Linear and nonlinear optical properties of multifunctional $PbVO_3$ thin films

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Lead vanadate ($PbVO_3$) is a multifunctional material which is both polar and magnetic. Its optical properties, important for linear and nonlinear optical spectroscopy of the material, are presented. Using spectroscopic ellipsometry, the refractive index and absorption versus wavelength of lead vanadate thin films at 295 K is reported. Using optical second harmonic generation, the nonlinear optical coefficients were determined to be $d_{15}/d_{31}=0.20\pm0.02$, $d_{33}/d_{31}=316.0\pm4.4$, and $|d_{33}|=10.40\pm0.35$ pm/V at a fundamental wavelength of 800 nm. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2943283]

The search for a single phase multiferroic material with coupled polarization and magnetic order parameters has attracted significant research interest in this field.[1,2] Lead vanadate, $PbVO_3$ (PVO), belongs to the family of ABO_3 perovskites and has been predicted to be an antiferromagnetic ferroelectric with large spontaneous polarization P_s $\sim 152\ \mu C/cm^2$.[3–5] The lone pair of the divalent A cation (Pb^{2+}) induces polarization while the transition metal B cation (V^{4+}) gives rise to a magnetic moment.[2] Linear and nonlinear optical spectroscopy provides a good tool to study the different order parameters in such materials.[6,7] For example, using optical second harmonic generation (SHG), a predicted magnetic transition was recently observed at 110 K.[7] The linear and nonlinear optical constants of PVO (in bulk or thin film state) often required for such studies have not yet been reported. In this study, we report the wavelength dependence of complex refractive index as well as second order nonlinear optical coefficients for PVO thin films.

Epitaxial PVO (001) (tetragonal notation) thin films were synthesized by pulsed-laser deposition (PLD) from a target with nominal stoichiometry $Pb_2V_2O_7$ in reducing environments at temperatures ranging between 450–650 °C on single crystal substrates of $(La_{0.18}Sr_{0.72})(Al_{0.59}Ta_{0.11})O_3$ (001) (LSAT) (tetragonal notation) and $NdGaO_3(110)$ (orthorhombic notation), as described in Ref. 8. The films studied here are epitaxial with orientation relationship PVO(001)‖LSAT(001) and PVO(001)‖$NdGaO_3(110)$. The linear optical properties of PVO films on LSAT substrate were measured. Since LSAT is noncentrosymmetric, the nonlinear optical properties were measured on PVO films grown on centrosymmetric $NdGaO_3$ substrate. These (001) oriented films have nearly single crystalline perfection, with three well-defined crystallographic x-[100], and y-[010] axes within the film plane, and the z-[001] axis normal to the plane which allows us to extract nonlinear coefficients precisely without ambiguity.

Ellipsometric spectra in (Δ,Ψ) were collected *ex situ* for a PVO film prepared by PLD on LSAT at three angles of incidence $\theta_i=45°$, 65°, and 75° using a variable-angle rotating-compensator multichannel spectroscopic ellipsometer[9,10] with a spectral range from 200 to 1670 nm. The optical properties (n,k) shown in Fig. 1 and the corresponding dielectric function spectra $(\varepsilon_1,\varepsilon_2)$ are extracted by using a least squares regression analysis and a weighted root mean square error,[11] to fit the ellipsometric spectra to a three-medium optical model consisting of a semi-infinite LSAT substrate/bulk film/air ambient structure. The free parameters correspond to the bulk film thickness and a parameterization of the PVO dielectric function as shown in Table I. The dielectric function parameterization of PVO consists of a combination of a Lorentz oscillator,[12] a Tauc–Lorentz oscillator,[13,14] and a constant additive term to ε_1 denoted by ε_∞. The Lorentz model for dielectric function parameterization is given by

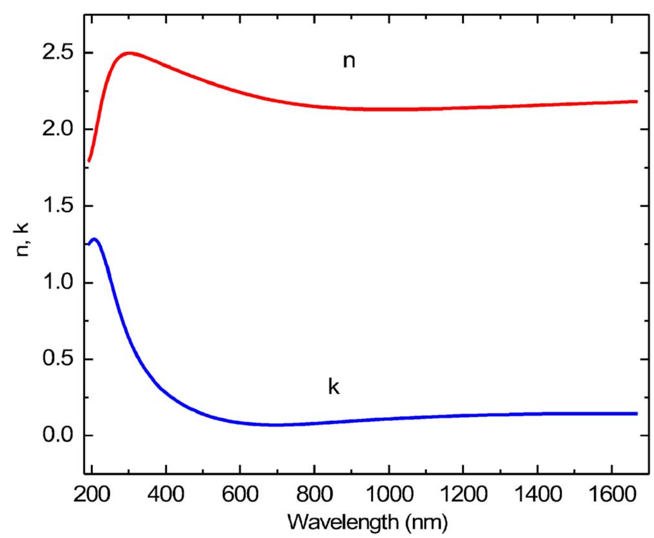

FIG. 1. (Color online) Index of refraction (n) and extinction coefficient (k) for PVO over a spectral range from 200 to 200 to 1670 nm. These values correspond to a parameterized PVO dielectric function obtained by fitting measured ellipsometric spectra in (Δ,Ψ) of a PVO film deposited on a LSAT substrate at three angles of incidence ($\theta_i=45°$, 65°, and 75°) to a three-medium optical model consisting of a semi-infinite LSAT substrate/bulk film/air ambient structure.

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TABLE I. Optical model parameters corresponding to PVO microstructure and dielectric functions represented by a combination of a Lorentz oscillator, Tauc–Lorentz oscillator, and ε_∞. (Mean square error $\chi=12.06$). Using the model, the thickness was estimated to be 122.03 ± 0.06 nm.

	E_0 (eV)	Γ (eV)	A (eV)	E_g (eV)	ε_∞ (Å)
1	5.76 ± 0.01	4.76 ± 0.04	46.23 ± 0.43	1.52 ± 0.01	1.37 ± 0.01
2	1.16 ± 0.01	2.10 ± 0.03	1.06 ± 0.01	⋯	⋯

$$\varepsilon=\frac{AE_0}{E_0^2-E^2-i\Gamma E}, \quad (1)$$

where the parameters include an oscillator amplitude A, a broadening parameter Γ, and a resonance energy E_0. The corresponding parameterization for the Tauc–Lorentz model is given by

$$\varepsilon_2=\begin{cases}\dfrac{AE_0\Gamma}{(E^2-E_0^2)^2+\Gamma^2E^2}\dfrac{(E-E_g)^2}{E}, & E>E_g\\ 0, & E>E_g,\end{cases}$$

$$\varepsilon_1=\frac{2}{\pi}P\int_{E_g}^{\infty}\frac{\xi\varepsilon_2(\xi)}{\xi^2-E^2}d\xi, \quad (2)$$

where the parameters include those of the Lorentz oscillator with the addition of the Tauc gap E_g.

We obtain the linear complex indices from this model to be $\tilde{N}_f^{\omega}=2.151+0.080i$ and $\tilde{N}_f^{2\omega}=2.420+0.287i$ for corresponding wavelengths of 800 and 400 nm, respectively. It should be noted that although PVO is uniaxially anisotropic, only the optical properties of the ordinary index of refraction have been obtained for this film. The optical axis of PVO epitaxially grown on LSAT is perpendicular to the surface, in which case the contributions to the ellipsometric spectra from the projection normal to the surface are small and a good estimate of the optical properties in the ordinary projection can be obtained.[15]

The crystal symmetry of epitaxial PVO(001) films has been shown to be point group 4*mm* using optical SHG and diffraction techniques.[7] Optical SHG (Ref. 16) involves the conversion of light (electric field E^{ω}) at a frequency ω into an optical signal at a frequency 2ω by a nonlinear medium, through the creation of a nonlinear polarization $P_i^{2\omega}\propto d_{ijk}E_j^{\omega}E_k^{\omega}$, where d_{ijk} represent the nonlinear optical coefficients. PVO film with thickness of about 120 nm grown on $NdGaO_3(110)$ substrates was used for this study. $NdGaO_3$ is centrosymmetric (point group *mmm*) and does not contribute SHG signals of its own for the incident powers used. The SHG experiment was performed with a fundamental wave generated from a tunable Ti-sapphire laser with 65 fs pulses of 800 nm wavelength incident from the film side at variable tilt angles θ to the sample surface normal.

As shown in Fig. 2, the crystallographic x-z plane in the PVO film was aligned with the incidence plane. The polarization direction of incident light is at an angle ϕ from the y axis, which was rotated continuously using a half-wave plate. The intensity $I_j^{2\omega}$ of the output SHG signal at 400 nm wavelength from the film was detected along either $j=p,s$ polarization directions as a function of polarization angle ϕ of incident light. The resulting polar plots of SHG intensity for p and s polarized output at tilt $\theta=50°$ are shown in Figs. 2(a) and 2(b), respectively. If the incident beam has intensity I_0 then the nonlinear polarizations for PVO(001) film with y axis perpendicular to the plane of incidence are given by

$$P_x^{NL}=I_0f_xf_zd_{15}\sin^2\phi\sin 2\theta,$$

$$P_y^{NL}=I_0f_yf_zd_{15}\sin 2\phi\sin\theta,$$

$$P_z^{NL}=I_0[d_{31}(f_x^2\sin^2\phi\cos^2\theta+f_y^2\cos^2\phi)+d_{33}f_z^2\sin^2\phi\sin^2\theta], \quad (3)$$

where d_{ij} are nonlinear coefficients and f_i are linear Fresnel coefficients. The measured intensity of the p and s polarized SHG in transmission geometry (neglecting birefringence) is proportional to nonlinear polarization. The expected SHG intensity expressions for p and s output polarizations in the predicted 4*mm* symmetry system of PVO are

$$I_s^{2\omega}=K_1^2\sin^2 2\phi,$$

$$I_p^{2\omega}=(K_2\sin^2\phi+K_3\cos^2\phi)^2, \quad (4)$$

where

$$K_1=I_0f_yf_z\tilde{f}_y^Tf_{s,e}d_{15}\sin\theta,$$

$$K_2=I_0f_{p,e}(\tilde{f}_x^Tf_xf_zd_{15}\sin 2\theta+\tilde{f}_z^Tf_x^2d_{31}\cos^2\theta+\tilde{f}_z^Tf_z^2d_{33}\sin^2\theta),$$

$$K_3=I_0f_{p,e}\tilde{f}_z^Tf_y^2d_{31}. \quad (5)$$

Here, K_1, K_2, and K_3 are coefficients that are functions of the nonlinear coefficients d_{ij}, refractive indices n of the film

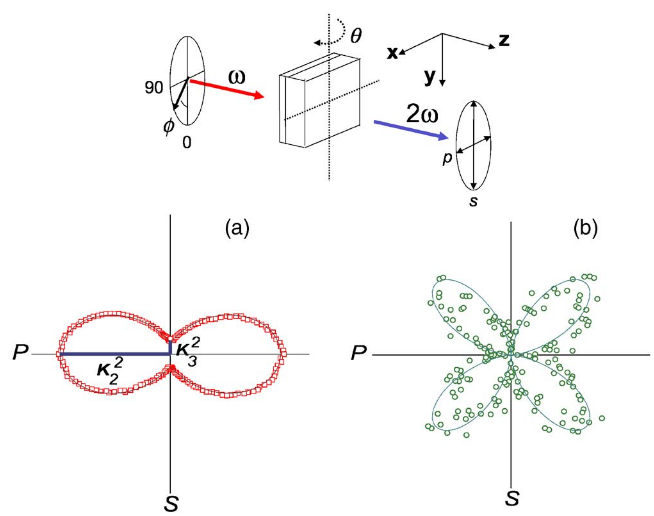

FIG. 2. (Color online) Variation of (a) p and (b) s polarized SHG intensity with incident polarization angle ϕ for a PVO(001)‖NGO(110) film with y axis perpendicular to the plane of incidence for tilt angle $\theta=50°$ about the Y axis of the film.

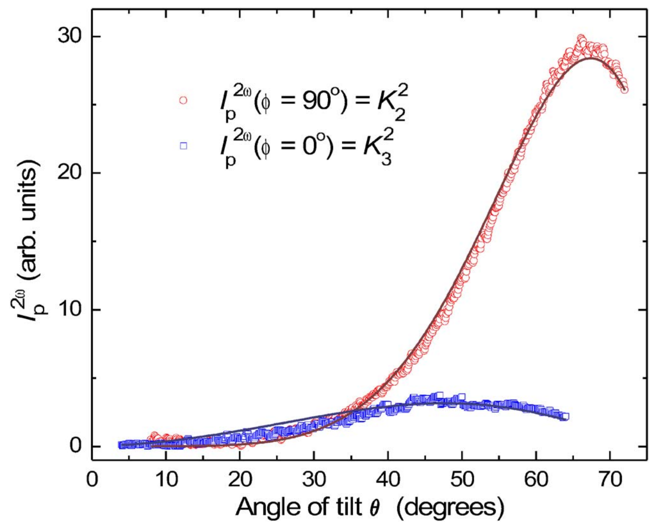

FIG. 3. (Color online) Variation of $K_2^2[I_p^{2\omega}(\phi=90°)]$ and $K_3^2[I_p^{2\omega}(\phi=0°)]$ as a function of tilt angle θ. The solid lines show theoretical fits to the data using which the ratios of nonlinear optical coefficients is extracted.

and the substrate, and incidence angle θ. The terms f_x, f_y, and f_z are linear Fresnel coefficients for transmission of light with frequency ω through the *incident* air-film interface while I_0 represents the incident intensity of the input beam. The terms $f_{s,e}$ and $f_{p,e}$ are linear Fresnel coefficients for s and p polarized SHG signals, respectively, in transmission through the *exit* substrate-air interface. The terms $\tilde{f}_x^T$, $\tilde{f}_y^T$, and $\tilde{f}_z^T$ are the nonlinear Fresnel coefficients.[17] Theoretical fits to the experimental polar plots based on Eq. (4) are excellent both in normal incidence and tilted configuration, as shown in Figs. 2(a) and 2(b), respectively, for both p and s polarized SHG output.

The K_2 and K_3 parameters, which contain the nonlinear coefficients, are experimentally obtained by collecting the p-in-p-out $I_p^{2\omega}(\phi=90°)$ and s-in-p-out $I_p^{2\omega}(\phi=0°)$ SHG signals for different angles of tilt θ about the x axis. The experimental data for K_2 and K_3 parameters (Fig. 3) is then fitted to Eq. (5) to extract the ratios $d_{15}/d_{31}=0.20\pm0.01$ and $d_{33}/d_{31}=316.0\pm4.4$. Using the $d_{22}=1.672$ pm/V coefficient of a single crystal z-cut $LiTaO_3$ as a reference[18,19] and taking absorption into account, an estimated effective value for $|d_{33}|=10.4\pm0.35$ pm/V was calculated. Note that only the signs of the ratios d_{15}/d_{31} and d_{33}/d_{31} were determined unambiguously. The absolute signs of the d_{ij} coefficients were not determined, except to state that all coefficient have the same sign. Since there are 180° domains, these numbers are the lower limit. Since no single crystal optical data for PVO exists, a comparison between films and crystals is not possible.

To conclude, we report the complex index of refraction versus wavelength and optical SHG coefficients in PVO thin films. These studies will be important in performing further linear and nonlinear optical spectroscopy of the magnetism and ferroelectricity in this material. By studying the variation of linear and nonlinear optical coefficients with temperature, one can identify phase transitions. The polarization symmetry of the SHG signal sheds light on the crystallographic and magnetic symmetry of the lattice. Wavelength dependence of the absorption and SHG coefficients will enable electronic spectroscopy in the material. Measurement of these optical properties under electric and magnetic fields may reveal spin-polarization coupling. These are interesting possible directions for future studies.

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