the paraelectric phase produce a strong decrease in the overall Er^{3+} luminescence above T_C : The remaining luminescence in this phase can be solely attributed to the Er^{3+} (A_2) and Er^{3+} (B_2) ions.^{20–22} On the other hand, Daldosso *et al.*²³ have reported that the Er^{3+} ions in SBN60 and SBN50 enter substitutionally in B_1 and/or B_2 sites (which in the pure crystal are occupied by Nb^{5+} ions) where, due to the great difference in the electrostatics and size between the pentavalent Nb^{5+} ions and the trivalent Er^{3+} ions, they are expected to induce a great deal of local disorder in the crystal structure. Also in this case, above T_C the B_1 sites become dead sites and the emission of the Er^{3+} ions in them is quenched^{19–23} with the remnant of the luminescence being due to the reduced fraction of Er^{3+} ions in B_2 sites. Our results for the emission spectra at 295 K and 355 K, shown in Figures 1–4, are fully consistent with the microscopic picture just presented and thus they support the occurrence of the ferroelectric to paraelectric phase transition in the host nanocrystals in this temperature region.

To the best of our knowledge, our results for SBN constitute the first time that the phase transition from the ferroelectric to the paraelectric phase has been observed in glass-ceramics samples. We note here that other authors have previously tried unsuccessfully to observe the ferroelec-

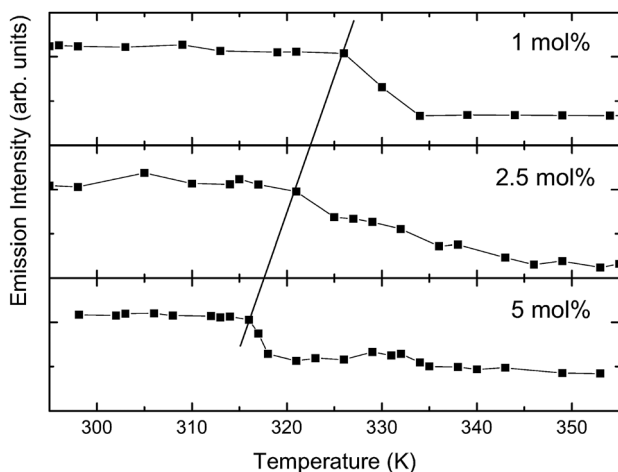


FIG. 4. Integer area of the emission spectra obtained for the different concentrations of Er^{3+} ions as a function of the temperature.

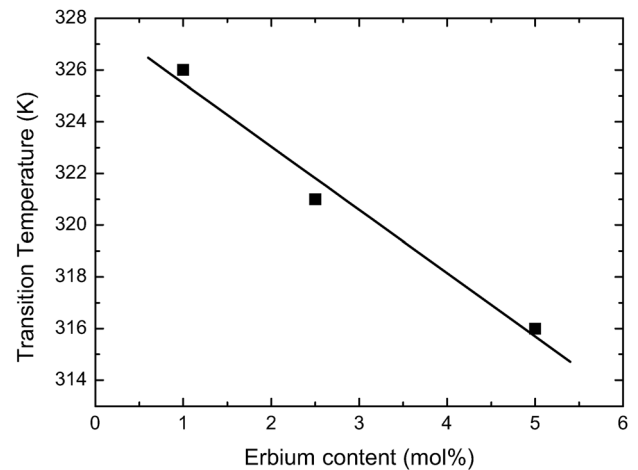


FIG. 5. Transition temperature as a function of the erbium content in SBN glass ceramic. The line is the linear fit to the experimental data.

tric phase transition in $\text{Li}_2\text{Ge}_7\text{O}_{15}$ (LGO) nanocrystals (where the spontaneous polarization is weaker than in SBN nanocrystals) embedded in a glassy matrix.¹⁷ The failure to observe any indication of the transition was explained as originating from the suppression of the process of the spontaneous ordering of the polarization in the system of LGO nanocrystals clamped inside the dense medium. We must conclude that such suppression mechanism is not effective in the SBN systems studied by us.

Dopants are known to significantly influence the transition temperature from the ferroelectric to the paraelectric phase of SBN crystals. This result was previously found, e.g., doping with Eu^{3+} ion²² or Cr^{3+} ions.^{15,24} In Figure 4, we show the integer area of the emission spectra for the different concentrations of Er^{3+} ions. As can be seen, the Curie temperature decreases as the Er^{3+} content increases. The results of these measurements for the different concentrations are summarized in Figure 5. The transition temperature T_i depends linearly on the Erbium concentration c_{Er} ,

$$T_i = -2.4c_{\text{Er}} + 327.9 \quad (c_{\text{Er}} \text{ in mol\%, } T_i \text{ in K})$$

Thus, Erbium, besides affecting the optical properties, turns out to be an effective tool for tailoring the phase transition of SBN.

IV. CONCLUSIONS

Photoluminescence measurements were performed on Er^{3+} doped SBN glass ceramic samples. These samples were obtained from the precursor glass by thermal treatment and were doped with different contents of Er^{3+} ions. The optical properties of Er^{3+} ions were reported under 532 nm excitation and the luminescence changes were analyzed as a function of the temperature. They were examined in the temperature range around the Curie temperature, when the system passes to para-electric phase from ferro-electric phase. Some optical transitions were sensitive to the change in the ferroelectric properties and they were reported. By

doping SBN with rare earths, the Curie temperature can be varied which implies a change in the ferroelectric properties.

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