Phonon decay in BaSnO₃ perovskite

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Available at: https://doi.org/10.1063/5.0092179
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Decays of Raman active vibrations have been directly traced in time in technologically important BaSnO$_3$ semiconducting crystal. Time-domain coherent Raman technique with excellent time and spectral resolutions has been applied to selectively measure ultrafast decay rates of optical phonons within 350-1300 cm$^{-1}$. The phonon mode damping rates are found to be within 1.27 - 1.59 ps$^{-1}$ at room temperature indicating that the homogeneously broadened Raman linewidths are within 6.7-8.4 cm$^{-1}$. Phonon decay mechanisms are being discussed within the framework of parametric phonon interactions due to the lattice anharmonicity. Characteristics of the Raman active modes are essential in understanding limiting factors for achieving high carrier mobility.

Wide band-gap semiconducting oxides have strong expectations in providing the high mobility while retaining their properties at heterojunction interfaces that is critical for microelectronic device applications. Recently, measurements in bulk BaSnO$_3$ (BSO) perovskite demonstrated significantly higher room temperature mobility with values within 100-320 cm$^2$/V·s range$^{1-4}$. Though ionized impurity scattering is a dominant contribution that limits the mobility at high doping levels, the impact can be avoided by using effective doping techniques. That leaves the inelastic carrier-phonon scattering to affect the mobility as only the polar optical (LO) phonons can mediate energy exchanges between the hot carriers and the lattice. In this case, the mobility values can be as high as 500 cm$^2$/V·s for electron concentrations $> 1 \times 10^{19}$ cm$^{-3}$$^5$. Knowledge of mechanisms for polar phonon interactions and phonon decay routes at different temperatures in the system where screening of ionic potential is relatively weak is essential. From the fundamental point of view, lattice vibrations (LO- and TO- phonons) and their characteristics is key in quantifying and modeling the oxide material’s complex dielectric function$^6$$^7$. The phonon-damping rate ($\Gamma$) is more important and critical parameter than the vibration frequency ($\Omega$). The damping rate relates straightforwardly to homogeneous linewidth $\Delta\nu[cm^{-1}] = \Gamma/2\pi c$ for Raman resonances that are usually studied using traditional(spontaneous) Raman scattering spectroscopy techniques. Transparent oxides have been a subject of a few theoretical and experimental studies. In particular, cubic lattice BSO has been modeled using density functional theory (DFT) to predict lattice parameters, band structure, carrier scattering rates, vibrational spectra, and dielectric function$^5$$^7$$^9$$^{11}$. With regard to the experimental studies, some of the earlier optical measurements indicated a presence of strong Raman active modes$^2$.$^9$$^{11}$

In this letter, we present results on direct time-dependent measurements of the phonon decay in single-crystal BaSnO$_3$ perovskite. Ultrafast time resolution and excellent sensitivity of the three-color Coherent Anti-Stokes Raman Scattering (CARS) technique provided valuable insight into the dynamics of multiple phonon lines within the frequency range of 350-1300 cm$^{-1}$. The superior approach that had been applied for this type of material led to important knowledge about the damping of Raman active vibrations in intrinsic wide-bandgap oxide crystal. Damping rates of the characteristic Raman active modes have been determined with an excellent precision that is not attainable using other experimental methods. The obtained information is valuable both from the standpoint of problems in fundamental physics and understanding carrier transport properties, including mechanisms that put limits to achieving high electronic mobility that is critical for device applications.

The time-resolved CARS process can be regarded as scattering of a delayed probe pulse with amplitude $E_3$ and carrier optical frequency $\omega_3$ on the coherence created in the material by a pair of time synchronized $E_1(t)$ and $E_2(t)$ pulses applied at an earlier time. Fig. 1 provides a schematic of the CARS setup for time-domain measurements in BSO crys-
and phase-in vibrations at around \( \Omega_{\text{PO}} \). The \( \text{OPO}_{1,2} \) spectra used for the calculations are presented in the inset. The OPOs are tuned to different wavelengths in order to target and phase-in vibrations at around \( (\omega_1 - \omega_2) \approx 390 \text{ cm}^{-1} \). Dashed vertical lines indicate frequency positions for zone center phonons in BSO crystal according to results of recent theoretical and experimental studies\(^9\).

A high-average-power femtosecond Ti:S oscillator, running at 76 MHz, is utilized to synchronously and simultaneously pump two lab-built \( \text{OPOs}^{12,13} \), another small portion of the oscillator is used as a delayed probe pulse \( E_3(t) \). The broadly tunable \( \text{OPO}_{1,2} \), utilizing quasi-phase-matched materials with high nonlinear gain, provide continuously tunable outputs at corresponding wavelengths \( (\lambda_1, \lambda_2) \) to target frequencies \( (\omega_1 - \omega_2) \) that match Raman shifts \( (\Omega_{\text{R}}) \) within 350-1300 cm\(^{-1}\). Collinearly propagating beams and focusing conditions ensure that nearly zero-wavevector phonon states are excited and probed. Excellent time synchronization of the three pulses is ensured by the nature of synchronous pumping and active OPO cavity length adjustments on sub-micron scale. Monochromator and bandpass spectral filtering are used before detecting the signal at \( \omega_{\text{det}} = \omega_1 + (\omega_1 - \omega_2) \) with a low-noise CCD detector. The CARS signals (Fig.1, left inset) are primarily due to the non-resonant ultrafast electronic nonlinearity and the coherence is fast decaying. The data show that our time resolution is better than 120 fs while the signal-to-noise ratio is such that the CARS transients can be traced within \( \sim 75 \text{ dB} \). With regard to the spectral data (lower right panel), precision for detected CARS spectra is within \( \pm 1.4 \text{ nm} \) \( \sim 26 \text{ cm}^{-1} \). The ultrashort pulses \( (130-190 \text{ fs}) \) that are being used within this arrangement result in a fairly broadband macroscopic coherence. Fig.2 shows the calculated spectrum for the coherent amplitude \( Q(t) \) that is the result of an action of pulse pair from \( \text{OPO}_{1,2} \) that are tuned to \( \lambda_1 = 1015 \text{ nm} \) and \( \lambda_2 = 1053 \text{ nm} \) thus targeting Raman active vibrations at \( (\omega_1 - \omega_2) \sim 390 \text{ cm}^{-1} \). Details of the calculations are presented in Supplement\(^14\). Density functional theory calculations for Raman active mode frequencies\(^8,9\) and the typical bandwidths of our pulses result in involvement of at least two phonon modes within the coherent excitation envelope shown in Fig. 2. Therefore, spectrally resolved measurements are key to differentiate decays of different Raman active vibrations within the broadband CARS signal.

FIG. 2. Spectral envelope for the coherent amplitude \( Q(\omega_1 - \omega_2) \) produced in a material by two femtosecond pulses from \( \text{OPO}_{1,2} \). (a) The \( \text{OPO}_{1,2} \) spectra used for the calculations are presented in the inset. The OPOs are tuned to different wavelengths in order to target and phase-in vibrations at around \( (\omega_1 - \omega_2) \sim 390 \text{ cm}^{-1} \). Dashed vertical lines indicate frequency positions for zone center phonons in BSO crystal according to results of recent theoretical and experimental studies\(^9\).

The BSO single crystals have been grown using a PbO-based flux method. The oriented crystal dimensions are \( 1.7 \times 1.7 \times 1 \text{ mm}^3 \) with facets polished for normal incidence along \( (100) \) direction. Fig. 3 presents time and spectrally resolved CARS signals for the phonon modes at \( \sim 465 \text{ cm}^{-1} \) and \( \sim 630 \text{ cm}^{-1} \). Based on the spectral data we can state that the detected signals are within the phonon energies identified by the DFT studies as \( \text{LO}_2 \) and \( \text{LO}_3 \) modes\(^8,9\). Time-resolved CARS spectra for the \( \text{LO}_2 \) mode are shown in Fig. 3(b) while the corresponding CARS transient is shown in red circles in Fig. 3(a). The important decay constants for investigated vibrations can be obtained with best precision by fitting the experimental data with a model for time-resolved CARS signal \( S(t_d) \).
is inside’s step function, $T_{\text{cal}}$ curve for at half maximum (FWHM) linewidths for the Raman active envelope for the pulsed electric field with pulsewidth $t_p \pm 8.25$ (decay time constant of Fig. 3(a) show perfect single exponential decay for the strength of a Raman active resonance. The transients contribute to the third-order optical nonlinearity due to the much slower decaying part representing the resonant cays by a few decades in less than 500 time is due to non-resonant third-order nonlinearity that de-

additional details are provided in the Supplement.

The measurement yields in the corresponding damping rate $\Gamma = 1.34 \pm 0.05 \text{ps}^{-1}$.

We probed even higher frequency ($\sim 950$-$1250 \text{ cm}^{-1}$) phonon modes in our BSO experiments. Fig. 5 shows CARS transients and spectra for the case of the coherently driven vibrations within the indicated range. The time-resolved signals shown in Fig. 5 (a), (b) are obtained for the experimental condition when $OPO_{1,2}$ pulses have been tuned to 1014 nm and 1142 nm wavelengths. This drives vibrations within the broadband ($\sim 230 \text{ cm}^{-1}$) range at around 1100 cm$^{-1}$. The corresponding CARS spectra (Fig. 3 (d)) show two-component spectra at longer delay times which can be attributed to Raman active vibrations at $\sim 946 \text{ cm}^{-1}$ and 1068 cm$^{-1}$. The two phonon states decay at different rates as can be seen from the corresponding time-resolved CARS data shown in Fig. 5 (a) and (b) correspondingly. Experiments with even longer wavelength tuning ($>1150 \text{ nm}$) indicate the absence of Raman active resonances within $\sim 1100$-$1250 \text{ cm}^{-1}$ range of frequencies as the CARS signals show time-resolution limited response within 60-70 dB (Fig. 5(c)).

We will discuss the results within the framework of theories that consider both dephasing processes and parametric phonon interactions within the crystal lattice$^{15-17}$. These correspond to changes in the phase (pure dephasing) and the amplitude of the individual vibrations. Lattice vibration phase shifts are due to spatial modulation of crystal and the amount of excess carriers that may affect the intrinsic phonon mode. In good quality samples, processes induced by spatial disorder and free carrier plasma play a negligible role. Hall measurements for our BSO crystal show that the estimated excess carrier density is less than $\sim 10^{14} \text{ cm}^{-3}$ and the corresponding plasma frequency ($< 0.56THz$ or $\sim 3 \text{ cm}^{-1}$) is well below the frequencies of the BSO crystal LO-phonon modes. Thus, pure dephasing mechanism can be ruled out. Phonon mode amplitude dynamics is determined by efficiency of parametric phonon interactions caused by anharmonic crystal potential. As a good approximation to quantify the amplitude-damping rate, the decay of a zone-center (i.e., $q \sim \vec{0}$) LO-phonon into other phonons is considered in terms of the lowest-order anharmonic term in the crystal potential$^{16,17}$:

$$\Gamma(Q, T) = \sum_{i,j} \langle 3 \rangle (Q) \rho_{\omega_{i}\omega_{j}} [1 + n(\omega_{i}, T) + n(\omega_{j}, T)]$$

In the equation, $n(\omega_{i}, T) = (e^{(\hbar \omega_{i} / k_{B} T)} - 1)^{-1}$ terms stand for the lower energy phonon occupation numbers at

![FIG. 4. Time-resolved CARS signal under an excitation condition of targeting Raman shift at $\sim 830 \text{ cm}^{-1}$. The $OPO_{1,2}$ central wavelengths have been tuned to $\lambda_1 = 1014 \text{ nm}$ and $\lambda_2 = 1107 \text{ nm}$. The slow decaying spectral trace was centered at $\lambda_{\text{ar}} \sim 765 \text{ nm}$ corresponding to a phonon mode at $\sim 790 \text{ cm}^{-1}$. The theoretical fitting curves for different phonon decay times ($T_2$) are shown in solid, dashed, and dash-dotted lines.](image-url)
crystal temperature \(T\). The corresponding phonon wavevectors result in the total momentum conservation \(\langle \vec{q}_i + \vec{q}_j = \vec{0}\rangle\). The coupling coefficients \(s^{(3)}_{ij}(\omega)\) are tied to the third derivative of the crystal potential. Due to the density of states factor \(\rho(\omega)\) zone-edge phonons (with \(\vec{q}_i = -\vec{q}_j\)) are expected to provide highest contribution in the decay process. Analyzing our time-resolved CARS data for the phonon decay at \(\sim 465 \pm 27\) \(cm^{-1}\) we should state that the Raman active line is \(80\) \(cm^{-1}\) blue shifted compared to the calculated zero-wavevector \(LO_2\)-phonon energy provided in Ref [8]. Comparison of the detected value with the calculated \(LO_2\)-phonon energy provided in Ref [9] shows slightly red shifted \(\sim 25\) \(cm^{-1}\) vibration while the experimental results of this work identify the \(LO_2\)-phonon position at \(\sim 408\) \(cm^{-1}\).

With regard to the observed phonon dynamics in our CARS experiment, we can identify a straightforward decay route. The traced \(465\) \(cm^{-1}\) vibration can decay into lower energy phonons with energies of \(\sim 300\) \(cm^{-1}\) and \(\sim 160\) \(cm^{-1}\). Using formula (2), knowing from our data that \(\Gamma = 1.59\) \(ps^{-1}\) (at \(T = 300K\)), and calculating the final phonon occupation numbers, we can estimate a zero-temperature decay rate of \(0.73\) \(ps^{-1}\). This results in a linewidth of \(3.89\) \(cm^{-1}\). With regard to the detected \(\sim 630\) \(cm^{-1}\) vibration, its frequency position matches well with the theoretical predictions of Refs [8, 9]. The DFT results of Ref [9] show that there might be at least two different decay channels. These are the overtone paths resulting in final phonons with equal energy \(\sim 315\) \(cm^{-1}\) and the opposite wave-vectors and the combination channel involving two \(LO\)-phonons with energies of \(\sim 480\) \(cm^{-1}\) and \(\sim 160\) \(cm^{-1}\). The DFT calculations of Ref. [8] also suggest that there might be more than one combination channel for the decay. This is the phonon pair involving \(LO\)- and \(TO\)-vibrations with energies around \(\sim 385\) \(cm^{-1}\) and \(\sim 240\) \(cm^{-1}\) as well as another possibility that involve final phonon states at \(\sim 490\) \(cm^{-1}\) and \(\sim 140\) \(cm^{-1}\). The above arguments together with data presented in Fig. 3 for the \(\sim 630\) \(cm^{-1}\) mode yields the decay rate at zero-temperature to be within \(0.63-0.89\) \(ps^{-1}\) \((2.38-3.36\) \(cm^{-1}\) for linewidths). The ratio factor \(r\) mentioned above and the DFT calculations lead us to a conclusion that the CARS transient presented in Fig. 4 is due to a two-phonon state. Indeed, the resonant part is weaker as the ratio drops from \(r = 3.7 \times 10^{-2}\) for the \(\sim 465\) \(cm^{-1}\) mode to \(r = 2.5 \times 10^{-4}\) for the mode at \(\sim 792\) \(cm^{-1}\). The two-phonon state is formed by two \(LO_2\) phonons \((385-420\) \(cm^{-1}\)). Theoretical and experimental studies show the two-phonon states may even have comparable Raman scattering cross-section [18-20]. This is especially true for the case of wide-bandgap materials. The cross-section was found to be dependent on ratio of material’s bandgap to the probe photon energy and the increase is nonlinear with the ratio [19]. Similarly, we believe that the results presented in Fig. 5 (a,b) show dynamics of the two-phonon states with the rates governed by low energy lattice vibrations that form the two-phonon states combining \(LO_2\) and \(LO_3\) phonons.

In conclusion, we reported results on direct measurements of the decay of lattice vibrations in wide-bandgap semiconducting \(BaSnO_3\) single crystal. The intrinsic vibrations decay via mechanisms of parametric phonon interaction. Time-resolved coherent Raman measurements offered exceptional precision and resulted in an equivalent spectral resolution that is extremely difficult to achieve in traditional Raman scattering studies. In particular, the experimental data allowed important estimates for zero-temperature decay rates for the primary \(LO\)-phonons to within the range of \(0.63-0.89\) \(ps^{-1}\). In the spectral domain, this corresponds to linewidths range for Raman resonances of \(2.38-3.36\) \(cm^{-1}\). We believe that the studies provide very important information on a class of materials within the transparent semiconducting oxides that are being actively considered for high power solid-state device applications.

ACKNOWLEDGMENTS

This material is based upon work supported by the United States Air Force Office of Scientific Research under award No: FA9550-18-1-0273. Crystal growth was supported by the center for Quantum Materials Synthesis (cQMS), funded by the Gordon and Betty Moore Foundation’s EPiQS initiative through grant GBMF10104, and by Rutgers University. The authors acknowledge help with experiments from Dinusha Senarathna and Helani Singapura of URI.

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