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Large optical nonlinearity in $CaCu_3Ti_4O_{12}$ thin films

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Abstract $CaCu_3Ti_4O_{12}$ (CCTO) thin films were successfully prepared on $LaAlO_3$ substrates by pulsed laser deposition technique. We measured the nonlinear optical susceptibility of the thin films using Z-scan method at a wavelength of 532 nm with pulse durations of 25 ps and 7 ns. The large values of the third-order nonlinear optical susceptibility, $\chi^{(3)}$, of the CCTO film were obtained to be 2.79×10^{-8} esu and 3.30×10^{-6} esu in picosecond and nanosecond time regimes, respectively, which are among the best results of some representative nonlinear optical materials. The origin of optical nonlinearity of CCTO films was discussed. The results indicate that the CCTO films on $LaAlO_3$ substrates are promising candidate materials for applications in nonlinear optical devices.

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1 Introduction

Nonlinear optical films with large optical nonlinearity and ultrafast response are required as promising candidates for future integrated photonics applications, such as image processing, all-optical switching, data storage, fiber optical communication, etc. [1–3]. Thin films with perovskite related structures have attracted special attentions due to their sufficient physical properties and useful applications including large spontaneous polarization, high dielectric constant, and remarkable optical nonlinearity. Over the past few years, thin films of perovskite related structures, such as Ce:$BaTiO_3$ [4], $SrBi_2Ta_2O_9$ (SBT) [5], $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) [6, 7], $Bi_2Nd_2Ti_3O_{12}$ (BNT) [8], $PbLaTiO_3$ (PLT) [9], have been extensively studied for nonlinear optical applications. In recent years, high-dielectric-constant $CaCu_3Ti_4O_{12}$ (CCTO) thin films with perovskite-like structure have been widely researched due to their potential applications in microelectronic devices [10–12]. However, the nonlinear optical properties of CCTO films have not been reported to our knowledge.

In this paper, we report the nonlinear optical properties of CCTO films on $LaAlO_3$ substrates using Z-scan technique in picosecond and nanosecond time regimes at 532 nm. The results show that CCTO films possess large nonlinear optical absorption and negative nonlinear refraction effects.

2 Experimental

CCTO films were fabricated on $LaAlO_3$ (001) substrates by pulsed laser deposition (PLD) technique. A XeCl excimer laser beam (308 nm, 27 ns, 4 Hz) was focused on a spot at a 45° incidence angle on the surface of a rotating CCTO target, which was prepared by conventional ceramic sintering process. The pulsed laser energy fluence was about 2.5 J/cm^2. The films were deposited at 820°C under 30 Pa oxygen pressure, followed by the annealing for 30 min under the same conditions. X-ray diffraction (XRD) along

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with Raman scattering measurements was performed to determine the crystal structure and crystallinity of the films. The thicknesses of the samples were measured to be about 230 nm by Dektak 8 surface stylus profiler (Veeco Company).

The linear optical transmittance of the samples was investigated in the wavelength range of 0.3–3.0 μm at room temperature with a Spectrapro500i spectrophotometer (Acton Research Corporation) and PTS-6000 Fourier transform infrared spectroscopy (FTIR).

The nonlinear optical properties of the films were characterized using single beam Z-scan method, which is an effective tool to determine the magnitude and sign of the real and imaginary parts of the third-order nonlinear optical susceptibility [13]. In the experiments, a Nd:YAG mode-locked laser (532 nm, 25 ps) and a Nd:YAG Q-switched laser (532 nm, 7 ns) were used as light sources for the measurements in picosecond and nanosecond time regimes, respectively. The focal length of the lens was 150 mm. The radius of the beam waist (ω_0) was 30 μm, which was calculated from the equation $\omega(z)^2 = \omega_0(1 + z^2/z_R^2)$, where $z_R = \pi\omega_0^2/\lambda$ is the Rayleigh length. Hence the values of z_R were both calculated to be 5.3 mm, which were much longer than the film plus substrate thickness. The peak intensities I_0 used in the experiments were 4.4 GW/cm^2 and 18.6 MW/cm^2 for picosecond and nanosecond pulse excitation, respectively. The transmitted-beam energy, the reference beam energy, and the ratios of them were recorded using an energy ratiometer (EPM 2000, Coherent Inc.) simultaneously to remove the laser fluctuations. The linear transmittance of the far field aperture, S, defined as the ratio of the pulse energy to the total energy, was measured to be 0.25. The pulse repetition rate was set to 1 Hz to reduce the possible thermal accumulative effect.

3 Results and discussion

Figure 1 shows a typical θ–2θ scan profile of the CCTO films. It is clear that there are no diffraction peaks from impurity phases or randomly oriented grains except $LaAlO_3$ (00l) and CCTO (00l) peaks, which indicated that the deposited CCTO films are single phase and c-axis oriented. Raman scattering spectroscopy of CCTO films was also performed at room temperature, not shown here. The main peaks confirmed that the CCTO films are with pure chemical phase and perovskite-like structure [14, 15].

The linear optical transmittance spectrum of CCTO films was shown in Fig. 2. The oscillating transmittance indicates the film has a flat surface and a uniform thickness. The linear refractive index n_0 was determined from the transmittance curve using the envelope method [16]. The values of n_0 and absorption coefficient α of the films at 532 nm

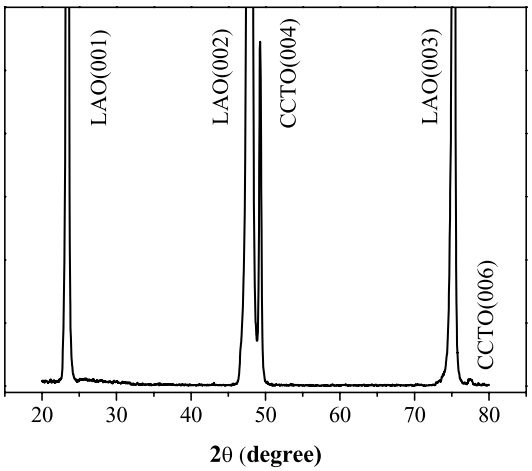

Fig. 1 X-ray diffraction (XRD) pattern for the CCTO films grown on $LaAlO_3$ (001) substrates. Only $LaAlO_3$ (00l) and CCTO (00l) peaks were found indicating the single phase and c-axis oriented CCTO films

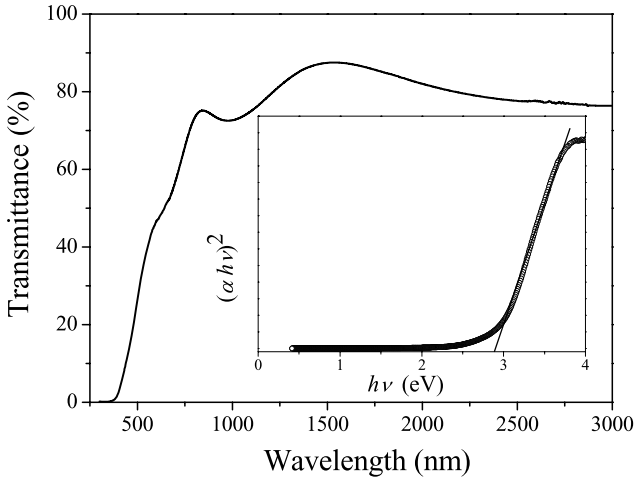

Fig. 2 Linear optical transmittance of the CCTO films on $LaAlO_3$ (001) substrates. The inset shows the plot of $(h\nu\alpha)^2$ vs. $h\nu$ for the films

were determined to be $n_0 = 2.85$ and $\alpha = 4.50 \times 10^4$ cm^{-1}, respectively. The optical band gap energy E_g of the film was calculated to be about 2.88 eV using Tauc's formula $(h\nu\alpha)^2 = \text{const}(h\nu\alpha - E_g)$ assuming a direct transition between the bands, where $h\nu$ is the incident light's photon energy. The graph of $(h\nu\alpha)^2$ vs. $h\nu$ was shown in the inset of Fig. 2.

Figure 3 shows the typical open-aperture (OA) and closed-aperture (CA) Z-scan curves of the CCTO films in 25 ps- and 7 ns-durations, respectively. The OA curves show normalized transmittance valleys indicating the presence of nonlinear absorption in the CCTO films. The CA profiles, obtained after division of closed-aperture data with the open-aperture data to eliminate the contributions of nonlinear absorption, have peak-valley configures corresponding to negative nonlinear refractive index (n_2). Because

the $LaAlO_3$ substrates have very small nonlinear optical response that can be neglected, the high nonlinear optical properties result from the CCTO films. The measurements were performed at several laser intensities both in picosecond and nanosecond time regimes, and the relations of $\Delta n = n_2 - n_0$ versus the peak input irradiance I_0 show straight lines, which indicate that the nonlinear optical effects are the third-order responses. The relative uncertainty of the results is estimated to be ~20–30% for the Z-scan measurements.

The data were analyzed with the procedures described in reference [13]. The nonlinear absorption coefficient β(m/W) was obtained by the theoretical fitting the OA data using the equation

$$T(Z) = 1 - \frac{\beta I_0 L_{\text{eff}}}{2\sqrt{2}(1 + z^2/z_R^2)} \tag{1}$$

where I_0 is the input irradiance at the focus, $L_{\text{eff}} = [1 - \exp(-\alpha L)]/\alpha$ is the effective thickness of the films. The relation between β(m/W) and the imaginary part of $\chi^{(3)}$, Im $\chi^{(3)}$(esu) is shown as follows

$$\text{Im}\,\chi^{(3)}(\text{esu}) = \frac{c^2 n_0^2}{240\pi^2\omega}\beta(\text{m/W}) \tag{2}$$

where c is the speed of light and ω is the angular frequency of light field. The refractive index n_2(m^2/W) and the real part of $\chi^{(3)}$, Re $\chi^{(3)}$(esu), are given by

$$n_2 = \frac{\lambda \Delta T_{\text{pv}}}{0.812\pi(1-S)^{0.25} L_{\text{eff}} I_0}, \tag{3}$$

$$\text{Re}\,\chi^{(3)}(\text{esu}) = \frac{n_0^2 c}{120\pi^2} n_2(\text{m}^2/\text{W}), \tag{4}$$

where ΔT_{pv} is the difference between the normalized peak and the valley transmittance and can be obtained by the best theoretical fit from the Z-scan CA curves. The calculated absolute values of $\chi^{(3)}$ and figure of merit (FOM), defined as $\chi^{(3)}/\alpha$, were summarized in Table 1. The difference values of $\chi^{(3)}$, obtained under 25 ps- and 7 ns-durations, originates from the relative contributions of slower and faster $\chi^{(3)}$ components [17].

It is worth noting that the values of $\chi^{(3)}$ in the CCTO films are among the best results of some representative third-order optical materials, such as ferroelectric materials [4–9], metal-doped composite films [18–20], transitional metal oxide films [17], and organic polymer films [21–23], but smaller than a few exceptions measured using degenerate four-wave mixing (DFWM) [24–26]. The results indicate that the CCTO films have potential applications for nonlinear optical devices.

The origin of nonlinear optical response of the CCTO films was discussed briefly here. In general, there are two processes that can contribute to the nonlinear absorption: free carrier absorption and multiphoton absorption. Because the concentration of free carriers is very low in CCTO film as a high-constant-dielectric material, the free-carrier absorption effect can be negligible. Since, the band gap in the CCTO films on $LaAlO_3$ substrates of 2.88 eV is larger

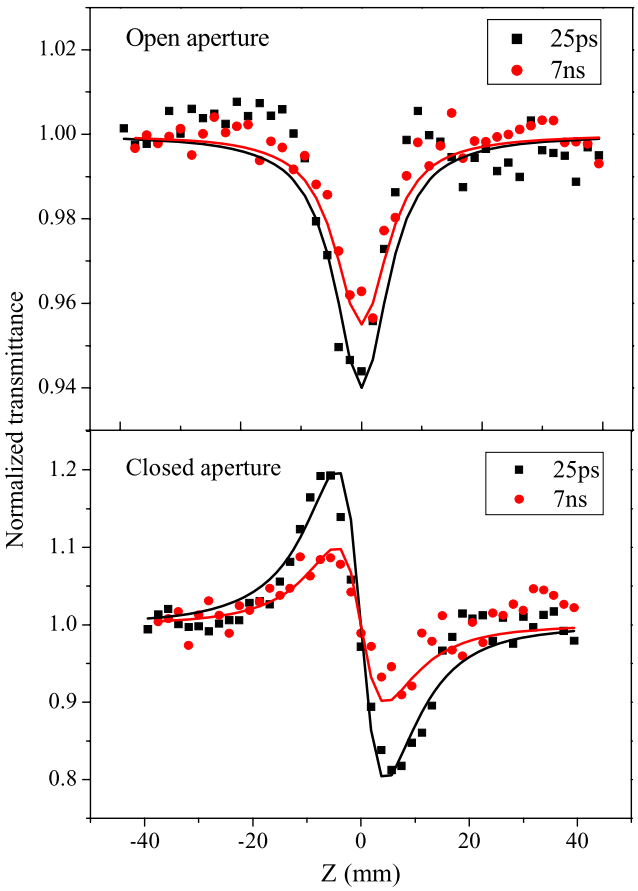

Fig. 3 Experimentally measured (*symbols*) and theoretically fitted (*lines*) transmittance variations of the CCTO film versus scan position for the open and closed aperture Z-scan

Table 1 Nonlinear optical properties of the CCTO films at 532 nm with pulse durations of 25 ps and 7 ns

Time regime	β (10^{-7} m/W)	n_2 (10^{-14} m^2/W)	Im $\chi^{(3)}$ (10^{-7} esu)	Re $\chi^{(3)}$ (10^{-7} esu)	$\lvert\chi^{(3)}\rvert$ (10^{-7} esu)	$\lvert\chi^{(3)}\rvert/\alpha$ (10^{-11} esu · cm)
25 ps	0.269	1.32	0.0234	0.278	0.279	0.0620
7 ns	47.4	156	4.22	32.7	33.0	7.33

than the photon energy of the laser (2.34 eV) and smaller than two-photon energy of the laser (4.68 eV), two-photon absorption (TPA), as the lowest multiphoton absorption, is considered to be the dominant contribution to the nonlinear absorption. To discuss the origin of the nonlinear optical refraction of the CCTO films, the bond-orbital theory of nonlinear optical response is taken into account [27]. For transition metals, Cu and Ti, the s, p, and d orbitals in conduction band contribute to nonlinear response. If the bond length between transition metal and oxygen $D \geq 2.3$ Å, the third-order nonlinearity is mainly contributed from sp orbitals, and d orbital contribution is negligible. However, when $D \leq 2.0$ Å, the contribution from d orbitals rapidly increases and exceeds the sp-orbital contribution. The nonlinear optical refractive index could be expressed by the equation as follow [27, 28]

$$n_2 = \frac{25 f_L^3 D^2 (n_0^2 - 1)}{n_0 E_s^2(\text{eff})} \times 10^{-13} \quad (5)$$

where $f_L = (\varepsilon + 2)/3$ is the Lorentz local field factor, ε is the dielectric constant of the films, E_s(eff) is the common 'one-parameter' Sellmeier gap and a fix value for a given material. There are six Ti-O bonds in TiO_6 octahedra and four oxygen atoms bonded to a Cu atom in CCTO structure. The bond lengths of Ti-O and Cu-O are both around 1.96 Å at room temperature, smaller than 2.0 Å [29]. The Ti^{4+} ion has low-lying, empty 3d orbital and Cu^{2+} ion provides one unoccupied outer d electronic state. So the nonlinear refraction of CCTO film is mainly contributed from these unoccupied d-orbital electronic states. For Ca^{2+}, the Ca-O bond length is about 2.6 Å [29], mainly sp-orbital contributions to nonlinear optical response. However, there are only two valence electrons in the outer electronic shell to be distorted in response to the optical electric field, and small charge displacement can be produced, which leads to the low hyperpolarizability.

4 Conclusions

In summary, $CaCu_3Ti_4O_{12}$ films with perovskite related structures were fabricated on $LaAlO_3$ substrates by pulsed laser deposition technique. The third-order optical nonlinearity of the films was investigated using the Z-scan technique at a wavelength of 532 nm with laser durations of 25 ps and 7 ns, respectively. Large third-order nonlinear optical susceptibilities in $CaCu_3Ti_4O_{12}$ films were observed. The origin of the nonlinear optical response of the films was discussed. The results suggest that $CaCu_3Ti_4O_{12}$ films are promising for applications in nonlinear optical devices.

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