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Defect dynamics and spectral observation of twinning in single crystalline LaAlO₃ under subbandgap excitation

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We have investigated the photoluminescence and ultrafast dynamics of LaAlO₃ crystal. The photoluminescence consists of a broad spectrum and two sharp peaks, which arise from various defect levels within the bandgap. A doublet splitting of roughly 6 nm is seen in these two sharp peaks. An Al displacement of 0.09 Å in a sublattice, which is possible because of twinning, is adequate to explain the spectral splitting. Femtosecond pump probe experiments reveal further that many of these defect levels have a few picosecond decay times while the lowest defect states have decay times longer than nanosecond to the valence band. © 2011 American Institute of Physics. [doi:10.1063/1.3543840]

The low microwave losses,¹ good lattice matching with many common oxides (pseudocubic $a=3.79$ Å),^{2,3} wide bandgap (5.6 eV), and thermal stability have made LaAlO₃ (LAO) crystals a strategically important substrate.¹⁻⁴ The optical characteristics in the infrared and microwave regions have been widely studied for the rare-earth LAO on account of their deployment in the fabrication of high temperature superconductor based microwave devices.⁵⁻⁷ More recently, there has been a resurgence in the interest in LAO due to the observation of a quasi-two-dimensional electron gas at the interface of LAO and SrTiO₃ (STO) crystals for the polar nature of LAO and the requirements to avoid a polarization catastrophe.⁸ LAO exhibits a cubic to rhombohedral phase transition at 820 K and at temperatures below this value the crystal develops twins.⁹ The twinning could result in the formation of crystalline domains where the cations may be displaced from their equilibrium sites. Such displacements could potentially affect the electronic energy levels which may show up in various spectroscopic measurements. Recent observations of resistive switching in oxides,¹⁰ high mobility electrons,^{8,11} and unusual magnetic phenomena¹² at the LAO/STO interfaces underscore the role of defects within the bandgap of these oxides and the need for careful characterization of these defects, namely, their location, energy width, and electron lifetimes. Transient absorption and photoluminescence (PL) in the picosecond to femtosecond time scale are powerful tools for studying the dynamic coupling of electron and lattice and for detecting localized defect states for wide bandgap crystals such as STO and LAO.^{13,14}

Based on the PL and transient absorption many interesting carrier dynamics studies have been reported for the doped and undoped STO.¹⁵⁻¹⁷ However, as far as we know, few ultrafast dynamics and PL studies have been reported on LAO crystals.^{18,19} Kawabe *et al.*¹⁸ found that under 266 nm excitation there were two distinct components, a fast UV one

arising from band-band excitation and a broad component involving oxygen defect levels. Kanai *et al.*¹⁹ found by using 248 and 193 nm excitations a series of five different PL peaks which were associated with defect levels inside the gap. In both papers the electrons were pumped to the conduction band and the resultant PL was dominated by emission from conduction band to various defect levels. Under this condition the PL spectrum was dominated by broad peaks with very little distinguishable features. In this paper, we investigate the dynamics of electron relaxation and defect PL from single crystal LAO by using subbandgap excitation (400 nm) which selectively probes certain defect levels revealing features not seen in the previous studies. We see consistent doublet features on more than one PL peak and we believe this to arise from the twin splitting of the defect energy band, which, in turn, enable us to estimate the size of the cationic displacements within the twins in LAO.

For this study, doubly polished (100) LAO single crystals (Crystec GmbH, Berlin, Germany), 1 × 1 cm in size and 0.5 mm thick, were used as received. The femtosecond transient absorption and pump probe experiments were performed by using a Spectra-Physics Ti:sapphire oscillator seeded amplifier laser system. The amplifier gives an output with a central wavelength of 800 nm, a pulse duration of 60 fs, and a repetition rate of 1 kHz. The output beam was split into two portions. A larger portion passed through a β-BaB₂O₄ crystal to generate a 400 nm beam by second harmonic generation to act as a pump beam. Another portion was focused at a sapphire plate to generate a white light continuum. The white light beam was split into two portions: one as probe and the other as a reference to correct for pulse-to-pulse intensity fluctuations. Both the pump and probe beams were focused onto the same position on the sample with diameters of about 350 and 200 μm, respectively. The delay between the pump and probe pulses was varied by using a computer-controlled translation stage. The temperature dependent PL experiments were carried out using the same 400 nm laser excitation source. The PL signal was collected through a Princeton Instruments SP 2300i Spec-

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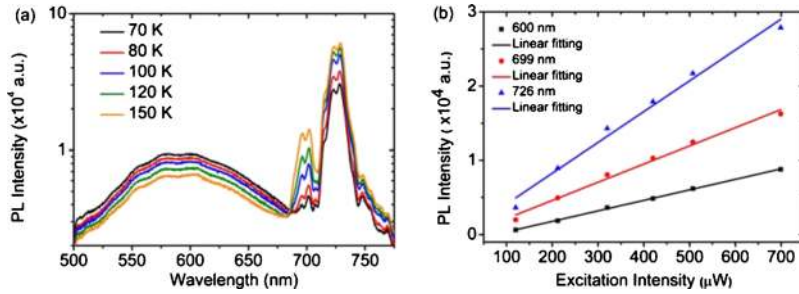


FIG. 1. (Color online) (a) Photoluminescence data for LAO crystal at different temperatures under 400 nm laser excitation. (b) Photoluminescence intensity at 600, 699, and 726 nm under different excitation intensities at room temperature.

trometer with a charge-coupled device detector. The spectral resolutions were 0.14 nm for PL measurement and 5 nm for transient absorption measurements.

In Fig. 1(a) three distinct peaks were observed in the PL intensity, a broad spectrum at high energies from 550 to 650 nm and two sharp peaks at lower energy range centered at 699 and 726 nm. Both sharp peaks show a doublet splitting of ~ 6 nm. The splitting is also likely to be present in the peak centered at 600 nm but is not observable due to the peak broadening. Such a splitting has not been reported in the previous studies probably due to low spectral response of the detector at longer wavelengths (Kawabe) or inadequate spectral resolution (Kanai).^{18,19} As the photon energy of the 400 nm excitation is below the bandgap, the electrons can reach the conduction band only via a two-photon process. Figure 1(b) clearly shows that the PL intensities at three different wavelengths follow a linear dependence on the excitation intensity. The linearity suggests that PL arises from the excitation of the valence band excitation to some intermediate defect levels followed by decay down to various lower defect levels. The PL intensity at 726 and 699 nm increases with temperature, while the PL intensity for the broad spectrum from 550 to 650 nm decreases linearly with increasing temperature. This interesting effect indicates that the PL for the broad spectrum and the two sharp peaks originate from different electronic processes.

This is better illustrated in Fig. 2 where we have taken the calculated defect levels from Lou *et al.*²⁰ and have matched the observed PL with possible energy levels. The broad peak at 600 nm is likely due to the electronic transition from singly charged oxygen interstitial defect levels to valence band; the 726 nm peak is likely due to La interstitial and/or the Al antisite at the La position to the valence band. The different temperature dependences of these peaks may be related to the relative temperature redistribution of the

density of the defects. With increasing temperatures one would infer from these data an increase in the La interstitial and/or the Al antisite at the La position defects and a decrease of oxygen interstitial.

The spectral splitting of the peaks at 699 and 726 nm is quite interesting and may be related to the twin formation in LAO. At around 820 K, LAO undergoes a transition from a high temperature cubic phase to a low temperature orthorhombic phase with a rhombohedral primitive unit cell through a $Pm3m \leftrightarrow R3c$ octahedral tilting.²¹ This symmetry breaking transition leads to a buildup of high stress in the crystal which is relieved by the formation of eight energetically equivalent domain states, of which there are only four macroscopically observable twins. Any pair of the four twin states will have twin boundaries along the (100) or (110) planes. However, it has been found that the (100) twins are energetically more favorable than the (110) twins due to lesser strain.²² These twin states may have significant displacement of the cations from their equilibrium sites which may affect the electronic energy levels. To shed more light on the effect of this cation displacement, first-principles calculations based on density functional theory (DFT) are employed for the position of energy level in the bandgap. The DFT calculations include the generalized gradient approximation,²³ using a plane wave basis (kinetic energy cutoff of 400 eV) and projector augmented-wave pseudopotential.²⁴ One oxygen atom was removed from a $3 \times 3 \times 3$ supercell to model the oxygen vacancy defect in LAO. This defect level was found at around 2.23 eV above valence band maximum (without shifting the Al or La). When the Al atom was shifted from the original site with respect to the other atoms in their original sites, the position of the defect level changed significantly. The defect level shifted about 15 meV from original position when the Al atom was displaced 0.09 Å from the original site (Fig. 3), while a similar displacement at the La site did not lead to any

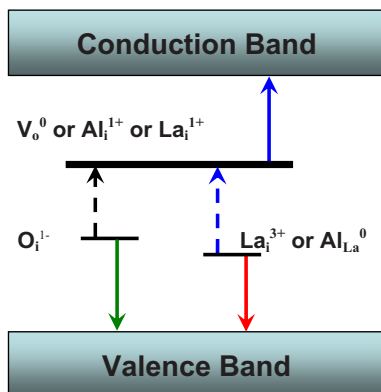


FIG. 2. (Color online) Illustration for the possible origin of the PL (down arrow) and the transient absorption (up arrow) peaks with the calculated defect levels from Lou *et al.* (Ref. 20).

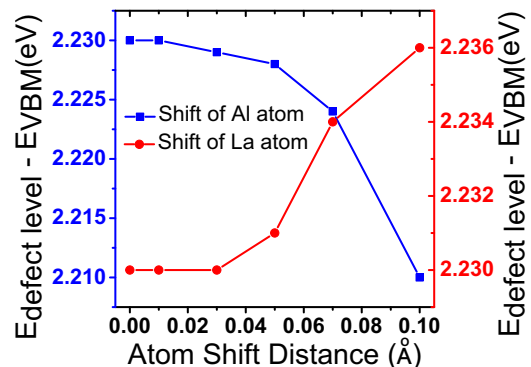


FIG. 3. (Color online) First-principles calculated defect levels with shifting Al and La atoms.

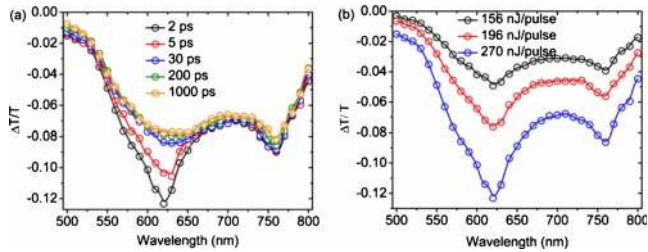


FIG. 4. (Color online) (a) Transient absorption spectrum for the single LAO crystal under 270 nJ/pulse, 400 nm femtosecond laser excitation at room temperature. (b) Transient absorption spectrum under different excitation intensities with 2 ps delay time.

significant shift of the defect level. Hence, the twinning could result in two different Al sites, one shifted and the other not, leading to the observed 6 nm splitting in the defect PL.

The transient absorption spectra of the defect dynamics for the LAO crystal under excitation at 400 nm at the room temperature are shown in Fig. 4. Two transient absorption bands at 620 and 760 nm were observed at different excitation intensities. It is interesting to note that the two bands behave differently with evolution of time. The transient absorption band at 620 nm under high excitation intensity (270 nJ/pulse) decays with two different time scales, a fast decay with a time constant of 4 ps followed by a slow decay with time constant over 1 ns. However, the transient absorption band at 760 nm only shows one slow decay component. This difference in the time evolution behaviors indicates that the 620 and 760 nm bands originate from different electronic processes. Figure 4(b) shows excitation intensity dependent transient spectra at a time delay of 2.0 ps. The excitation intensity dependence indicates a hybrid of one- and two-photon excitation processes with a larger two-photon component for the 620 nm band (power of 1.6) than the 760 nm band (power of 1.4). As the excitation intensity increases, the amplitude of the fast decay components for 620 nm band also increases. The two-photon excitation at high excitation intensities will promote the electrons onto the conduction band. The initial decay from the conduction band to upper defect level is believed to be very fast (~ 100 fs and not observed in our data), which is followed by decay to lower defect level with time constants of 4 ps and subsequent decay back to valance levels with a very slow decay components (>1 ns). Figure 4 shows that the relaxed transient spectra, say at 30 ps, became similar to the initial (e.g., at 2 ps) transient spectra under lower excitation intensities. The one-photon excitation (which will dominate at the low excitation intensity) can only promote electrons to the midgap defect level (top thick solid horizontal line in Fig. 2). The 620 nm band arises from two different electronic transitions, first one from the upper defect level to the conduction band absorption with a short decay time constant (4 ps) (solid up-arrow in Fig. 2) and the second from the lowest defect levels to the upper gap defect level excitations with a slow decay time constant (>1 ns) (dashed up-arrow on the right side of Fig. 2). The 760 nm transient absorption is from the lowest defect levels to the upper defect level with a slow time constant (>1 ns) (dashed up-arrow on the left side of Fig. 2). Hence, this confirms that the upper defect level centered at 3.1 eV has a fast electron decay time (~ 4 ps), while

the two lower defect levels centered at 2.1 and 1.7 eV have long (>1 ns) decay times.

The study of wide bandgap oxides and the defects lying within the bandgap may be better studied by using subbandgap excitation rather than a band to band excitation. We have shown this to yield exciting new data for the case of LAO where a doublet splitting is seen in the various defect levels with different dynamics processes. These splittings give us an idea of the cationic displacements in LAO as a result of structural phase transitions which are responsible for the commonly observed twins in this system. The femtosecond pump probe studies are able to distinguish the widely differing electronic lifetimes of the various defect levels. Hence, PL and optical pump probe spectroscopic techniques can shed new information on these wide bandgap materials.

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