

# Temperature dependence photo-luminescence of Nd<sup>3+</sup> doped PLZT ceramic

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**Abstract** Temperature dependence of photo-luminescence for Nd<sup>3+</sup> doped PLZT(9/65/35) was measured across its structural phase transition temperature. The absorption corresponding to  $^4I_{9/2} \rightarrow ^4F_{5/2}$ ,  $^2H_{9/2}$  energy level near 808 nm was used for exciting the sample. The major emission bands at 0.9, 1.06, and 1.34  $\mu\text{m}$  were observed. No shift in the peak position of these emission bands was observed across the diffused structural transition with increase in temperature. However, a 10% increase in FWHM was observed. The absence of any discernible peak shift is attributed to the shielding of the intra-configurational 4f-4f transitions, in trivalent Nd<sup>3+</sup> ions, by external 5 s and 5d orbitals. The red shifted phonon side bands appeared with increase in temperature.

**Keywords** Ferroelectrics · Luminescence · PLZT · Ceramics · Dielectric

## 1 Introduction

Lanthanum modified lead zirconate titanate (PLZT) ceramic, has been known for its applications in electro-optical devices such as modulator, amplifier, and switches [1]. Recently, neodymium (Nd<sup>3+</sup>) doped  $\text{Pb}_{0.91}\text{La}_{0.9}(\text{Zr}_{0.65}\text{Ti}_{0.35})_{0.9975}\text{O}_3$ ,

PLZT (9/65/35), has been investigated for its potential application as a laser-host active medium [2]. Studies have shown that its low phonon energy, negligible excited state absorption losses and very low down-conversion and up-conversion losses mark it out as a suitable laser host material [2, 3]. In addition, being a ferroelectric material it can introduce an emission modulation by application of electrical field [4]. Though PLZT as a host material has possibility of emission modulation but it has strong temperature dependence of the electro-optic and electro-mechanical properties around room temperature [1, 5]. This temperature dependence is due to a diffuse structural transition observed in PLZT (9/65/35) near 80°C. This transition is accompanied by a change in the crystal field which may change the electronic energy levels of optically active Nd<sup>3+</sup> ion and as a consequence a shift in the emission lines is expected. First report on temperature dependence of emission spectra for Nd<sup>3+</sup> doped PLZT (9/65/35) ceramic was published by Murakami et al. [6] in the year 2000. They studied the temperature dependence of line width and thermal shift of emission lines in the temperature range 10–300 K. However, there is no report on temperature dependence of emission spectra above room temperature, especially across the phase transition temperature. In the present work, we have carried out measurements on the temperature dependence of photo-luminescence of Nd<sup>3+</sup> doped PLZT ceramic across the phase transition temperature.

## 2 Experiment

PLZT (9/65/35) powder doped with 1 mol%Nd<sub>2</sub>O<sub>3</sub> was synthesized by conventional dry route. High purity (>99%) PbO (Alfa), La<sub>2</sub>O<sub>3</sub> (Aldrich), ZrO<sub>2</sub> (Aldrich), TiO<sub>2</sub> (Fluka), and Nd<sub>2</sub>O<sub>3</sub> (Aldrich) powders were used as starting

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materials. Three mole percent of excess PbO was added to compensate for the lead loss during sintering. The oxide precursors were ball-milled, calcined at 900°C (4 h) to get the single phase perovskite PLZT powder. The calcined powder was again ball-milled to break agglomerates and reduce the particle size. It was then compacted in the form of a disk of diameter 25 mm and thickness ~12 mm. Pressure assisted sintering of the green pellet (disk) was carried out by uniaxial hot-press (10 MPa) at 1175°C. Single-phase formation was confirmed by powder X-ray diffraction using  $\text{CuK}\alpha$  radiation. The samples obtained after hot-pressing were cut in the form of rectangular plates of size ~10mmx8mm and thickness ~1 mm. Dielectric measurement was carried out at different temperatures and frequencies using a HP4194A impedance analyser. The samples were polished and transmission spectrum of 0.5 mm thick rectangular plates was measured using Shimadzu make spectrophotometer between 300–1000 nm. The absorbance of the sample was calculated from transmission spectra. Photoluminescence (PL) of the sample was measured by exciting it by a diode laser operating at 808 nm. The signals were filtered in a 1/4 m monochromator and collected by a germanium (Ge) photodiode. The band pass of the monochromator was kept about 4 nm. The PL measurements were carried out in reflection mode at six different temperatures between 30–200°C in the range of 850–1600 nm wavelength. A variation of  $\pm 3^\circ\text{C}$  in temperature was observed during the single measurement.

### 3 Results and discussion

The variation of dielectric permittivity with temperature at four different probing frequencies is shown in Fig. 1. It shows a diffuse phase transition near 80°C with dispersion in dielectric maxima temperature. An increase in the

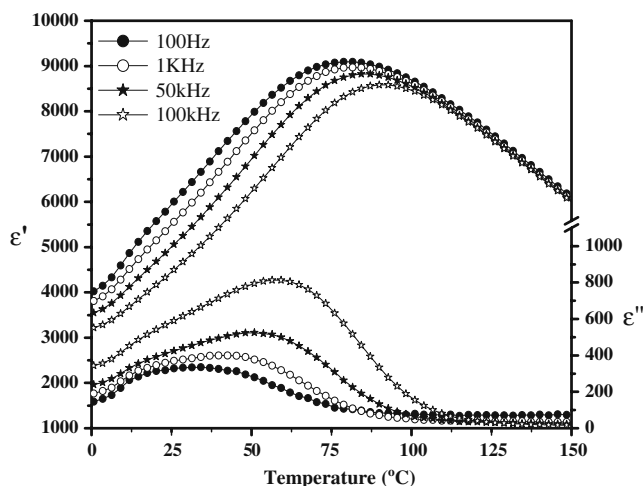


Fig. 1 Temperature dependence of dielectric permittivity for Nd:PLZT

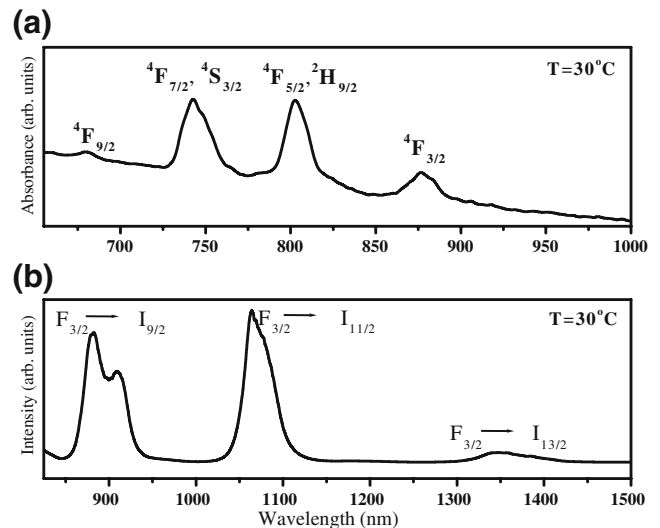


Fig. 2 Room temperature (a) absorbance and (b) PL spectrum Nd:PLZT

dielectric constant is observed from the room temperature. Similar to the dielectric constant, other properties like electro-optic coefficient is also expected to show a variation with temperature [1, 5]. The dispersion in dielectric maximum temperature is attributed to the relaxor like behaviour of PLZT [7].

Figure 2(a & b) shows the room temperature absorbance and photo-luminescence spectra of Nd:PLZT. A number of absorption peaks were observed as transitions to the different excited states, viz.,  $^4F_{3/2}$ ,  $^4F_{5/2}$ ,  $^2H_{9/2}$ ,  $^4F_{7/2}$ ,  $^4S_{3/2}$ , and  $^4F_{9/2}$ , from the ground  $^4I_{9/2}$  state. These are practically identical to those previously reported [2, 3]. We have used absorption of  $^4I_{9/2} \rightarrow ^4F_{5/2}$ ,  $^2H_{9/2}$  corresponding to 808 nm for exciting the sample for photo-luminescence (PL) measurement. The full width at half maximum (FWHM) of this peak is ~14 nm. The major emission bands were observed at 0.9, 1.06, and 1.34  $\mu\text{m}$  correspond to the  $\text{Nd}^{3+}$  transitions from level  $^4F_{3/2} \rightarrow ^4I_{9/2}$ ,  $^4F_{3/2} \rightarrow ^4I_{11/2}$ , and  $^4F_{3/2} \rightarrow ^4I_{13/2}$ , respectively [2]. The full width at half maximum (FWHM) of the emission band at 1.06  $\mu\text{m}$  ( $^4F_{3/2} \rightarrow ^4I_{11/2}$ ) is ~33 nm. The emission band for 0.9  $\mu\text{m}$  ( $^4F_{3/2} \rightarrow ^4I_{9/2}$ ) consists of two sub-bands with FWHM 21 and 19 nm. These high FWHM values in absorption and emission spectra are due to the polycrystalline nature of the host material [3].

Figure 3 shows the photoluminescence spectra of Nd:PLZT at four different temperatures. Although we performed the experiment at seven different temperatures but the PL spectrum on four temperatures is presented for the sake of clarity. It is interesting to note that along with the main emission lines weak side bands, red shifted with respect to the main emission bands, are also seen in Fig. 3. These red shifted bands appear more prominently when the same spectrum is plotted on a logarithmic scale (inset Fig. 3). With increase in temperature the intensity of

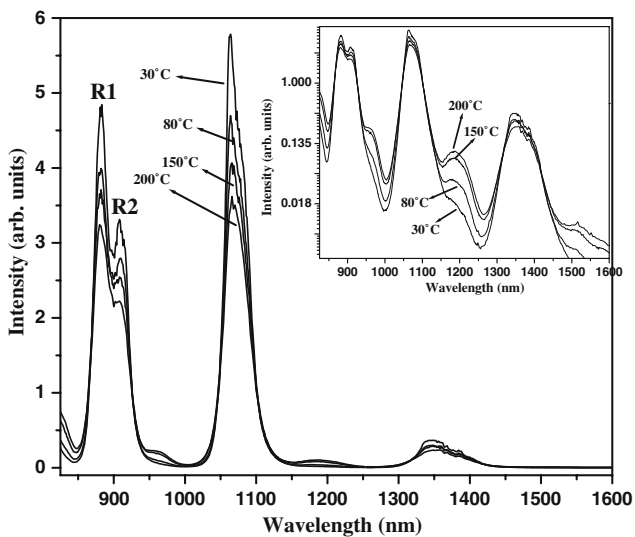


Fig. 3 PL spectrum of Nd:PLZT at different temperatures

main transition bands decreases while the intensity of the red shifted side bands increases. The peak position of these side bands is found to be independent of temperature. These red shifted side bands observed in photo-luminescence measurements can be attributed to the phonon assisted vibronic transitions [8]. The energetic differences between these side bands and the main pure electronic transitions,  ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$ ,  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ , and  ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$  (also called zero-phonon lines) give a direct measure of the local phonon energies acting on the Nd-ion. It has been observed that these side bands are  $\sim 110$  meV red shifted from the zero-phonon lines which is quite close to the reported phonon energy of PLZT ( $\sim 100$  meV) [9]. The red shift of the vibronic bands is indicative of phonon generation process. This would account for the observed increase in the intensity of vibronic side bands with increase in temperature and a corresponding decrease in the intensity of main transition bands. Moreover, the phonon scattering processes at higher temperature lead to broadening of emission bands in Nd:PLZT ceramics [8].

The temperature dependence of the full width at half maximum (FWHM) and peak position of main two emission lines corresponding to  ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$  and  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  are shown in Figs. 4 & 5. The  ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$  emission band is a clearly a superposition of two sub-bands marked as R1 and R2 respectively (see Fig. 3). We have used non-linear fitting to extract FWHM of each peak. There is no significant shift in the peak positions of emission bands with increase in temperature from 30°C to 200°C, however a 10% increase in FWHM is observed. The absence of any discernible peak shift in emission bands suggests that the crystal field alterations arising due to structural transition in PLZT have no significant effect on 4f-4f transition levels of  $\text{Nd}^{3+}$  ion. This could be due to the screening of intra-

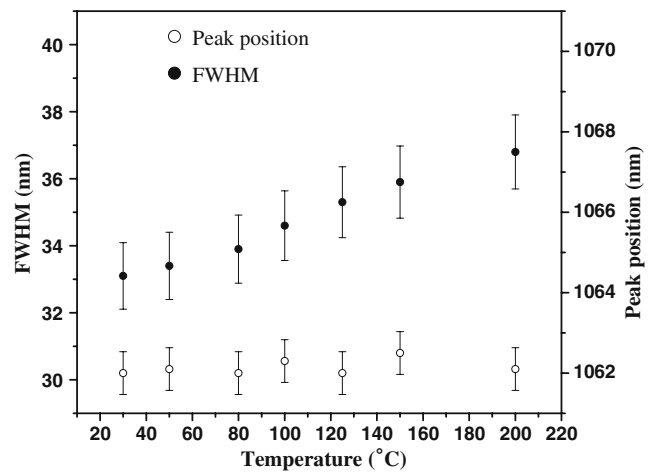


Fig. 4 Temperature dependence of Peak position and FWHM for  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  transition

configurational 4f-4f transitions, in trivalent  $\text{Nd}^{3+}$  ions, by external 5 s and 5d orbitals.

#### 4 Conclusion

Temperature dependent photo-luminescence measurements on  $\text{Nd}^{3+}$  doped PLZT across its diffuse structural transition show no shift in the peak position of the emission spectrum. While at one end it augurs well for the temperature stability of the laser output, it also rules out the possibility of tuning the operational frequency of the laser by a change of temperature. The red shifted phonon side bands appeared with increase in temperature and are responsible for decrease in intensity and broadening of main emission lines.

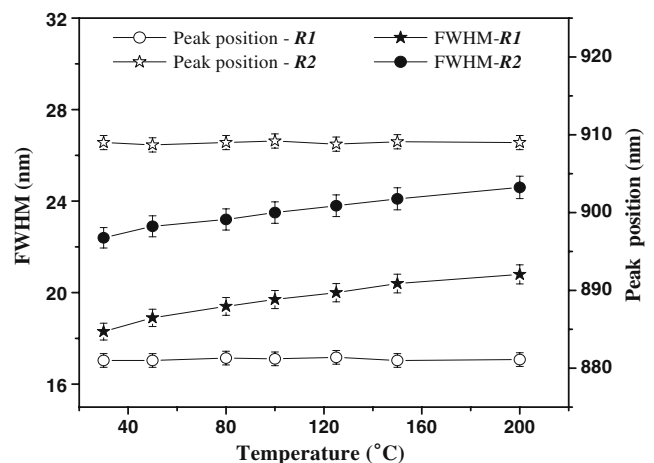


Fig. 5 Temperature dependence of Peak position and FWHM for  ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$  transition

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