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Pingxiong Yang

Jianfeng Xu

Robert W. Schwartz
Missouri University of Science and Technology

David L. Carroll

et. al. For a complete list of authors, see http://scholarsmine.mst.edu/mec_aereng_facwork/3451

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Optical limiting in $SrBi_2Ta_2O_9$ and $PbZr_xTi_{1-x}O_3$ ferroelectric thin films

Pingxiong Yang[a] and Jianfeng Xu
Center for Optical Material Science and Engineering Technology, Department of Physics and Astronomy, Clemson University, Clemson, South Carolina 29634

John Ballato and Robert W. Schwartz
Center for Optical Material Science and Engineering Technology, School of Material Science and Engineering, Clemson University, Clemson, South Carolina 29634

David L. Carroll
Center for Optical Material Science and Engineering Technology, Department of Physics and Astronomy, Clemson University, Clemson, South Carolina 29634

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Optical limiting effects in $SrBi_2Ta_2O_9$ (SBT) and $PbZr_xTi_{1-x}O_3$ (PZT) ferroelectric thin films have been observed with nanosecond laser pulses at 1.064 μm. Limiting thresholds were found to be 5.84 J/cm^2 for SBT and between 4.53 and 5.93 J/cm^2 for PZT, depending on composition, whereas saturation thresholds for the films were about 2.92 J/cm^2 and between 2.27 J/cm^2 to 2.97 J/cm^2, respectively. Damage thresholds around 10.0 J/cm^2 and between 10.37 J/cm^2 to 10.54 J/cm^2, respectively for SBT and PZT, were also determined. A possible mechanism for the observed limiting, nonlinear optical scattering from the ferroelectric domains, is discussed. These results elucidate the origin of the nonlinear optical properties in perovskite-type ferroelectric thin films and show the potential role such materials can play in photonic devices based on nonlinear optical effects. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1477618]

Ferroelectric oxides possessing a perovskite crystal structure are a very attractive class of materials for numerous electronic and electro-optic applications due to their large spontaneous polarization, high dielectric constants, and optical nonlinearities. In recent years, there has been particular interest in the nonlinear optical properties of ferroelectric thin films for planar waveguide and integrated-optic devices.[1] Ferroelectric thin films of $SrBi_2T_2O_9$ (SBT), which have a layered perovskite structure and are being considered for nonvolatile memories due to their fatigue-free properties, and $PbZr_xTi_{1-x}O_3$ (PZT) both have been extensively investigated and reported.[2–6] However, the nonlinear optical (NLO) properties of these materials, in particular, the origin of the optical nonlinearity, have been less well studied.[7–9] Optical limiting is an area of increasing interest. Materials that exhibit optical limiting have potential applications, especially in military theaters where eye and optical sensor protection from exposure to sudden intense light beams is a growing concern. Optical limiting has been observed in various kind of materials, such as the carbon family of materials, organometallic, and organic materials.[10–16] The origin of the optical limiting in these materials has been proposed to arise from the formation of microplasmas in carbon black suspensions and carbon nanotubes,[11] beam fanning in photorefractive materials, and reverse saturable or two-photon absorption in absorbing or transparent materials.[14–16]

In this letter, reflection-mode optical limiting properties of SBT and PZT ferroelectric thin films are reported. These results then are used to gain insight into the origin and understanding of nonlinear optical effects in perovskite-type materials.

SBT and PZT thin films were prepared on platinized silicon ($Pt/Ti/SiO_2/Si$) substrates using pulsed-laser deposition. The platinized silicon substrates were synthesized by wafers of (111) oriented Si with a layer of thermally grown 2000 nm SiO_2, then coated with 30 nm Ti and 800 nm Pt using an ultrahigh vacuum electron-beam evaporator (Balzers UMS500p) from a Ti and Pt target, respectively. SBT and Pb-rich PZT ceramics were used as targets for the thin films deposited, respectively. The deposition processes were equivalent to our previous reports.[17] X-ray diffraction showed these films to have a well-crystallized perovskite structure. Compositional analysis was performed on the films using an inductively coupled plasma quantemeter and showed the ratio of Sr:Bi:Ta to be 1.0:1.98:2.0 for the SBT, and Pb:Zr:Ti to be about $0.97{:}x{:}(1-x)$ ($x=0.30,0.53,0.80$) for the PZT. Scanning electron microscopy observations of the surface and cross section of the films show that the films exhibit smooth surfaces and dense microstructures. The thickness of the films was determined to be about 0.20 μm for SBT, and 0.30 to 0.35 μm for PZT, and a average grain size of 200 nm was observed.

Optical limiting of the thin films was measured in reflection; an extension of more standard transmission techniques. Similar to conventional optical limiting techniques, a modification to the spatial profile of the incident beam upon reflection by the film is monitored using an energy detector placed in the far-field region. A *Q*-switched Nd:YAG laser was used as the light source (fundamental wavelength of 1.064 μm and pulse width of 8 ns full width at half maximum). The laser emission was focused using a 20 cm focal

[a]Electronic mail: pxyang@clemson.edu

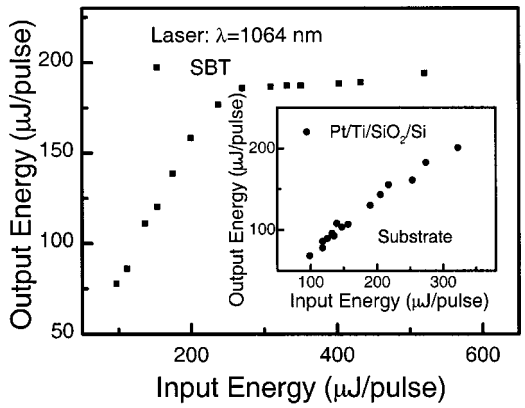

FIG. 1. Optical limiting of SBT ferroelectric thin film and the platinized silicon substrate (inset) measured at 1.064 μm with 8 ns laser pulses.

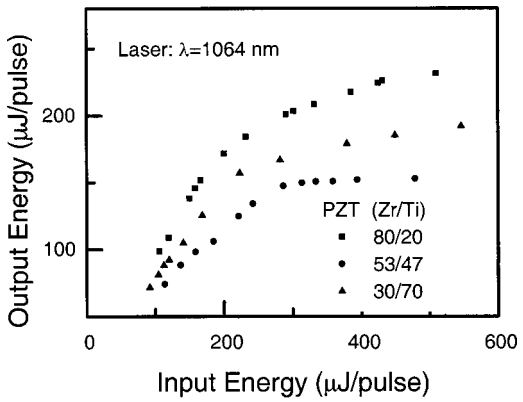

FIG. 2. Optical limiting of PZT ferroelectric thin films with varied Zr content ($x=0.30$, 0.53, and 0.80) at 1.064 μm with nanosecond laser pulses.

length lens such that the $1/e^2$ radius of the beam was about 45 μm at the focal point. The sample was placed at the focal point during the limiting measurements. Input and output energies were measured by two energy meters (Laser Probe Inc. Rj-7620 Energy Ratiometer). The input pulse energy was varied by rotating a polarizer. In order to avoid cumulative thermal effects, data were collected in single-shot mode.

Figure 1 shows the optical limiting behavior of the SBT thin film on a platinized silicon substrate. For input energies less than 271.5 μJ/pulse ($\approx$4.27 J/cm^2, the relative error in the measured fluence is mainly due to the uncertainty in determining the spot sizes), the output energies increase linearly with incident energy. However, in excess of 271.5 μJ/pulse, the output energy (E_{out}) is nearly a constant value of 185.6 μJ/pulse ($\approx$2.92 J/cm^2 average fluence). Saturation occurs at $E_{out}<2.92$ J/cm^2 for higher inputs and functionally appears as typical limiting behavior. In our experiment, when the increasing incident energy was over a certain value, it was found that the output energy was less and the surface damage of sample can be visibly observed. The damage threshold for the SBT thin film was around 650 μJ/pulse ($\approx$10 J/cm^2). In order to confirm that the behavior results from the film rather than the platinized silicon substrate, optical limiting of the substrate was measured under identical conditions. The inset to Fig. 1 shows the data for the platinized silicon substrate. The results in the inset of Fig. 1 indicate that the substrate does not show any limiting effects. In addition, the Pt layer is thick enough so that incident light does not propagate through this layer. The contribution from the substrate can be neglected, as has been done previously.[3,4] Thus, the NLO limiting behavior observed here results solely from the SBT films.

Figure 2 shows the optical limiting of $PbZr_xTi_{1-x}O_3$ thin films on the same platinized silicon substrates. Saturation output energies are approximately 167.78 μJ/pulse, 144.15 μJ/pulse, and 188.61 μJ/pulse for $x=0.30$, 0.53, and 0.80, respectively. The same as observed for SBT, the sample surfaces of PZT are also damaged when the input energy increasing is over certain value. The damage thresholds for PZT thin films were around 660 to 670 μJ/pulse (10.37 to 10.54 J/cm^2), depending on composition.

In order to compare with other materials, we define here the limiting threshold as the input energy at which the ratio of output energy with input energy goes down to half of its linear transmission. The limiting threshold for SBT and PZT thin films are 5.84 J/cm^2 and 4.53 J/cm^2 to 5.93 J/cm^2, respectively. The large limiting thresholds compare favorably with other representative optical limiting materials, such as carbon-based systems and organometallics polymers, as is shown in Table I.

Several mechanisms have been proposed for optical limiting in materials such as the carbon family and organometallics.[10–16] Optical limiting in ferroelectric thin films remains, however, a relatively undeveloped area of study. According to Robertson *et al.*,[6] a band gap for SBT of 5.1 eV was found and arises from the valence band maximum of the O *p* states and some Bi *s* states and the conduction band minimum of the Bi *p* states, and for PZT, the valence band edge arises from hybridized Pb *s* and O *p* states for all compositions, while the conduction band edge changes from a Ti *d*-like $\Gamma_{25'}$ state to a Pb *p*-like X_1 state with increasing Zr content, with a band gap of 3.0 to 3.5 eV. These electronic structures indicate that nonlinear absorption from excited states may not be the mechanism of optical limiting for the thin films at 1.064 μm (1.16 eV) due to mismatch between the band gaps and photon energy.

Based on these arguments, we believe that the observed optical limiting in the films may result from a scattering of the incident light by the ferroelectric domains in the films. In

TABLE I. Some representative optical limiting materials.

Materials	Incident wavelength (μm)	Limiting threshold (J/cm^2)	Sample form[a]	Reference
C_{60}	0.532	1.30	S*l*	11
C_{60}–Mo/C_{60}–Cr	0.532	0.06	S*l*	10
Carbon nanotube	1.064	10.0	S*l*	11
Carbon nanotube	0.532	1.00	S*l*	11
CuPc–C_{60}	0.532	0.20	S*l*	12
CuPc	0.532	0.18	S*l*	12
Pt:ethynyl	0.615	1.20	S*l*	13
[(R-APPC)Cd]*Cl*[b]	0.532	1.4~3.0	S*l*	14
P3OT/[6,6]PCBCR[c]	0.760	0.30	S	15
Stilbene 3 doped gel glass	0.600	~0.8	L	16
SBT	1.064	5.84	S	present study
PZT	1.064	4.53~5.93	S	present study

[a]S1=Solution, S=Solid, and L=Liquid.
[b]Asymmetric pentaazadentate porphyrin-like cadmium complexes.
[c]Phenyl-C61-butyric acid cholesteryl ester.

our samples, 180° domain walls dominate in SBT thin films, while non-180° domain walls are primary in PZT thin films,[17] due to domain structure formation depending on the grain size of thin films.[2,5] In the illumination process, photogenerated carriers can lead to a change of the domain configuration in the thin films. For SBT thin films, the defect traps include electrons trapped at the Ta^{5+} ion, the Ta^{4+} center, and holes trapped at the Bi^{3+} ion, the Bi^{4+} center, with a shallow level of ~0.2 eV for both.[5] During laser illumination, the photogenerated carriers partially compensate the trapped electrons and holes, resulting in the restoration of Ta^{5+}, Bi^{3+} ions given the shallowness of the level (~0.2 eV). This can result in an increase in number of the domain walls due to the polarization mainly from Ta and Bi ions in SBT. Consequently, the increased number of domain walls now more strongly scatter light from the propagated beam, leading to the decrease in the measured output light energy. In literature, light scattering of La-doped in PZT is minimized when the ferroelectric domains are aligned and maximized when remanent polarization is about zero.[18] For PZT thin films, non-180° domain walls, including 90° walls in tetragonal structure or 71° and 109° walls in rhombohedral structure, are pinned easily. Photogenerated carriers from laser illumination pin the domain walls due to the walls being more easily pinned.[19] The pinning of domain walls lessens the alignment of domains in the thin films, resulting in more strongly scattered light.

As is shown in Fig. 2, the optical limiting of PZT is dependent upon the Zr/Ti ratio. This demonstrates that the origin of the limiting is not from the nonlinear absorption of thin films, since as described herein, the electronic structure of PZT primarily derives from the Pb states rather than the ratio of Zr/Ti. The mechanism of nonlinear scattering from the domain walls can account for the compositional (Zr/Ti ratio) dependence of the optical limiting for PZT films. In PZT, the 53/47 ratio of Zr/Ti defines the morphotropic phase boundary (MPB) that separates the tetragonal (*T*) phase (high Ti content) from the rhombohedral (*R*) one (high Zr content). The MPB represents a boundary where there is the coexistence of two phases; rhombohedral and tetragonal.[20,21] The phase activity (between *T* and *R* phase transition) leads to some unique characteristics of the films with compositions near the MPB such as high polarizibility, high dielectric constants, and maximized piezoelectric coefficients.[20,21] Thus, the nonlinear scattering in the PZT 53/47 thin film is strongest due to greater ease of reorienting the ferroelectric domains in films of this composition. This results in stronger optical limiting, as is suggested by the saturation output energy minimum and the sharpness of the onset that are evident in Fig. 2. Compared with PZT 80/20 film, the pinning number of domain walls in PZT 30/70 film is larger, due to more photogenerated carriers resulting from the Pb^{3+} hole center becoming more shallow as the the Zr content dropped. Thus, it has been observed that the curve 30/70 film is located between curves 53/47 and 80/20 in Fig. 2.

The measurement of optical limiting in single-crystal PZT also was performed. The result was an oblique straight line, indicating that the behavior may be a sensitive function of the fabrication process and conditions since these affect defect populations in sample. Comparing Figs. 1 and 2, it was noted that limiting threshold was lower for PZT than SBT films. This implies that optical limiting in ferroelectrics may be dependent on material classes as well as the film fabrication process.

In conclusion, reflection optical limiting properties of SBT and PZT thin films were studied in the infrared spectral region with nanosecond laser pulses. The limiting, saturation, and damage thresholds for the films were determined. The mechanism of the effect is believed to arise from nonlinear scattering of ferroelectric domain walls. The results show ferroelectric thin films to be promising materials for applications in optical limiting devices.

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