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# Characterization of optical properties of nanocrystalline doped PZT thin films

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**Abstract**

High optical transmittance and refractive index together with strong electro-optic Kerr effect of the ferroelectric lead-zirconate-titanate (PZT) films can be utilized in various active optical applications like optical shutters, modulators and waveguides. Pulsed laser deposition (PLD) with XeCl-excimer laser with a wavelength of 308 nm and Nd-modified PZT target were used for the optical thin film fabrication. The films were deposited on single-crystal MgO (1 0 0) substrates. The crystal structure and grain size distribution were studied using XRD technique. The optical transmission spectra of the films were measured at UV–vis–NIR wavelengths, which was utilized to obtain the refraction index $n$ dispersion, extinction coefficient $k$, and the value of the band gap $E_g$. Electro-optic coefficients were determined by ellipsometric technique. In the case of polycrystalline films, mean grain size was between 9 and 20 nm. At the wavelength of 633 nm the refractive index varied from 2.28 to 2.46 as a function of mean grain size. Also, the electro-optic coefficient showed dependence on grain size distribution increasing from $0.37 \times 10^{-18}$ to $2.49 \times 10^{-18}$ $m^2/V^2$ with increasing mean grain size.


*Keywords:* Films; Grain size; Optical properties; PZT; Electro-optics

## 1. Introduction

High optical transmittance and strong Kerr electro-optic effect of the ferroelectric lead-zirconate-titanate (PZT) films can be utilized in various active optical applications like acousto-optic Bragg deflectors based on SAW technology, light-beam switching shutters, modulators and waveguides. In the Kerr effect, the change of the refractive index $\Delta n$ of the PZT film is proportional to the square of the applied electric field $E^2$, thus making the control of the polarized light propagation in the PZT film possible by using very simple electrode structures.[1] Especially, La-doped PZT ceramics has been reported to have excellent optical properties also in the form of thin films.[2] Together with the properties of the substrate material and PZT thin-film thickness, the optical properties are greatly affected by the crystal structure, orientation of the crystals, the grain size distribution, packing density, and the morphology of the film surface.[3,4] Some of these parameters are also strongly dependent on the film deposition and the thermal heat-treatment processes. In the case of polycrystalline PZT films grown by PLD, the films are typically composed of nanometer sized crystals.[5]

The influence of the heat-treatment process on the crystal size, orientation, and subsequently, on the optical properties of the PZT thin films were considered in this study. Especially the dependence of refractive index $n$ and electro-optic Kerr effect was investigated as a function of grain size distribution. Characterized PZT films were deposited from Nd-modified target used in PLD process. The effect of the Nd-addition on the mechanical and electrical properties of PZT is comparable to La-doping due to the equal valence (+3) and similar ionic radius.[6]

## 2. Experimental

A pulsed XeCl-excimer laser with a wavelength of 308 nm and $Pb_{0.97}Nd_{0.02}(Zr_{0.55}Ti_{0.45})O_3$ target with density

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of $7.4 \times 10^3$ kg/m$^3$ were used to deposit amorphous Nd-modified lead-zirconate-titanate (PNZT) thin films on MgO (1 0 0) substrate. The deposition was carried out at room temperature at a pressure of 6 mPa. The substrate and the target were placed parallel at a distance of 30 mm. The repetition rate of laser pulses was 25 Hz and the duration of the single pulse was 30 ns. After deposition, the PNZT thin films were post-annealed either at 700, 800 or 900 °C for 20 min under the inverted zirconia crucible together with some PNZT powder. The heating and cooling rate of 400 °C/h was used in every temperature profile. After the annealing, crystal structure of the PNZT films was studied by X-ray diffraction (XRD) measurements and the mean grain size was calculated using Warren-Averbach method.[7] A polycrystalline silicon sample with a large grain size was used as a standard for measurement of instrumental function, and Lorentz polarization correction was made for the raw XRD data. Results of microstructure analysis by X-ray diffraction, atomic force microscopy, and scanning electron microscopy of the post-annealed PNZT films are presented in our previous studies.[8]

Optical transmission spectrum at the wavelength range from 180 to 3000 nm was measured using Varian Cary 5000 spectrophotometer. External field induced birefringence shift $\Delta n$ was measured with setup similar to one proposed by Adachi and Wasa.[2] Metal electrodes forming a gap were vacuum deposited on the PNZT film. The measurement is based on determining the phase difference between perpendicular polarization states, when polarized light at 45° angle relative to electric field passes through PZT thin film. The used light source was 633 nm He–Ne laser. Electric fields up to 30 kV/cm were used for the measurements of otherwise unpoled samples. Refractive index $n$ and extinction coefficient $k$ were calculated from transmission data fitted with multiple Lorentz-oscillator model using SCI Film Spectrum software.

## 3. Results and discussion

Measured and fitted optical transmission $T(\lambda)$ spectra in UV–vis–NIR wavelengths of PNZT film with the thickness of 450 nm and annealed at 700 °C is presented in Fig. 1 together with transmission spectra of the MgO (1 0 0) substrate with the thickness of 500 μm. Lorentz multiple oscillator model was fitted to the data with an error of RMSE = 0.4899. In Fig. 2, there are calculated values of refractive index $n$ and extinction coefficient $k$ as a function of wavelength obtained from measurement data shown in Fig. 1. Refractive index shows a typical dispersion curve at UV–vis region and saturates to the value of 2.49 at IR wavelengths. The absorption band edge was around 318 nm in Fig. 2, but it was observed to be film thickness dependent so that, with the thicknesses below 100 nm, the edge was shifted towards shorter wavelengths. This possibly indicates the thickness dependent energy band gap that was also found in the case sol–gel-derived $SrTiO_3$ thin films by Bao et al.[9] Using Tauc-plot analysis,

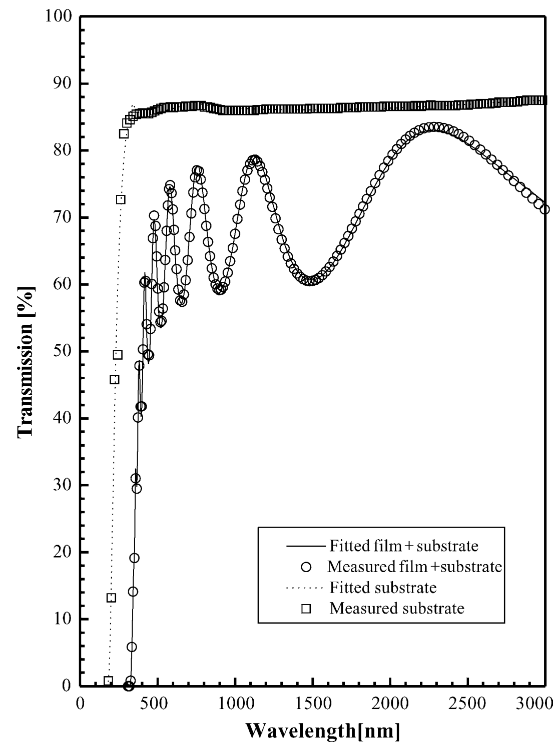


Fig. 1. Measured and fitted transmission spectra of MgO single-crystal substrate and PNZT thin film on MgO substrate post-annealed at 700 °C.

the energy band gap value $E_g$ = 3.95 eV was calculated from the extinction coefficient data shown in Fig. 2, and for the other samples $E_g$ varied between 3.79 and 3.975 eV. These values are high compared to the values reported for various PZT compositions but comparable with Nb-doped PZT films deposited by the PLD technique.[10,11]

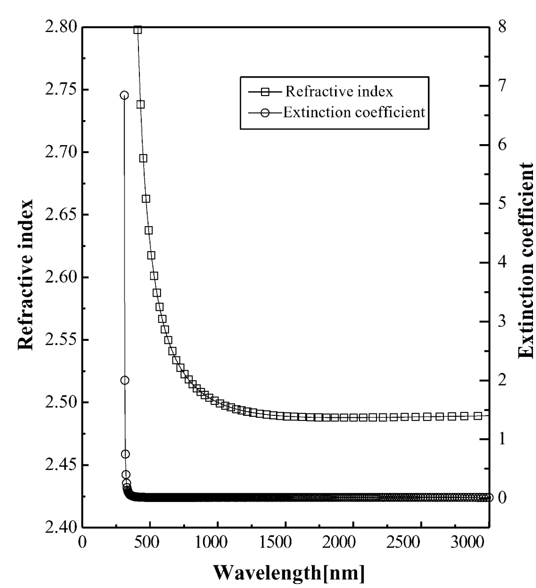


Fig. 2. Calculated refractive index $n$ and extinction coefficient $k$ of PNZT thin film on MgO substrate post-annealed at 700 °C.

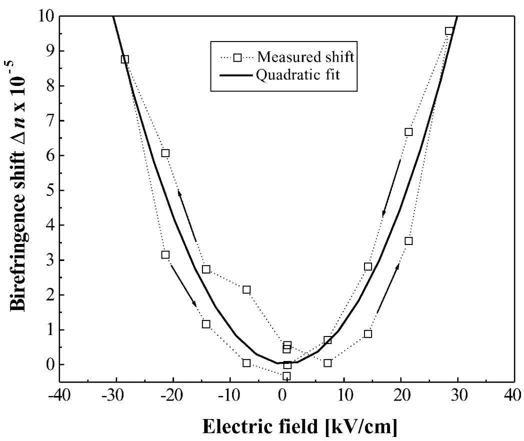


Fig. 3. Measured birefringence shift $\Delta n$ and quadratic fit as a function of applied electric field of PNZT thin film on MgO substrate post-annealed at 700 °C.

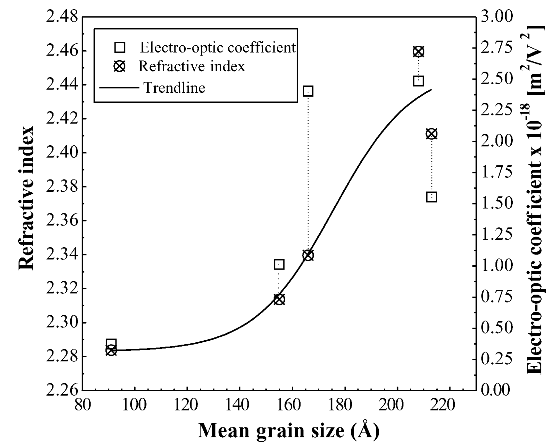


Fig. 4. Refractive index $n$ and electro-optic coefficient $R$ as a function of mean grain size of the PNZT thin films post-annealed at temperatures from 700 to 900 °C.

Electro-optic properties of the PNZT thin films were characterized by measuring the birefringence shift $\Delta n$ as a function of applied electric field. In Fig. 3, an electro-optic response with quadratic fitting curve of PNZT film with the thickness of 270 nm and annealed at 700 °C is shown. Birefringence shift $\Delta n$ and second order electro-optic coefficient $R$ are related according to equation:

$$\Delta n = \frac{1}{2} n^3 R E^2, \quad (1)$$

where $n$ is the refractive index and $E$ is the applied electric field.[2] In all measurements the birefringence shift had the same sign in both directions of electric field having nearly quadratic form with the shift magnitude around $\Delta n = 7 \times 10^{-5}$ at 25 kV/cm electric field. This quadratic behavior in unpoled PZT films is also reported in other studies.[2] Using Eq. (1) with $n = 2.41$ determined from transmission measurement data at 633 nm wavelength, the value of $R = 1.6 \times 10^{-18}$ m$^2$/V$^2$ was calculated. The hysteresis in birefringence shift in Fig. 3 indicates the ferroelectricity of the PNZT thin films.

The effects of the microstructure and grain size on the optical and electro-optic properties of the nanocrystalline films were also studied. It was found from the Warren-Averbach analysis made for the PNZT thin films using (0 0 1) and (0 1 1) reflections of $\theta$–2$\theta$ XRD measurements that the mean grain size varied between 91 and 213 Å with increasing post-annealing temperature. Also, the crystal orientation was found to change favoring the bulk ceramic like random orientation in films post-annealed at temperature of 700 °C, but having a strong tetragonal orientation in the films annealed at 900 °C.[8] Both refractive index and electro-optic coefficient were found to increase with increasing mean grain size, as is shown in Fig. 4. Value of the electro-optic coefficient increases from $0.37 \times 10^{-18}$ to $2.49 \times 10^{-18}$ m$^2$/V$^2$ with increasing mean grain size. Corresponding birefringence shift spans now from $1.4 \times 10^{-5}$ to $12 \times 10^{-5}$ at the electric field of 25 kV/cm. These values of $R$ are small compared to electro-optic coefficient of PLZT (9/65/35) with the value of $9.1 \times 10^{-16}$ m$^2$/V$^2$ for bulk ceramic and $7.2 \times 10^{-16}$ m$^2$/V$^2$ for pulsed-laser-deposited films with same composition.[12] For sputtered prepared PLZT thin films with compositions of (9/65/35) and (28/0/100), the reported values are $1.0 \times 10^{-16}$ and $0.6 \times 10^{-16}$ m$^2$/V$^2$, respectively.[2] However, the values are comparable to the properties of sol–gel deposited PLZT films.[13] Correspondingly, the value of refractive index increased from 2.28 to 2.46 with increasing mean grain size. In the films with the mean grain size above 200 Å the refractive index approaches typical values of PZT with various compositions.[10]

The dependence of the electro-optic coefficient on crystallite size distribution can be explained by the decrease in the lattice constant ratio $c/a$ of tetragonal ferroelectric unit cell. The critical crystallite size when ferroelectric tetragonal phase transforms to paraelectric cubic phase for $PbTiO_3$ was estimated to be around 70 Å by Chattopadhayaya et al.[14] This size effect diminishes various ferroelectric properties, for example, remanent polarization, low frequency dielectric constant and piezoelectric constants. Because the mean grain size of the films with weak electro-optic coefficients are around 100 Å the part of the grains is assumed to be already in paraelectric cubic phase and thereby not contributing to electro-optic effect. Cubic crystal structure can have influence on refractive index due to different unit cell structure and lattice constant. Furthermore, the volume occupied by the amorphous grain boundaries increases in the films with decreasing grain size. Since the total dielectric constant of the film is a combination of dielectric constants of grain boundaries and various crystallite phases, the electric field inducing birefringence shift is assumed to be lower in films with small grains. On the other hand, the refractive index related to the high frequency dielectric constant is also assumed to be dependent on mean grain size due to change in volume ratio of grain boundary and bulk grain, together with the volume fraction of cubic phase.

## 4. Conclusions

Pulsed laser deposition (PLD) with XeCl-excimer was used for Nd-modified PZT thin film fabrication on MgO (1 0 0) substrates. After deposition, the PNZT thin films were post-annealed either at 700, 800 or 900 °C to obtain different degree of tetragonal orientation and grain size distributions. The crystal structure and grain size distribution were studied using XRD technique and Warren-Averbach analysis. The optical transmission spectra of the films were measured at UV–vis–NIR wavelengths. Refraction index dispersion and extinction coefficient were calculated using multiple Lorentz-oscillator model. Electro-optic coefficients were determined by the ellipsometric technique. Both refractive index and electro-optic coefficient were found to increase with increasing mean grain size. Value of the electro-optic coefficient increased from $0.37 \times 10^{-18}$ to $2.49 \times 10^{-18}$ m$^2$/V$^2$ and the value of the refractive index increased from 2.28 to 2.46 with increasing mean grain size from 91 to 213 Å, respectively. The refractive index and electro-optic effect were found to be dependent on mean grain size of the films possibly due to change in volume ratio of grain boundary and bulk grain together with the lattice constant shift and consequent diminish of the ferroelectricity in phase transition occurring in grains with small volume.

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