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Strong electro-optically active Ni-substituted
 $\text{Pb}(\text{Zr}_{0.35}\text{Ti}_{0.65})\text{O}_3$ thin films: toward integrated
active and durable photonic devices†Minmin Zhu,^a Zehui Du,^c Soon Siang Chng,^a Siu Hon Tsang^c and
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Ferroelectric materials for precise control of light from lasers to optical communications have sparked great interest owing to their large electro-optic (EO) coefficients, low propagation loss, and fast switching time. Here, we report the deposition of highly oriented Ni-doped lead zirconate titanate (PZT) thin films on glass substrates as a novel way to seamlessly connect the electrical, optical, and magnetic domain. Small dielectric dispersion, low dielectric loss, and a large dielectric constant ranging from 10^2 Hz to 10^6 Hz were observed at a Ni content of 0.5 mol%. These films show well-saturated ferroelectric hysteresis with a large spontaneous polarization ($>30 \mu\text{C cm}^{-2}$) and a high Curie temperature ($>350^\circ\text{C}$). In addition, optical measurements indicate a large refractive index (~ 2.43), a low propagation loss ($\sim 4.14 \text{ dB cm}^{-1}$), a fast response time ($4.02 \mu\text{s}$), and an effective EO coefficient (167.7 pm V^{-1}), which are five times larger than those of the current standard material for EO devices (LiNbO_3). More importantly, such films can work well up to 250°C and retain above 80% of the EO performance at 10^4 Hz. Finally, the substitution of Ni^{2+} at the Ti^{4+} site shows distinct magnetic behaviors. The integration of EO active films could pave the way for future power-efficient, ultrafast switches, and compact integrated nanophotonic and magneto-optic devices.

Introduction

Ferroelectric oxide thin films (*i.e.*, $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, $(\text{K}_x\text{Na}_{1-x})\text{NbO}_3$ and BaTiO_3) and their derivative materials have attracted considerable attention for a variety of applications owing to their excellent piezoelectric, pyroelectric, ferroelectric, and electro-optic properties.^{1–3} Among them, EO materials allow the modulation of a beam of light without any degrading effects on laser linewidth and stability, and are widely used in photonic devices from lasers to optical telecommunications, such as optical modulators, beam deflectors, telecommunication switches, and mode-locking of lasers.^{4,5} Generally, EO effects are based on electric-field-controllable optical properties through the material, such as the phase, frequency, amplitude, or polarization of the beam. As for the thin film EO modulator, the optical wave phase ($\Delta\Phi$) changes in

response to an applied voltage (E), thereby leading to a change in the refractive index (Δn). Hence the refractive index $n(E)$ as a function of E is given by:⁵

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

where r_c and R are the linear Pockels and quadratic Kerr effect coefficients, respectively. Notably, the Kerr effect is a second-order electric-field effect and can be ignored when compared to the first-order Pockels effect. Thus, the equation above can be reduced as follows:

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

Herein, the effective Pockels coefficient, r_c , is a close approximation to the true coefficients which are always tensor quantities. However, they are the material's composite EO coefficient that allows the evaluation of the EO material's device performance in practice. Apparently, large r_c means more compact, lower consumption, and potentially less-expensive EO devices.

Lithium niobate (LiNbO_3 , LNO) as the current standard EO material has been used for EO modulators, realizing high-speed (over 10 Gbps) and wide band optical modulations.^{6,7} However, its primary drawback is a relatively low Pockels coefficient ($r_c =$

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30 pm V⁻¹),⁶ indicating that high voltages or thick materials should be used in LNO-based EO devices. Owing to the large EO coefficient (~ 148 pm V⁻¹), there have been numerous efforts to create thin film modulators with lead-free BaTiO₃ (BTO) and its derivatives ((Ba,Sr)-TiO₃, BST) as the modulating medium.^{8,9} One inherent problem in BTO and BST, however, is their Curie temperature (T_c , ferroelectric transition temperature) which lies just above room temperature. This seriously limits the stabilities of BTO-based modulators while operating over a wider temperature range. Therefore, ferroelectric thin film modulators with a larger EO coefficient and a higher transition temperature are desirable. Of all perovskite oxides, PZT combines a very high transition temperature (> 400 °C) and a large EO coefficient (> 200 pm V⁻¹),^{10,11} and may offer potential for compact thin-film modulators to operate over a wide temperature range. In general, highly-oriented or textured PZT films are usually required to obtain a large EO effect, because most of these complex oxides are naturally optically anisotropic. George *et al.* revealed an excellent linear effective Pockels coefficient of 240 pm V⁻¹ in (100)-oriented PZT thin films.¹¹ Our previous work also confirmed that epitaxial (100) PZT thin films possess a large EO coefficient of ~ 270 pm V⁻¹.⁴ Moreover, the epitaxial or textured growth of PZT thin films is also desirable for reducing light scattering caused by numerous grain boundaries existing in polycrystalline films.^{5,12} In addition, PZT thin films with a ABO₃ perovskite-structure can easily introduce A-site and B-site doping, leading to extra functionality that can widen the application scope of the materials. For example, for highly oriented (100) PZT thin films with Fe⁺ doping concentrations from 0.1% to 2%, the value of magnetization increases from 0.14 to 0.51 emu cm⁻³.¹³ Khorrami *et al.* also found the presence of magnetism in Pb(Zr_{0.52}Ti_{0.43}X_{0.05})O₃ (X = Fe, Ni, Co),¹⁴ revealing the coexistence of ferroelectric and ferromagnetic orderings which is the mutual exclusion in nature for multiferroic materials.¹⁵ Until now, systematic study on Ni-doped PZT thin films has been inconsistent, and the impacts of the Ni content on their ferroelectric, electro-optic, and magnetic properties remain unclear. In this work, pure perovskite-structured and highly-oriented Ni-doped PZT thin films have been deposited on the Corning glass substrate by magnetron sputtering using highly oriented (Pb_{0.86}La_{0.14})TiO₃ as the seeding layer. We systematically investigate the influences of the Ni substitution on the microstructure, and ferroelectric, optical, electro-optic, and magnetic properties of highly textured PZT thin films. More importantly, the Ni-substituted PZT thin films exhibit high heat tolerance and frequency durable EO behaviours, which is useful for high-speed modulator devices that operate over a wide working range. Such thin films can possess more than one ferroelectric, ferromagnetic, ferroelastic, and electrooptic ordering simultaneously and have attracted a lot of interest because of their fundamental physics and potential application in optoelectronic and magneto-optic devices.

Experimental section

Seeding layer preparation

(Pb_{0.86}La_{0.14})TiO₃ (PLT) sols were synthesized by using dehydrated lead acetate (Pb(CH₃COO)₂·3H₂O), titanium isopropoxide

(Ti[OCH(CH₃)₂]₄), and lanthanum nitrate (La(NO₃)₃·6H₂O) as precursors and 2-methoxyethanol (CH₃OCH₂CH₂OH, 2-MOE) as the solvent. Notably, 5 mol% of Pb excess was added to compensate the lead loss during the annealing process. Lead acetate was firstly dissolved in 2-MOE, followed by the addition of titanium isopropoxide. After refluxing at 120 °C for 4 h, the solutions were mixed with lanthanum nitrate and stirred for 2 h. Subsequently, PLT seeding layers were deposited on the Corning 1737 glass by spin coating, pyrolyzed at 450 °C for 10 min and subsequently annealed at 575 °C for 20 min.

Thin film deposition

Pb(Zr_{0.35}Ti_{0.65})_{1-x}Ni_xO₃ (PZTN) thin films with different Ni-doping contents were prepared by radio frequency (RF) magnetron sputtering. The substitution is performed on Zr or Ti sites so that the nominal formula of the sample is Pb(Zr_{0.35}Ti_{0.65})_{1-x}Ni_xO₃ ($x = 0\%$, 0.5%, 1.0%, 1.5%, and 2%, namely PZT, PZTN5, PZTN10, PZTN15, and PZTN20). Prior to the deposition of PZTN films, the sputtering chamber was first evacuated to a base pressure of 1.6×10^{-6} Torr following which the mixed gases of 10% oxygen and 90% argon were introduced. The pressure and RF power were 15 mTorr and 150 W, respectively. The typical growth time was 1 h and the thickness was about 1 μ m. The as-grown PZTN films were annealed at 600 °C for 10 minutes in oxygen to obtain high-quality crystallinity.

Electro-optic measurement

The electric field induced optical modulation of the PZTN thin film was characterized by a customized ellipsometric setup using a 632 nm He-Ne laser as the light source. In this setup, an input laser beam is focused through the film at an incident angle of 45° onto the top electrode. Under the applied electric field, the laser beam propagates through the PZTN thin film. An oscilloscope converts this phase shift ($\Delta\Phi$) into an intensity modulation, which is measured using a photodetector locked to the frequency of the excitation voltage.

Characterization

X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM6340) and transmission electron microscopy (TEM) were performed to investigate the crystallinity and microstructure of the PZTN thin films. Dielectric property measurements were carried out using a traditional interdigital technique. A standard Radiant RT6000HVS type ferroelectric tester was used to study the dielectric and ferroelectric properties of the samples. The measurement area is 0.3 mm in diameter and is coated with 100 nm platinum (Pt) by sputtering. The chemical states and surface compositions of the as-deposited PZTN thin films were analysed by X-ray photoelectron spectroscopy (XPS) with Al K radiation at an energy of 1486 eV. The refractive index and propagation loss of the PZTN films were determined using a prism coupler (Metricon 2010, Metricon). The EO properties were investigated by the Senarmont method with a He-Ne laser. Coplanar type gold electrodes with a gap of 10 μ m were deposited on the films for applying the electric field. The magnetic properties were examined using a

vibrating sample magnetometer (VSM7404) in the field range of $H = 0$ to ± 7000 G at room temperature.

Results and discussion

Highly (100)-oriented PLT films have directly grown on the glass from the sols after aging for 1–2 days, as confirmed by XRD analysis shown in Fig. 1a. The as-prepared PLT films from sols aging 2 days or less exhibited only the (100) peak, indicating distinct oriented textures, although there was no lattice matching between the films and substrates. Notably, Corning glass is the more preferred substrate due to its low refractive index (1.5) and low cost, as compared to common single crystal substrates such as SrTiO_3 , MgO , and Al_2O_3 which are more expensive.¹⁶ Another factor is that PLT has a matched thermal expansion coefficient (TEC, $4.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) to that of PZT films ($3.7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$).¹⁷ More importantly, such (100) oriented PLT with a tetragonal phase ($a = 0.402$ nm and $c = 0.412$ nm) is more desirable for the growth of textured PZTN thin films as only one seeding layer is required owing to a low lattice mismatch of 2.2%,¹⁸ when compared with that of tetragonal $\text{Pb}(\text{Zr}_{0.35}\text{Ti}_{0.65})\text{O}_3$ thin films ($a = 0.4107$ nm and $c = 0.4116$ nm).^{19,20} A typical grain structure is observed in the as-grown PZT thin films, as shown in Fig. 1b. Energy dispersive spectroscopy (EDS) analysis reveals the presence of O, Pb, Zr, and Ti, as well as the stoichiometric ratio of Zr/Ti close to 65 : 35 (the inset of Fig. 1b). It can be seen from Fig. 1c that the film is dense with a uniform thickness of $\sim 1 \text{ } \mu\text{m}$.²¹ Fig. 1d shows the HRTEM image of the films, further confirming the excellent crystallinity of the as-prepared films. The d spacing of the PZT thin film was ~ 0.290 nm, which can be attributed to the (110) planes of PZT.^{22,23} The dot-like selected area electron diffraction (SAED)

pattern (the inset of Fig. 1d) can be indexed to the (001), (110) and (111) diffractions of the tetragonal PZT, further confirming that the sample is crystalline.²²

Utilizing the highly (100)-oriented PLT as the seeding layer, highly textured Ni-substituted PZT thin films are expected. Fig. 2a shows the XRD patterns of the as-deposited PZTN thin films with different Ni contents ranging from 0% to 2%. As noted above, the PZTN thin films with a pure-perovskite structure (ABO_3) and without any metaphase such as pyrochlore ($\text{A}_2\text{B}_2\text{O}_7$) will seriously degrade the ferroelectric performance (Fig. S1, ESI†).²⁴ As the Ni content increases, a shift to a larger angle at the (100) peak of the PZTN film (as shown in Fig. 2b) is observed when compared to the pure PZT thin film, indicating a smaller lattice (a) of the PZTN thin film which can be derived from the Bragg equation ($n\lambda = 2d \sin \theta$). Fig. 2c exhibits the derived lattice a and c of the PZTN films as a function of Ni content. The former slightly reduces from 0.4064 to 0.4038 nm as the Ni content increases, whereas the latter increases from 0.4043 to 0.4116 nm. To evaluate the degree of the grain orientation, the orientation parameter α can be defined as:²⁵

$$\alpha = [\sum(I_{00n}/I_{00n}^*) + \sum(I_{00n}/I_{n00}^*)]/[\sum(I_{hkl}/I_{hkl}^*)] \quad (3)$$

where n is the number of reflections, I_{hkl} is the measured intensity of the (hkl) peak for the PZTN films, I_{hkl}^* is the intensity of the power diffraction data of the films. The value α of the PZTN films decreased from 86.6% to 79.8% when increasing the Ni content from 0.5% to 2% (Fig. 2d). These facts reveal that the films using PLT as a seeding layer are improved due to alignment with the substrates. More interestingly, the orientation α can remain at approximately 80% with a Ni content of 2 mol%. In addition, the surface roughness is measured at approximately 2.6 nm and no pores between irregular-shaped grains were observed (the inset of Fig. 2d), indicating that the films are very smooth and homogeneous,

Fig. 1 XRD patterns of seeding layer PLT on the 1737 Corning glass during 0 and 2 days. The inset is the perovskite structure with the Pb/La atom at the corner, the O atom at the face center, and Ti in the center. (b) SEM image of the PZT thin film with typical grain domains. The inset is the corresponding EDS spectrum. (c) Cross-section SEM image of PZT thin films grown on the PLT-coated substrate. (d) HRTEM image of the PZT thin film. The inset shows the SAED pattern.

Fig. 2 (a) XRD patterns of the as-prepared PZTN with Ni contents from 0 to 2%. (b) A comparison of the (100) diffraction peak position for the patterns. (c) Lattice parameters of PZTN thin films. (d) Orientation degree α of the PZTN films as a function of Ni content. The inset is the AFM image of the PZTN thin film.

thereby minimizing the propagation loss due to surface scattering.

Fig. 3a shows the Raman spectra of PZTN thin films. The tetragonal PZTN belongs to space group C_{4v} ($P4mm$), which regularly yields $3A_1 + B_1 + 4E$.²⁶ Some typical phonon modes of E(2TO), E(silent) + B_1 , A_1 (3TO) and E(3LO) for the PZT thin films are observed which are in agreement with those reported in ceramic samples.²⁷ It is believed that the two-phonon (2P, TO + LO) mode at $\sim 950\text{ cm}^{-1}$ and the two-magnon (2M) mode at 1490 cm^{-1} arise from the nickel.^{28,29} There is a pronounced frequency variation in the E(2TO), E(silent) + B_1 , and E(3LO) mode (Fig. 3b) being observed, which may come from either the fluctuation of the domain size or the distributions of Ni-doped B-site ions (Ti,Zr) in thinner films. To confirm the existence of Ni and its possible oxidation states, high-resolution XPS measurements have been carried out on PZTN films. Fig. 3c shows the corresponding full spectra. The characteristic peaks of Pb 4f_{7/2} (137.5 eV), Pb 4f_{5/2} (142.3 eV), Zr 3d_{5/2} (180.9 eV), Zr 3d_{3/2} (183.2 eV), Ti 2p_{3/2} (457.4 eV), Ti 2p_{1/2} (463.1 eV), Ni 2p_{3/2} (854.7 eV), Ni 2p_{1/2} (872.8 eV), and O 1s (530.4 eV) were observed, which are consistent with a previous report on sputtered PZT thin films.³⁰ The systematic shifts of the spectra were corrected with the help of the carbon 1s (284.6 eV) line.³¹ As shown in Fig. 3d, the observed binding energy difference between the Ni 2p doublet spectra, i.e., 2p_{3/2} and 2p_{1/2}, is found to be $\sim 18.6\text{ eV}$,

Fig. 3 (a) Raman spectra of PZTN thin films. (b) Raman intensities of E(2TO), E + B_1 , E(3LO) as a function of Ni content. (c) Full XPS spectra of the as-grown PZTN thin film. (d) XPS spectrum of the nickel element in the PZTN film. (e) A $2 \times 2 \times 4$ supercell adopted in the theoretical study, where one Ti^{4+} ion is replaced by nickel dopants and one oxygen vacancy (O^{2-}) is located at the spatial center. In this case, local electroneutrality is maintained.

whereas the standard doublet separation is 18.4 eV for NiO and 17.4 eV for metallic Ni.³⁰ Thus, it seems that there is a clear presence of Ni–O bonding with the possible occupation of Ni at the center of the BO_6 octahedral. Fig. 3e illustrates the doping behaviour of Ni in the PZT matrix. In the supercell, a Ti^{4+} ion is replaced by a Ni^{2+} ion. To maintain charge neutrality, an oxygen vacancy is produced ($\text{N}'_{\text{Ti}} - \text{V}''_{\text{O}}$). In fact, low valence state ions such as Fe^{3+} and Ni^{2+} ions are considered for acceptor doping to replace B-site ($\text{Zr}^{4+}/\text{Ti}^{4+}$) atoms, creating oxygen vacancies during the annealing process. By contrast, high valence state ions including W^{6+} or Nb^{5+} are for donor doping, leading to the lead vacancy.^{32,33}

Such acceptor doping can result in the change of the element's valence in the PZT thin films. The chemical compositions of the PZTN thin films were further analyzed by XPS. The high-resolution spectra of Pb 4f, Zr 3d, Ti 2p, and O 1s are simulated by fitting their peaks using the multi-peak Gaussian method. Fig. 4a–d show the rescaled XPS spectra of Pb 4f, Zr 3d, Ti 2p, and O 1s, respectively. The XPS peaks of Pb 4f_{7/2}, Zr 3d_{5/2}, and Ti 2p_{3/2} photoelectrons located at 138.3, 181.3, and 457.8 eV (Fig. S2, ESI†) are in agreement with the values previously reported.^{34,35} Note that the spin–orbit split Pb 4f peaks exhibited two typical binding states: one at $\text{Pb}(4f_{7/2}) = 138.3\text{ eV}$ and another at $\text{Pb}(4f_{7/2}) = 137.7\text{ eV}$ (Fig. S2a, ESI†), which are typical values for the Pb–O binding.³⁵ The intensity of all Pb 4f, Zr 3d and Ti 2p reduces as the Ni content increases. Moreover, the intensity of O 1s also shows a similar trend (Fig. 4d). The O 1s peaks can be identified as a combination of two peaks. The first peak is located at approximately 531.00 eV which is derived from the adsorbed oxygen of the sample, whereas the second peak is located at $\sim 529.00\text{ eV}$ which is ascribed to oxygen in O1/O2 sites in the unit cell (Fig. S2d, ESI†).³⁶ As shown in

Fig. 4 High resolution spectra of (a) Pb 4f, (b) Zr 3d, (c) Ti 2p, and (d) O 1s, photoelectrons for PZTN thin films. Peak shift of (e) Pb 4f_{7/2} and O 1s as a function of Ni content, as well as (f) Zr 3d_{5/2} and Ti 2p_{3/2}.

Fig. 4e, the O peak shifts from 530.0 to 529.5 eV, indicating the change of the oxygen valence state due to the presence of oxygen vacancy. In addition, it is seen from Fig. 4f that the Zr peak shifts from 181.4 to 181.1 eV while the Ti peak shifts from 458.1 to 457.7 eV with increasing Ni doping. It is believed that the Ni substitution leads to the changes in the chemical valence state of Zr and Ti. Similar changes of the valence states have also been observed in the PZT thin films with other doping metals, such as W-doped PZT and Mo-doped PZT.³⁷

Typical polarization–electric field (P – E) hysteresis loops of the films measured at a frequency of 100 Hz along with the spontaneous polarization (P_s) and coercive field (E_c) derived from the hysteresis loops are shown in Fig. 5a and b. Well-saturated hysteresis loops in good square shapes are observed for all the current compositions, suggesting that majority of the domains in thin films are c -domains (Fig. 5a). As shown in Fig. 5b, pure PZT exhibits a well-defined square loop with a P_s of $\sim 34.5 \mu\text{C cm}^{-2}$ and an E_c of 81.5, slightly lower than the values previously reported in the epitaxial counterpart.⁴ A Ni substitution of 0.5 mol% results in a slightly reduced coercive field and spontaneous polarization. As the Ni-doping continues to increase, both the E_c value and the P_s value significantly reduces due to the larger lattice variation induced by Ni substitution. Fig. 5c shows the frequency-dependent relative dielectric permittivity (ϵ_r) and loss tangent ($\tan \delta$) of the PZTN thin films with different Ni contents at room temperature. Notably, the ϵ_r for all films is stable over a wide range of

frequency. The loss tangent is almost constant, <0.05 , in frequencies from 10^2 to 10^6 Hz; above 10^6 Hz, a drastic increase was observed in loss tangent with the increase of frequency. Compared to pure PZT, an improvement in dielectric loss was observed for PZTN thin films. Meanwhile, the dielectric constant becomes stable with small dispersion in a wide frequency range from 10^3 to 10^6 Hz. This is attributed to the existence of grain and roughness in the surface morphology. Table 1 lists the ferroelectric properties of highly oriented PZTN thin films. Fig. 5e shows the plot of the dielectric constant of the PZTN films as a function of temperature at frequencies 10k, 20k, and 50k Hz. In a normal ferroelectric thin film, the relationship between ϵ and T is given by the Curie–Weiss equation:²³

$$\frac{1}{\epsilon} = \frac{(T - T_c)}{C} \quad (4)$$

where ϵ is the dielectric constant, T is the temperature, T_c is the Curie temperature (the phase transition temperature from the ferroelectric phase to the paraelectric phase), and C is the constant. In this case, the responding $1/\epsilon$ versus $(T - T_c)$ curves in the PZTN20 thin films under different frequencies are also measured (the inset of Fig. 5e). Both exhibit a linear behaviour which agrees well with the Curie–Weiss relationship in typical ferroelectric thin films. It is noticed that the T_c of the PZTN20 film is calculated to be 318.5°C . Fig. 5f presents the dielectric constant and Curie temperature values for PZTN thin films. Although the T_c value changes from 396.1°C to 318.5°C , owing to the presence of nickel doping amounts, this value is much larger than that of lead-free BaTiO_3 ($T_c = \sim 120^\circ\text{C}$) and $(\text{Ba,Sr})\text{TiO}_3$ ($T_c = \sim 89^\circ\text{C}$) thin films.^{38,39} Apparently, such a high T_c indicates a wide operating range for piezoelectric and electro-optic applications.

Refractive index is one of the most important factors for the use of EO materials and is also required for the calculation of r_c based on eqn (2). Fig. 6a shows a schematic illustration of a prism coupler which can measure the refractive index and its anisotropy for the bulk or thin film sample with high accuracy. Fig. 6b shows the transverse electric (TE, parallel to the film surface) and the transverse magnetic (TM, perpendicular to the surface) guided-mode spectra of the PZTN5 films. Five TE and three TM modes have been excited in the PZTN5 thick films. The sharpness of the reflectivity dips indicates a good confinement of the incident laser in the PZTN waveguiding layer. Using all the TE and TM modes in the spectra, the refractive indices of the PZT films can be derived, shown in Fig. 6c. Apparently, both the ordinary (n_o) and extraordinary (n_e) reduces as the Ni

Fig. 5 (a) P – E hysteresis loop of PZTN films. (b) The spontaneous polarization (P_s) and electric field (E_c) of PZTN films as a function of Ni content. (c) The dielectric constant (ϵ) and dielectric loss ($\tan \delta$) of the films in a wide frequency range of 100 Hz–10 000 kHz. (d) The dielectric constant of the samples at 10k, 20k, and 50k Hz as a function of Ni content. (e) The dielectric constant of the PZTN20 film as a function of temperature. The inset is the $1/\epsilon$ vs. temperature curve. (f) Curie temperature (T_c) of the PZTN films as a function of Ni content.

Table 1 Ferroelectric properties of highly oriented Ni-doped PZT thin films

Samples	P_s ($\mu\text{C cm}^{-2}$)	P_r ($\mu\text{C cm}^{-2}$)	E_c (kV cm^{-1})	ϵ_r (10k Hz)	$\tan \delta$ (%)	T_c ($^\circ\text{C}$)
PZT	34.5	28.5	81.5	991.3	6.35	396.1
PZTN5	32.8	26.9	85.4	954.9	3.72	363.7
PZTN10	29.4	24.1	89.8	928.4	2.74	344.8
PZTN15	26.5	21.5	98.2	910.7	2.59	327.1
PZNT20	18.2	14.8	99.8	892.1	2.01	318.5

Fig. 6 (a) Schematic illustration of a prism coupler. (b) Refractive index of the films in the TE and TM modes. (c) Derived n_o and n_e of the as-grown samples as a function of Ni content. (d) The corresponding propagation loss as a function of Ni content. The inset is a schematic diagram of the experimental arrangement for propagation loss.

content increases. In addition, the optical propagation loss of the PZTN thin films can be determined by measuring the variation in the scattering intensity along the direction of the laser beam propagation (Fig. 6d). Although the loss slightly increased from 3.87 to 4.33 dB cm⁻¹, this value is still relatively low and is comparable to those of the submicron thick ferroelectric films such as Pb(Mg,Nb)O₃-PbTiO₃ (PMN-PT, 4.1 dB cm⁻¹) and BST (3.04 dB cm⁻¹) thin films.^{40,41} Table 2 summarizes the derived values of n_o and n_e for perovskite EO materials using a prism coupling method at room temperature, as well as their corresponding propagation loss. Our PZTN thin films have a refractive index ranging from 2.23 to 2.36 at 632.8 nm which is comparable to that of the pure PZT thin film ($n = 2.215$ – 2.431).⁴² It is lower than that of PMN-PT ($n = 2.599$) and very similar to that of (Pb,Li)(Zr,Ti)O₃ (PLZT, $n = 2.345$) using a prism coupler.^{25,43} Notably, the BO₆ octahedra in an oxygen-octahedral ABO₃ thin film dominates its corresponding optical properties and the lowest energy oscillator is the largest contributor to the dispersion of the refractive index.⁴ In addition, some void networks imposed by interface, surface roughness, and porosity inside the film are another cause for the refractive index variation in the PZTN films.

Table 2 Refractive index, EO coefficients, and half-wave voltage for common EO thin films

Materials	n_o	n_e	Loss (dB cm ⁻¹)	r_c (pm V ⁻¹)	λ (nm)	Ref.
BaTiO ₃	2.224	2.219	—	148	1539	8
BST	2.219	2.170	3.0	125	633	47
LiNbO ₃	2.233	2.203	—	30	633	6
KNN	2.247	2.216	—	17.4	633	48
BiFeO ₃	2.721	2.653	4.6	15.9	633	45
PLT	2.375	2.271	—	55	633	49
PLZT	2.365	2.345	4.0	152	633	50
PMN-PT	2.542	2.448	4.1	182	633	43
PZT	2.454	2.433	3.9	196.7	633	This work
PZTN5	2.417	2.384	4.1	167.7	633	This work

Using a 632.8 nm He-Ne laser as the light source, an ellipsometric amplitude modulator in a modified Senarmont compensator style is used to evaluate the electro-optic performance of the PZTN thin films.⁴⁴ Fig. 7a shows a schematic of the EO modulator-based PZT multilayer films. In this setup, the angle between the two polarizers is 90°, which can ensure that no modulated signal will be observed without any applied electric field. Under a certain applied electric field (AC or DC), modulation of the light transmitted through the PZT thin film can be received by a detector (Fig. 7b). The relationship between the field-induced birefringence shift (Δn) and the applied electric field (E) at room temperature is given by eqn (2), and hence r_c can be extracted. Most electro-optic materials belong to a broad range of transparent perovskite-structured ferroelectric materials. Fig. 7c shows the change in the birefringence (Δn) of the PZTN thin films as a function of E . All the samples exhibit a linear EO behaviour (Pockels effect) and strong structure-dependent EO effects can also be observed. Meanwhile, the corresponding switching time in the PZT thin film is approximately 5.72 μ s (The inset of Fig. 7c), which is comparable to the theoretical and experimental results in other EO materials such as BiFeO₃ (BFO) and PMN-PT.^{45,46} Fig. 7d shows the linear EO coefficient (r_c) and switching time (τ) as a function of Ni content. Generally, the linear Pockels coefficient strongly depends on the spontaneous polarization.⁴

$$r_{ijl} = 2P_s \epsilon_0 (\epsilon_{kl} - \delta_{kl}) g_{ijk} / \zeta^3 \quad (5)$$

where r_{ijl} is the linear EO coefficient, P_s is the spontaneous polarization, ϵ_0 is the dielectric permittivity, ϵ_{kl} is the dielectric tensor, δ_{kl} is the Kronecker delta, g_{ijk} is the temperature independent quadratic polarization-optic coefficient of the octahedral, and ζ is the packing density of the octahedral. For perovskite thin films, $\zeta = 1$. The r_c reduces from 195.2 to

Fig. 7 (a) Experimental setup for electro-optic coefficient measurements. (b) Electric-field-controllable optical modulation in the film under various applied electric fields. (c) Change in the birefringence (Δn) of the films at 5 Hz as a function of the applied electric field. The inset is the switching time of the PZT20 film. (d) The EO coefficient (r_c) and switching time (τ) of the films as a function of Ni content.

32.2 pm V⁻¹ as the Ni content changes from 0 to 2%. The spontaneous polarization P_s also exhibits a similar trend as the Ni content increases (Fig. 5b), which is consistent with eqn (5). Importantly, at a Ni content of 0.5 mol%, the PZTN5 thin films exhibit an effective EO coefficient of ~ 167.7 pm V⁻¹, which is five times larger than the current standard material for EO devices (LiNbO₃). On the other hand, as the Ni content increases, the switching time τ increases slightly due to the larger interface roughness induced by the Ni doping effect (Fig. S3, ESI†). Moreover, the differences between the (001)/(101) and (111) orientations in the PZT thin films may broaden the switching characteristics, which is expected to be responsible for the observed variation in the switching time.¹ These giant EO responses and fast switching time have made PZTN the material of choice for a variety of electro-optic applications ranging from laser to optical telecommunication.

A thin-film electrooptic modulator based on transparent perovskite oxides is a well-established device and is crucial in the telecommunication industry. Fig. 8a shows the comparison of the EO performance of PZT-based thin films with those of other common EO materials. It is noted that most of the state-of-the-art EO materials are based on lead-free and lead-based transparent perovskite-structured ferroelectrics. Generally, lead-free EO materials contain LiNbO₃,⁶ BaTiO₃,⁸ (Ba,Sr)TiO₃,⁴⁷ (K,Na)NbO₃ (KNN),⁴⁸ and BiFeO₃,⁴⁵ while lead-based EO ceramics include (Pb,Li)TiO₃ (PLT),⁴⁹ PLZT,⁵⁰ PMN-PT,⁴³ and PZT. As we have noted, lead-based PZT thin films have exhibited some excellent advantages including large Pockels coefficient. By contrast, most lead-free EO materials including LNO, KNN, and BFO possess a very relatively small EO coefficient value ($r_c < 30$ pm V⁻¹). Although BTO and its derivative (BST) demonstrate a large EO coefficient which is comparable to those of PLZT and PMN-PT, their phase transition temperature (T_c) is less than 120 °C, thereby indicating the instabilities of EO

modulators when operating at high temperature.^{32,51} Fig. 8b shows the comparison of T_c of PZT-based thin films with other EO materials. Compared to lead-free EO thin films such as BTO and BST, most lead-based EO counterparts always demonstrate a relatively high T_c (> 180 °C) such as PLZT and PZT, as well as a large EO coefficient of > 160 pm V⁻¹ at the same time. More importantly, the T_c of the PZT and PZTN20 thin films in our work are 396.7 °C and 318.6 °C, respectively, therefore indicating that our PZT-based devices possess a wide operating range. As shown in Fig. 8c, the EO coefficients exhibit a weak increase for PZT as the temperature increases from 20–200 °C and are nearly invariant for PZTN devices, indicating the excellent stability in a wide temperature range. The negligible temperature dependent properties may be associated with their dielectric constant and spontaneous polarization and are very attractive for integrated optic applications.⁴³

Many high-performance EO thin films such as PMN-PT and PLZT are relaxors in nature. Under the applied electric field, they often exhibit a quadratic EO behaviour (Kerr coefficient, R) which always shows a highly diminished EO performance at high frequency.²⁵ For example, the EO response of PLZT devices at 10⁴ Hz is less than half of the DC response.⁵² Conversely, PZT and its derivatives, PZTN thin films, do not display a relaxor EO effect, evidenced by temperature-dependent dielectric constant results (Fig. 5e). Fig. 8d shows the effect of operating the PZT and PZTN5 thin film modulator at higher frequencies. The measured r_c at 10⁴ Hz is about 140.6 pm V⁻¹, demonstrating that PZTN5 can maintain $> 80\%$ of its DC r_c , even at frequencies as high as 10⁴ Hz. All of this is particularly important as most EO modulators operate at relatively high driving frequencies. In addition, this kind of drop off is also found in other EO materials that rely on domain reorientation phenomena, such as lead-free BTO and KNN thin films which always demonstrate normal ferroelectric behaviours and hence comply with the Curie-Weiss equation in eqn (4).^{53,54} It has been reported that the BTO single crystal loses $\sim 3/4$ of its DC r_c value under high-frequency clamping conditions. Meanwhile, thin-film BTO results also show that the value of r_c at 10⁴ Hz is about 1/2 of the DC r_c .⁵⁴ On the other hand, the linear EO coefficient of the KNN-STO thin film at 10⁴ Hz remains at a relatively lower value, $< 50\%$ of its DC r_c . Apparently, in the frequency range reported here (up to 10⁴ Hz), the EO performances of both PZT and PZTN in our work are superior when compared to other normal ferroelectrics such as BT and PLZT. Therefore, in combination with high transparency, giant EO coefficient, fast switching response, and high transition temperature, PZT-based materials demonstrate the potential for fast-switching broadband electro-optics in a wide operating range.

Besides excellent ferroelectric and electro-optic performance, magnetism can also be observed in PZTN thin films. Magnetization (M) as a function of magnetic field (H) was measured using a VSM at 300 K. An anti-S-type M - H curve can be observed in the pure PZT thin films, which indicates the intrinsic diamagnetic nature of the pure PZT sample (the inset of Fig. 9).⁵⁵ In the presence of PZT thin films with the perovskite structure, the ferromagnetism may be due to defects

Fig. 8 Comparison of (a) electro-optic coefficient (r_c) and (b) Curie temperature (T_c) of well-known perovskite structured oxide materials. (c) Temperature dependence of the EO coefficients of PZT and PZTN5 thin films. (d) EO coefficient versus driving frequency in PZT and PZTN5 thin films.

Q4 Fig. 9 (a) Magnetization hysteresis loops of the PZTN thin film at room temperature. The inset is the M - H curve of the pure PZT thin film under the same conditions.

or oxygen vacancies.⁵⁵ Correspondingly, the diamagnetic contribution of the host PZT to these Ni-doped samples was corrected (Fig. 9). When Ni ions were introduced into the PZT thin films, typical magnetic hysteresis loops were obtained. Upon increasing the Ni content from 0.1% to 2%, the value of magnetization increases from 3.38 to 4.45 emu, while the corresponding coercive field changes from -2.47×10^{-5} to -1.12×10^{-5} Oe. The appearance of the typical S-type ferromagnetic hysteresis in the M - H curve with the increasing Ni-doping content indicates that these Ni-substituted PZT samples exhibit ferromagnetic properties even at room temperature. Moreover, increasing Ni-doping contents can lead to magnetization enhancement. Similar magnetic coupling behaviours were reported in Fe-doped PZT and PbTiO_3 nanocrystals.^{56,57} There are several mechanisms that can explain the origin of ferromagnetism in magnetic metal-doped PZT thin films. Firstly, the secondary phase formation such as the magnetoplumbite phase is attributed to the presence of magnetism. Kleebe *et al.* have observed the formation of a magnetoplumbite secondary phase ($\text{PbFe}_{12}\text{O}_{19}$) in Fe-doped PZT thin films by employing electron paramagnetic resonance (EPR) spectroscopy.⁵⁸ Another is the exchange interaction of ferric ions *via* an electron trapped in a bridging oxygen vacancy (F-center).⁵⁹ Theoretically, an electron trapped in the oxygen vacancy makes an F center, where the electron occupies an orbital which overlaps the d shells of both iron neighbours. For Fe^{3+} , $3d^5$ only has unoccupied minority spin orbitals, the trapped electrons will be spin down, and the two iron neighbours will be spin up.⁵⁹ The exchange interaction between two irons *via* the F center causes ferromagnetic coupling, where the F center is similar to the bound magnetic polaron. Therefore, it can be considered that the magnetic behaviour in the Ni-PZT system may arise from the second mechanism. In addition, further theories and experimental studies are required to better understand the magnetic mechanism implicated by the system. Such PZTN thin films combining ferroelectric, electrooptic and ferromagnetic orderings simultaneously may receive considerable

attention and elicit widespread interest in optoelectronic and magneto-optic fields.

Conclusions

Deposition of highly textured Ni-substituted PZT thin films on glass substrates as a novel way to seamlessly connect the electrical, optical, and magnetic domain. These films have shown stable dielectric behaviors and well-saturated ferroelectric hysteresis, with a large spontaneous polarization and Curie temperature. Optical and electro-optic analyses indicate a large refractive index, a low propagation loss, and a fast response time. An effective EO coefficient of 167.7 pm V^{-1} is observed in the PZTN5 film, which is five times larger than that of the current standard material for EO devices (LiNbO_3). Such PZTN5 films can work well up to 250°C and retain $>80\%$ of the EO performance at 10^4 Hz. Finally, the substitution of Ni^{2+} at the Ti^{4+} site shows distinct magnetic performances. Our study reveals that B-site substitutions in a model EO material PZT can provide an additional degree of freedom to further boost electro-optic and magneto-optic devices.

Conflicts of interest

There are no conflicts to declare.

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Supporting Information

Strong Electro-Optically Active Ni-substituted $\text{Pb}(\text{Zr}_{0.35}\text{Ti}_{0.65})\text{O}_3$ Thin Films: Toward Integrated Active and Durable Photonic Devices

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Electro-Optic Study:

The electric field induced optical modulations of PZTN thin films were then characterized by a customized ellipsometric setup using a 632 nm He-Ne laser as the light source. In this setup, an input laser beam is focused through film at an incident angle of 45° onto the top electrode. Under the applied electric field, the laser beam propagates through the PZTN thin film. Then an oscilloscope converts this phase shift ($\Delta\Phi$) into an intensity modulation, which is measured by a photodetector locked to the frequency of the excitation voltage. Therefore, the birefringence phase shift ($\Delta\Phi$) is given by:

$$\frac{I}{I_0} = \frac{1}{4} \sin^2 \left(\frac{\Delta\Phi \pi}{\lambda} \right) \quad (1)$$

where I_0 and I are the incident laser intensity and the laser intensity through EO thin films in applied electric field, respectively. The linear EO effect (Pockels effect) alters the refractive index of the EO materials, which give rise to a shift in phase and thus convert into intensity modulation. The relationship between the phase shift ($\Delta\Phi$) and the birefringence shift (Δn) is given by:

$$\Delta\Phi = \frac{2\pi}{\lambda} l \Delta n \quad (2)$$

where λ and l are the wavelength of laser and the light path, respectively.

For these electro-optic materials, the linear and quadratic EO effects are defined as:

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

where r_c , n , and E are the linear EO coefficient (Pockels coefficient), refractive index, and applied electrical field, respectively. Based on Equation (2) and (3) above, the linear EO coefficient (r_c) can be calculated:

$$r_c = \lambda \Delta \Phi / (\pi m^3 EL) \quad (4)$$

Fig. S1. XRD patterns of the as-grown PZT thin films with and without PLT seeding layer.

Fig. S2. High resolution spectra of (a) Pb 4f, (b) Zr 3d, (c) Ti 2p, and (d) O 1s photoelectrons for PZT thin film.

Fig. S3. (a) Roughness of PZTN20 thin film. (b) Roughness of PZTN thin films as a function of Ni content.