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# Phonon sideband spectroscopy and 1550 nm luminescence from $\text{Eu}^{3+}$ and $\text{Er}^{3+}$ -doped ferroelectric PLZT for active electro-optic applications

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## Abstract

This work reports the spectroscopic behavior of erbium- and europium-doped electro-optic PLZT. Fluorescence at  $1.55 \mu\text{m}$  from  $\text{Er}^{3+}$ : PLZT was found to be spectrally broad and flat in comparison to commercially utilized electro-optic materials such as  $\text{LiNbO}_3$ . Phonon sideband spectroscopy of the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$  pure electronic transition in  $\text{Eu}^{3+}$  showed the highest energy phonon from PLZT to be at  $750 \text{ cm}^{-1}$ . This reduced phonon energy, coupled with moderately high refractive indices inferring large radiative transition probabilities, mark PLZT as a candidate material for efficient lossless and/or amplifying electro-optic devices in optical communication networks. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Erbium; PLZT ceramics; Electro-optics; Europium; Phonons

## 1. Introduction

Ferroelectric materials that can be made optically transparent, such as lithium niobate ( $\text{LiNbO}_3$ ), meet current commercial requirements for optical modulators, switches, and filters [1], based on the electro-optic (EO) effect. However, future requirements for increasingly higher capacity photonic networks mandate next-generation analogs with greater value-added and at a lower cost. One way

of increasing functionality, while reducing complexity, is to make a normally optically passive device active through selective doping with light-emitting impurities. This enables a device then to double as an optical source, amplifier, or zero-loss element. These latter two points are of particular importance since optical communication systems will continue to require ever-greater information capacities and ever longer haul links. In order to lessen the network loss-budget, hence require fewer amplifiers and/or lower output powers from the source lasers, the components with high optical losses should be reconsidered. The silica optical fibers exhibit near-intrinsic losses of  $0.2 \text{ dB/km}$ . This is in sharp contrast to the EO modulators and switches which lose roughly  $0.05\text{--}0.1 \text{ dB/cm}$ ,

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corresponding to a difference of 4–5 orders of magnitude in attenuation. Doping with rare-earth (RE) ions to provide at least enough gain to offset the high attenuations would obviate these loss-limitations to the systems performance. Further, the gain profile at the amplifying wavelengths should be broad and flat. This is because optical systems maximize their capacity by transmitting signals over multiple wavelengths. This wavelength-division-multiplexing (WDM) is well recognized as a critical technology. Although a great deal of work has gone into materials and pump schemes to optimize the spectral breadth and flatness of the erbium-doped fiber amplifiers [2], very little work has investigated equivalent considerations in the other network components. LiNbO<sub>3</sub> (LN) has become the industrial workhorse for EO applications; however, it has been recognized that the emissions from RE dopants are less than ideal for many applications [3].

From a material point-of-view, the lanthanum-modified lead zirconate titanate compositions represent a model system to develop active EO devices. The general composition often is written  $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\square_{x/4}\text{O}_3$  and abbreviated as PLZT  $x/y/(1-y)$  (e.g., PLZT 8/65/35; all in mole percent). The symbol  $\square$  represents a vacancy [4] required for charge neutrality on substituting  $\text{La}^{3+}$  for  $\text{Pb}^{2+}$ . PLZT is a well-known transparent ceramic based on the perovskite structure of barium titanate and possesses numerous structural, dielectric, and optical phases depending on the temperature and composition. PLZT's electro-optic coefficients are up to 20 times larger than LiNbO<sub>3</sub> [i.e.,  $r_{33}$  (PLZT 8/65/35)  $\approx$  600 pm/V,  $r_{33}$  (LiNbO<sub>3</sub>)  $\approx$  31 pm/V] [5,6], it easily may be substituted with REs for La without any restrictions up to relatively high concentrations ( $\leq$  28 at%), and numerous synthesis techniques have been developed for both bulk and epitaxial thin film forms [7].

For these reasons, RE-doped PLZT (RE : PLZT) was investigated. More specifically, the 8/65/35 PLZT composition was chosen for this work because it lies near the  $\text{PbTiO}_3/\text{PbZrO}_3$  morphotropic phase boundary ( $\sim$ 8 mol% La) and has the maximum electro-optic coefficients for the material system [6]. This composition, therefore, represents the most logical choice for EO devices. Tri-

valent erbium ( $\text{Er}^{3+}$ ) was chosen because its  ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$  emission at 1550 nm overlaps the minimum loss window of silica optical fibers and, hence, dominates light sources and optical amplifiers for application in telecommunication systems. Trivalent europium ( $\text{Eu}^{3+}$ ) was used as an optical probe to determine the vibrational energies of PLZT. Excitation spectra of the  $\text{Eu}^{3+} {}^5\text{D}_2$  state contain phonon side bands (PSB). The energetic differences between these PSBs and the main pure electronic transition (PET, also called zero-phonon lines) of the  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$  excitation give a direct measure of the local phonon energies acting specifically on the rare earth. This phononic information, coupled with the erbium radiative emissions, will be shown to mark PLZT for prospective use as efficient optically amplifying or zero-loss electro-optic devices in telecommunication networks.

## 2. Experimental procedure

Erbium- and europium-doped samples of 8/65/35 PLZT (i.e., 8 mol% La, 65 mol% Zr, 35 mol% Ti) were prepared by the mixed-oxide method. The purity and origin of the components were, respectively, PbO, 99.99%, Hammond Lead Products (Hammond, IN); La<sub>2</sub>O<sub>3</sub>, > 99.99%, Unocal Molycorp (Mountain Pass, CA); ZrO<sub>2</sub>, 99.99%, TAM Chemicals (Niagara Falls, NY); TiO<sub>2</sub>, 99.9%, Whittaker, Clark, and Daniels, Inc. (New York, NY); Er<sub>2</sub>O<sub>3</sub> and Eu<sub>2</sub>O<sub>3</sub>, both 99.9%, Alfa Aesar (Ward Hill, MA).

The raw materials (1000 ppm rare-earth concentrations) were weighed to the nearest 0.01 g in 500 g batches, transferred to a polyethylene mill jar containing 1.3 cm diameter zirconia media, and milled for 2 h in 350 ml of distilled, de-ionized water. The slurry was transferred to a stainless-steel drying pan and dried at 180°C for approximately 1 h. The powder then was crushed, passed through a 60-mesh screen, placed in an alumina crucible, with an alumina cover, and calcined at 900°C for 1 h. The calcined powder was placed into a polyethylene mill jar with 1.3 cm zirconia media and milled for 4 h in 300 ml of distilled, de-ionized water. The PLZT slurry was transferred to a stainless-steel pan and dried at 180°C, again for about 1 h.

The PLZT powder (125 g) was cold pressed at  $\sim 27.5$  MPa into a slug 2.22 cm in diameter and 3.8 cm in length. The resulting slug was hot pressed in a SiC die at  $1200^\circ\text{C}$  for 16 h at  $\sim 20.7$  MPa. A constant vacuum was applied to the hot-pressing chamber from room temperature until  $700^\circ\text{C}$ . At  $700^\circ\text{C}$ , the chamber was back-filled with a steady flow of  $\text{O}_2$  ( $\sim 20$  cm<sup>3</sup>/s) for the duration of the hot pressing. The slugs were allowed to cool to room temperature before removal from the SiC die. The PLZT slugs were then cut into  $\sim 500$   $\mu\text{m}$  thick wafers, and polished to an optical finish with diamond paste.

The density of each hot-pressed PLZT slug was determined by the standard Archimedes immersion method using trichloroethylene as the liquid medium. X-ray diffraction patterns of the PLZT samples were obtained with a Scintag XDS 2000 (Cupertino, CA) diffractometer using nickel-filtered  $\text{Cu K}_\alpha$  radiation. The hysteretic characteristics of the samples were obtained using a voltage amplifier connected to a Radiant Technology RT-66A ferroelectric tester (Albuquerque, New Mexico).

Fluorescence measurements were performed on a SPEX Fluorolog II. The  $\text{Er}^{3+}$ -doped sample was excited with a 800 nm laser diode and the fluorescence was collected at  $90^\circ$  focused onto the slits of the spectrometer with 0.5 nm resolution and detected with a InGaAs detector. The spectra were corrected for wavelength sensitivity using a calibrated black body source. The  $\text{Eu}^{3+}$  fluorescence was obtained by exciting the sample at 465 nm from a Xe lamp and the SPEX monochromator and PMT with 0.5 nm resolution. The PSBs were measured by monitoring the 613 nm  $\text{Eu}^{3+}$  emission through a 550 nm long pass filter, while scanning the excitation wavelength from 420 to 500 nm with 1 nm resolution. All measurements were made at room temperature.

### 3. Results and discussion

Bulk densities for all the hot-pressed slugs were found to be greater than 99.8% of the  $7.82$  g/cm<sup>3</sup> theoretical value for the 8/65/35 composition. Proper phase formation was confirmed by XRD

and the inclusion of the RE was found not to modify the structure to any measurable extent. This was expected for the low dopant level. The dielectric constant,  $K$ , and loss factor,  $\tan \delta$ , were statistically equivalent between the doped and undoped PLZT wafers (Undoped:  $K = 3412$ ,  $\tan \delta = 5.5\%$ ; 1000 ppm  $\text{Er}^{3+}$ :  $K = 3422$ ,  $\tan \delta = 5.4\%$ ). The polarization versus electric field hysteresis curve also showed negligible differences between the doped and undoped materials. The hysteretic curvature proved slim-loop ferroelectric behavior, hence electro-optic, as is well known for this composition. In summary, the structural, dielectric, and ferroelectric nature of PLZT is maintained with the addition of RE ions at concentrations typically employed to optimize the spectroscopic performance [8].

Fig. 1 shows the photoluminescence spectrum at 1550 nm for  $\text{Er}^{3+}$ : PLZT. This  ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$  emission is spectrally broad, extending from 1450 to beyond 1650 nm, and is smooth compared to  $\text{Er}^{3+}$  doped LN (Corresponding spectrum for  $\text{LiNbO}_3$  can be found in Ref. [9]). However, since luminescence from a 3-level system, such as this erbium emission, is not indicative of the expected gain spectrum an estimate of the gain lineshape was simulated by normalizing and subtracting the 1550 nm  $\text{Er}^{3+}$ : PLZT absorption from the fluorescence (i.e., the “0” curve is the 1550 nm absorption spectrum, inverted. The “100” curve is

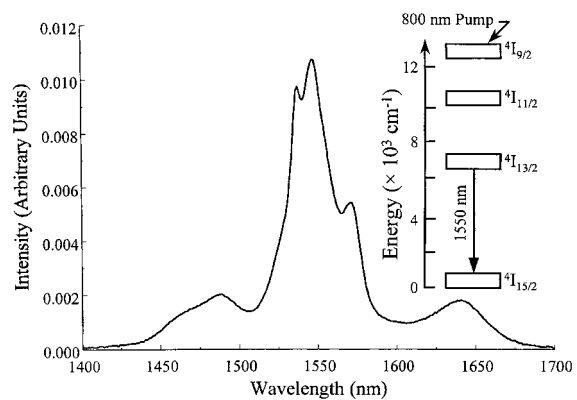


Fig. 1. Photoluminescence at 1550 nm from the  ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$  transition of  $\text{Er}^{3+}$ : PLZT. Inset depicts energy level structure for  $\text{Er}^{3+}$  with pump level and measured fluorescent transition.

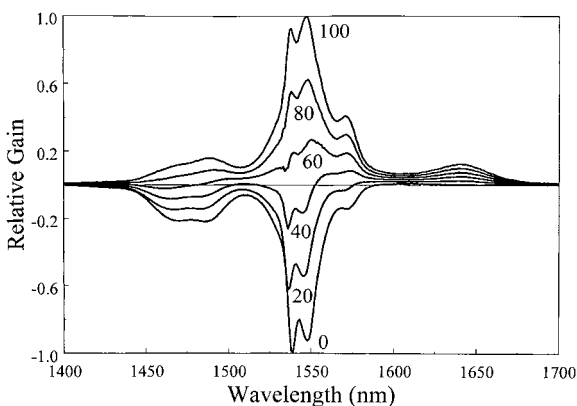


Fig. 2. Simulated relative gain spectra for  $\text{Er}^{3+}:\text{PLZT}$  for differing values of a fractional excited state ( $^4\text{I}_{13/2}$ ) population. Spectra calculated by normalizing and subtracting the 1550 nm  $\text{Er}^{3+}:\text{PLZT}$  absorption (not shown) from the fluorescence (Fig. 1).

the luminescence spectrum of Fig. 1. The other curves are fractionally weighted between these two spectra.) The resultant spectrum takes into account the influences of ground state absorption (GSA) and provides a more realistic concept of the gain profile expected from inverted  $\text{Er}^{3+}$  ions in a PLZT amplifier.

The simulated gain spectrum is shown in Fig. 2. There is a small but increasing gain in the 1450–1500 nm region so an  $\text{Er}^{3+}:\text{PLZT}$  planar amplifier would have to be highly inverted, and have a low background loss, to be useful in this part of the spectrum. There is a 25 nm wide window from 1550 to 1575 at 50% inversion that has a 20% gain variation, which could be promising. On the long wavelength side, the 1585–1660 nm band provides 75 nm of width, but with 55% gain variation, so this area could be useful with filtering. This spectral region is influenced by the  $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{9/2}$  excited

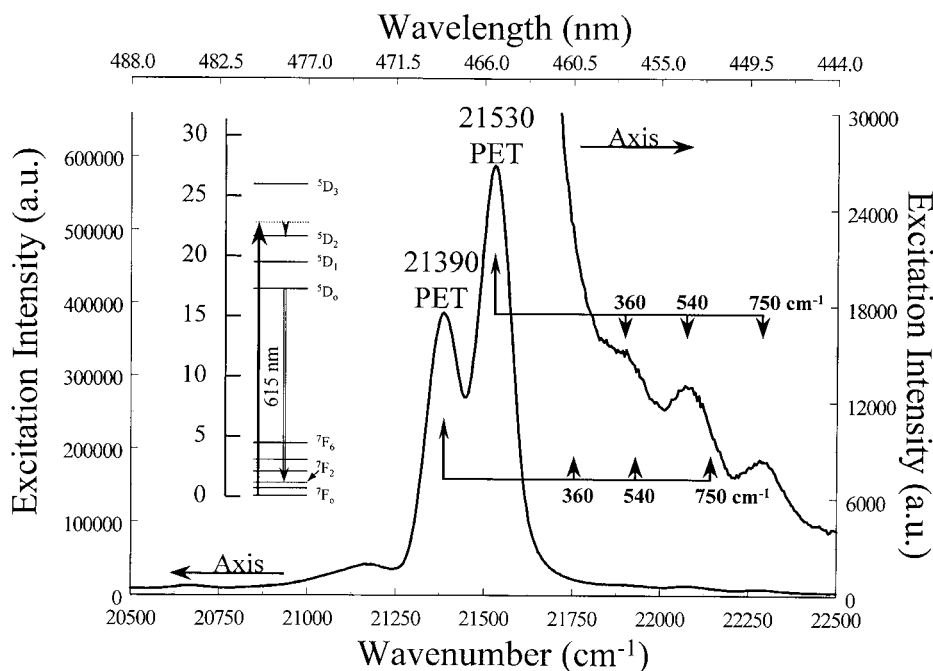


Fig. 3. Phonon sidebands to the  $^7\text{F}_0 \rightarrow ^5\text{D}_2$  pure electronic transition of  $\text{Eu}^{3+}:\text{PLZT}$  showing the highest energy phonon mode to be at  $750\text{ cm}^{-1}$ . The energy level structure and schematic of phonon excitation process for  $\text{Eu}^{3+}$  is shown in the left inset with ordinate values representing energies ( $\times 10^{-3}\text{ cm}^{-1}$ ). *N.B.*: The energies ( $\text{cm}^{-1}$ ) associated with the three phonon sidebands to the  $21\,390\text{ cm}^{-1}$  PET do overlap partly those of the  $21\,530\text{ cm}^{-1}$  PET. But given the relative intensity between the two PETs, the measured PSBs are dominantly assigned to the  $21\,530\text{ cm}^{-1}$  band.

state absorption at  $\sim 1650$  nm, which was not measured. This ESA would lower the efficiency of the amplifier, and would tend to increase with wavelength, so it would actually flatten the 1640 nm hump in the gain spectrum. Regardless, the gain is expected to be broader and reasonably flatter in comparison to conventional materials such as LN.

Since luminescence is a competition between radiative and nonradiative processes, the energy associated with the host phonon modes was measured using the phonon sidebands (PSB) of the  $^5D_2$  excitation in  $\text{Eu}^{3+}$ : PLZT. The results are shown in Fig. 3. The highest energy phonon mode in PLZT is located at  $750\text{ cm}^{-1}$  with lower energy modes at  $540$  and  $360\text{ cm}^{-1}$ . These values identically match those published for Raman spectra of equivalent compositions [10,11]. Of particular interest is the fact that the phonon energies of the electro-optic PLZT are comparable to telluride glasses [12] and other heavy-metal oxides currently of interest for optical amplifiers and light emitting devices. More important is the fact that the highest energy phonon is  $\sim 150\text{ cm}^{-1}$  less than that for  $\text{LiNbO}_3$ , which has a maximum phonon energy of  $900\text{ cm}^{-1}$ . Since the multiphonon emission rate is proportional to the exponential of this phonon energy, the nonradiative relaxation of RE excited states would be slower in PLZT than LN. This can be coupled with the fact that PLZT possesses relatively high refractive indices (at  $1550\text{ nm}$ ,  $n^{\text{PLZT}} = 2.404$ ,  $n_o^{\text{LN}} = 2.211$ ,  $n_e^{\text{LN}} = 2.139$ ) [13,14] that lead to greater Lorentz local field corrections to the radiative transition probabilities. Therefore, since the radiative quantum efficiency for an emission is maximized when emission probabilities are high and nonradiative rates are low, PLZT prevails over LN in both regards.

#### 4. Conclusions

Erbium- and europium-doped electro-optic PLZT were prepared. The inclusion of rare-earth dopants at concentrations typically necessary to optimize spectroscopic performance did not affect

the dielectric, hysteretic, or structural behavior. Emission at  $1550\text{ nm}$  from the  $^4I_{13/2} \rightarrow ^4I_{15/2}$  transition of  $\text{Er}^{3+}$ : PLZT was found to be spectrally broad and uniform in comparison to LN. The phonon sidebands that accompany the excitation of the  $^5D_2$  state in  $\text{Eu}^{3+}$  showed clearly the highest energy phonon mode in PLZT to be at  $750\text{ cm}^{-1}$ . With respect to  $\text{LiNbO}_3$  as a host for rare-earths, PLZT possesses a lower phonon energy and higher refractive index thereby reducing nonradiative relaxation rates and raising spontaneous emission probabilities, respectively. Therefore, we suggest RE: PLZT as a strong candidate for consideration in active electro-optic device in optical communication systems.

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