Influence of swift heavy ion irradiations on temperature dependent phononic behavior of epitaxial LaNiO_3 thin film

Sunidhi .¹, Vishal Sharma¹, Sunil K. Arora^{1}, Florencio Sánchez², Fouran Singh³ and Vasant Sathé⁴*

¹Centre for Nanoscience and Nanotechnology, Block-II, South Campus, Panjab University, Sector-25, Chandigarh-160014, India

²Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, Bellaterra 08193, Spain

³Materials Science Group, Inter-University Accelerator Centre, New Delhi 110067, India

⁴UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore-452001, India

*Corresponding author: aroras@pu.ac.in

ABSTRACT

The effects of Ag^{15+} (200 MeV) swift heavy ion irradiations on the structural and phononic properties of epitaxial LaNiO_3 (LNO) thin film have been investigated using High resolution X-ray diffraction (HR-XRD) and Raman spectroscopy. After irradiation, the decrease in out-of-plane lattice parameter of LNO towards its bulk value indicates the relaxation of epitaxial strain. The temperature dependency of phononic response for different ion irradiation doses was studied by performing the Raman measurements in temperature range 80K-300K. For pristine as well as irradiated samples of LNO, the observed phononic modes A_{1g} and E_g shows softening with an increment in the temperature. The temperature coefficient of both modes varies with ion fluence. For A_{1g} mode, temperature coefficient increases from $-0.087 \text{ cm}^{-1}\text{K}^{-1}$ for pristine to $-0.092 \text{ cm}^{-1}\text{K}^{-1}$ for maximum ion fluence $10^{12} \text{ ions/cm}^2$, while for E_g mode it decreases from $-0.022 \text{ cm}^{-1}\text{K}^{-1}$ for pristine to $-0.015 \text{ cm}^{-1}\text{K}^{-1}$ for $10^{12} \text{ ions/cm}^2$. Raman frequency shift for both the modes shows non-linear behaviour with temperature. This temperature dependent behaviour was quantitatively analysed by using a model which suggests that Raman shifts of A_{1g} mode emerged predominantly due to four phonon processes whereas, for the E_g mode, major contribution came from the thermal expansion effect. Ion irradiation did not change the dominating mechanism resulting in these temperature dependent Raman shifts, although the relative contribution of different processes got altered with ion fluence.

KEYWORDS: Raman Spectroscopy, Phonon anharmonicity, Ion Irradiation

I. INTRODUCTION

Correlated transition metal oxides (Rare earth nickelates, ReNiO_3 (Re = Rare earth)) among the functional materials have attracted tremendous attentions owing to their astonishing magnetic, electrical, and structural properties.¹ They offer various fascinating phenomenon such as metal to insulator (M-I) transition, charge, spin and orbitals ordering, colossal magneto-resistance and multiferroicity.² One of most exceptional property of these rare earth nickelates (except Re = La) is sharp M-I transition. However, Lanthanum nickelate (LNO) is the only nickelate perovskite structure, which shows no M-I transition and manifest the metallic behavior at all temperatures. This mesmerizing property of LNO made it a preferable applicant for electrode applications in electronics.³ LNO exhibits rhombohedral symmetry ($R\bar{3}c$) in the bulk form and become monoclinic ($C2/c$) in epitaxial thin film form because of strain induced from the substrate. This strain is accommodated in the structure either by distortion in bond length in $[\text{NiO}_6]^-$ octahedra or by fluctuation in octahedral distortion angle.^{4-6,8} The vibrational properties for LNO have been explored theoretically using density functional theory (DFT) calculations and experimentally using Raman spectroscopy.^{4-7,9,10} These studies featured A_{1g} and E_g as the pronounced modes where A_{1g} mode corresponds to the change in structural properties of $[\text{NiO}_6]^-$ while E_g mode is related to bending of oxygen octahedra. Both phononic modes are sensitive to the temperature and strain. The influence of mismatch strain on vibrational modes of LNO film grown epitaxially on different single crystalline substrates was investigated by using Raman spectroscopy and DFT calculations.⁶ Another study reported the vibrational and electronic properties of LNO using the DFT calculations.⁵ They computed the influence of temperature on the vibrational properties and showed that A_{1g} Raman mode can be used as a signature to characterize the magnitude of octahedral rotations in rhombohedral LNO. Chaban et al.⁴ performed temperature dependent Raman scattering for polycrystalline LNO thin film experimentally and discussed the notable redshift in Raman frequency of A_{1g} mode with temperature. In a previous study, we reported

softening of both the modes in epitaxial LNO thin films with increase in the temperature, and analysed this softening by a model including the contribution from thermal expansion effect, anharmonic decay of phonons, and thermal expansion coefficient (TEC) mismatch induced strain effect.⁷

In past couple of decades swift heavy ion (SHI) irradiations have become a very important and effective tool for the modifications of the properties of the materials.¹¹⁻¹³ The SHI irradiations have been used to alter the property of many oxide materials including high T_c superconductors, colossal magneto resistance (CMR) oxides, and many transition metal oxides owing to their ability of tailor materials properties via controlled introduction of defects in materials by selecting appropriate ion type and energy.¹⁴⁻²² There are reports in the literature where effect of irradiations on the structural, magnetic and electronic properties of LNO have been studied.²³⁻²⁵ Kumar et al. investigated the influence of heavy ion irradiations on the electrical, structural and magneto-transport properties of LNO thin films. They reported that with an increase in SHI fluence, hybridization between 3d orbital of Nickel and 2p orbital of Oxygen become strong leading to metallic and paramagnetic behaviour in irradiated film. Their work mainly focussed on the electrical properties (M-I) transition) of LNO where they studied the effect of irradiation on strength of hybridization leading change in conducting properties.

Raman spectroscopy being sensitive to structural distortions and strain, has been used to probe ion irradiation induced defects and their impact on phononic properties of oxide systems.¹⁷⁻²⁰ Hazem et al.¹⁷ used Raman spectroscopy to probe the crystalline to amorphous phase transition in irradiated TiO_2 thin film. Varshney et al.¹⁸ studied the effect of heavy ion irradiations in polycrystalline thin film of CeO_2 . They reported the formation of nanostructures on the surface of film when irradiated with Au^{13+} (175 MeV) ion beam. Thakur et al.¹⁹ studied the influence of SHI irradiations on electronic and structural properties

of TiO_2 film. By using structural characterization technique, they reported a phase transformation in TiO_2 from anatase phase to a mixture of rutile and brookite phases with increase in ion irradiation dose. Bajpai et al.²⁰ probed the effect of O^{8+} (100 MeV) SHI ions on phononic properties of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST_x) ceramics by using temperature dependent Raman spectroscopy. They found ion irradiation results in induction of strain and annihilation of oxygen vacancies in the structure. As far as we are aware, no study related to impact of SHI irradiation on the phonon modes of LNO is available in literature. Herein, we present a systematic study on the temperature dependency of vibrational properties of epitaxially grown LNO thin film irradiated with Ag^{15+} (200 MeV) ions probed through temperature dependent Raman spectroscopy.

II. EXPERIMENTAL METHODS

For this study, LNO thin film was grown epitaxially on (001) oriented LaAlO_3 (LAO) substrate ($10 \times 10 \text{ mm}^2$) by using Pulsed laser deposition (PLD). More details related to LNO thin film can be found in our previous study.⁷ The thin film of LNO was cut into four pieces, each with the size of $5\text{mm} \times 5\text{mm}$ so that after irradiation the growth condition of all samples under study remains the same for further studies. One piece was kept as pristine (reference) sample, while others were irradiated with different fluences of Ag^{15+} (200 MeV) ions i.e. 10^{11} ions/ cm^2 , 5×10^{11} ions/ cm^2 and 10^{12} ions/ cm^2 . The ion irradiation was performed in high vacuum conditions using 15 UD tandem accelerators at Inter University Accelerator Centre (IUAC), New Delhi. The uniform scanning of the ion beam was performed by a magnetic scanner over the area of $1 \times 1 \text{ cm}^2$. By collecting the total charge pulses falling on the sample, the fluences were measured and digital current integrator was used to integrate the total sample current. High resolution X-ray diffraction (HR-XRD) measurements of the thin film were performed by using a high resolution Bruker D8 advanced X-ray diffraction with Cu-K_α source. The low temperature Raman spectroscopy experiment was carried out using a micro-

Raman spectrometer (Jobin - Yvon, LabRAM HR-800 Horiba) using diode laser beam (473 nm, 3mW).⁷ A 50X objective with 0.5 NA was used to collect the scattered light which then dispersed using grating (1800 groove nm⁻¹), and thereafter, was detected by using a charged couple device (spectral resolution ~1 cm⁻¹). Silicon Raman peak at 520 cm⁻¹ was used to calibrate the system before performing the experiment. For pristine as well as irradiated samples, liquid nitrogen cryo-cooler (Linkam THMS-600, temperature stability ± 0.1 K) was used to perform temperature dependent measurements and the experimental conditions were kept same throughout the experiment at all temperatures.

III. RESULTS AND DISCUSSION

It is a well-known fact that when an energetic ion is incident on the target material, it can produce various kinds of defects (columnar and point) and modify the local strain in the material. During its passage through the material, energy loss occurs via two processes; Nuclear energy loss, S_n (elastic scattering) and Electronic energy loss, S_e (inelastic scattering). Thus, the total energy loss, dE/dx of the incident ion can be written as:

$$-dE/dx = S_n + S_e \quad (1)$$

Here, S_n and S_e are the principal energy loss mechanism in the low and high energy (energy > 1 MeV) regions, respectively.²⁶⁻²⁷ For SHI, loss in the energy is predominantly because of S_e . Depending upon the magnitude of S_e there could be formation of various types of defects in the material. If S_e is larger than a threshold S_e (S_{eth}), latent tracks and amorphization zones may be generated inside the material along the trajectory of incident ion. If the value of S_e is less than the S_{eth} , then mainly point defects and defect clusters are formed. It has been shown that the SHI irradiation can alter the strain state of the material (depending upon pristine state of material).²⁸⁻²⁹ To describe the relaxation of strain in the LNO films, we considered the thermal spike model.²⁸ According to thermal spike model, the

energy deposited by an incident ion beam creates secondary electrons along the path of incident ion. These electrons transfer their energy to phonon via electron-phonon coupling, resulting in a substantial increase of local temperature. In this way locally defects are created or if the system already contains such defects, then they can be annealed. The defects induced by SHI produce an additional strain in the material and is superimposed on the lattice strain present in the film. Depending on the magnitude of two strains, the overall strain in the material decreases or increases.²⁸⁻²⁹

By using Stopping and Range of Ions in Matter, SRIM 2013 code³⁰, we calculated the value of S_n and S_e of Ag^{15+} ions interacting with LNO as a function energy of incident ion and target depth as shown in Fig. 1(a) and (b).

FIG. 1. Variation of (a) energy loss of Ag^{15+} ions in LNO with energy of incident ion (b) nuclear and electronic energy loss of Ag^{15+} (200 MeV) ions in LNO (27nm)/LAO with target depth.

From Fig. 1(a) it can be clearly noticed that S_e increases as the energy of incident ion increases and become maximum (around 400 MeV) then decrease with further increase in energy whereas S_n exists only at low energy values and is almost negligible for energy above 10 MeV. From Fig. 1(a) calculated value of S_e and S_n for 200 MeV Ag^{15+} ions are 2.734 KeV/ Å and 0.007 KeV/ Å, respectively. From these values it is clear that the magnitude of S_n is three orders smaller than S_e , so all energy loss is mostly because of electronic excitations. Range of incident 200 MeV Ag^{15+} ions in LNO is calculated to be 11.86 µm. Thickness of film (27 nm) is much smaller than the range of ion, so ions will pass through the LNO without being implanted.

Figure 1(b) shows the change in S_e and S_n values with target depth. It can be clearly stated from this figure that in the region of thickness of LNO film (27nm), S_e mainly dominant over S_n and energy loss is mainly due to inelastic scattering resulting in electronic excitation or ionization. This passage of Ag ions through LNO generates the oxygen vacancies which increases further with increase in irradiation dose. The concentration of oxygen vacancies in LNO created by different fluences of Ag ions (200 MeV) i.e. 10^{11} ions/cm², 5×10^{11} ions/cm² and 10^{12} ions/cm² are 3.90×10^{17} cm⁻³, 1.95×10^{18} cm⁻³ and 3.90×10^{18} cm⁻³, respectively as calculated using SRIM 2013 code. These values correspond to 22.37 ppm, 111.83 ppm and 220.37 ppm concentration of oxygen vacancies in the lattice, respectively. Due to large tolerance factor of LNO (0.97), it is possible to accommodate large number of oxygen vacancies into crystalline network through cooperative rotation of octahedra as rigid units while maintain the stabilized perovskite structure. The displacement per atom (dpa) produced by 200 MeV Ag^{15+} ions in LaNiO_3 have been calculated using SRIM 2013 using the formula $dpa = (N_{dis}/N) * \Phi$ where, N_{dis} is Average number of displacements / (Angstrom-Ion), N is atomic density and Φ is fluence of incident ion.^{31, 32} For 200 MeV Ag^{15+} ions incident on LaNiO_3 , using $N_{dis} = 0.06$ / Angstrom-Ion and $N = 1.72 \times 10^{22}$ atoms/cm³ (calculated using

the formula $N = (\text{density} \times \text{Avogadro number}) / \text{Molar Mass}$, the calculated value of dpa for 10^{11} ions/cm², 5×10^{11} ions/cm² and 10^{12} ions/cm² are 0.34×10^{-4} , 1.70×10^{-4} and 0.34×10^{-3} dpa, respectively. Moreover, the increase in concentration of oxygen vacancies with ion irradiation have been confirmed by the stoichiometry and oxygen concentration determination through the ratio of atomic concentration of Ni⁺² and Ni⁺³ experimentally from XPS measurements. **(For more details please refer to Supplementary Figure S2 (a-f) and S3)**

To understand the influence of heavy ion irradiations on the structural properties of LNO, HR-XRD measurements were carried out for pristine as well as irradiated samples. Wide angular range θ - 2θ scan shows only (00 l) reflections of LNO confirming the formation of single crystalline phase as shown in Fig. 2. This shows the θ - 2θ scan around (002) reflection of LAO and LNO. The LNO (002) reflection occurs at a smaller angle than LAO (002) reflection. In the pristine film, the out of plane parameter of LNO, is calculated to be $c = 3.918$ Å. This value is larger than the cell parameter in bulk LNO ($a = 3.838$ Å). This tensile strain along the out-of-plane direction of LNO is due to compressive epitaxial stress caused by the LAO substrate ($a = 3.789$ Å). With increase in value of ion fluence, peak position of LNO shift towards higher angle from 46.29° for pristine to 46.56° for highest fluence 10^{12} ions/cm². This shifting towards higher angle of diffraction indicates that the ion irradiation results in relaxation of strain in the lattice.

Inset figure shows the change in the out of plane lattice parameter, c of LNO with ion fluences. The value of lattice constant, c for pristine, 10^{11} ions/cm², 5×10^{11} ions/cm² and 10^{12} ions/cm² are 3.918 Å, 3.913 Å, 3.904 Å and 3.896 Å, respectively. It can be clearly observed that with increases in ion fluences, lattice constant, c monotonically decreases from 3.918 Å for pristine sample to 3.896 Å for the highest fluence 10^{12} ions/cm².

FIG. 2. HR-XRD plots for pristine as well as irradiated LNO/LAO. Lattice constant of LNO plotted with different ion fluences (shown in inset).

This decrease in the out of plane lattice parameter towards bulk value signals release of strain in the lattice after irradiation. This variation in out of plane parameter can be explained due to oxygen vacancies created by ion irradiation in the lattice. The oxygen vacancies results in the decrease in out of plane lattice parameter of LNO when it is under compressive strain state.³³ This decrease in out of plane parameter with irradiation in oxides has been reported earlier also.^{18, 34} Kumar et al.²⁴ reported an increase in the out of plane lattice parameter of LNO film (200 nm) with increase in irradiation dose. This contrasting impact of irradiation noted by the authors may be explained due to distinct initial state of the much thicker film used in their study. The irradiation release or induce strain depending on the initial state of material. The thickness (200 nm) of LNO film used in their study is more than the samples used in current

study (27 nm). At 200 nm thickness, one expect the film to be completely strain relaxed⁶ and their results are manifestation of stoichiometric changes produced through irradiation. To understand in-plane strain of LNO film, we performed the X-ray Reciprocal space map (RSM) on pristine as well as irradiated samples (See **Supplementary Figure S1 (a-d)**). The asymmetric (103) reflection was used to perform the RSM in pristine as well as irradiated samples. From the analysis of RSM, we infer that for pristine sample, in-plane lattice parameters of LNO is equal to that of LAO substrate (3.789 Å) owing to similar value Q [100] value of LNO and substrate LAO, This confirms the existence of in-plane compressive stress in LNO. While Q [001] value of LNO is at smaller value than that of Q [001] for LAO due to out of plane tensile strain which are in line with HR-XRD results (Fig. 2). After SHI irradiation, Q [100] value for LNO remain at same value as that of pristine (2.63 nm⁻¹) indicating the presence of in-plane compressive strain even after irradiation due to constraints from substrate but Q [001] value of LNO alters from 7.64 nm⁻¹ for pristine sample to 7.66 nm⁻¹ for highest irradiation dose 10¹² ions/cm² representing the decrease in out of plane parameter towards its bulk value. So from both HR-XRD and RSM results we concluded that after irradiation, epitaxial strain is relieved only along out of direction while in-plane parameters of LNO remain locked to substrate due to epitaxial strain in in-plane direction.

Figure 3(a) depicts the Raman spectra of pristine as well irradiated LNO film at room temperature revealing A_{1g} and E_g as the phonon active modes of LNO. The A_{1g} mode represents the structural distortion in [NiO₆]⁻ octahedra whereas, E_g mode shows bending vibration of Ni-O bond in [NiO₆]⁻ octahedra (pictorial repersentaion of A_{1g} and E_g modes shown within Fig. 3(b)). Figure 3(c) shows the variation of peak positions of both modes with the ion fluence. For pristine film, A_{1g} mode is at 210 cm⁻¹ while E_g mode is at 415.3 cm⁻¹. With increase in fluence, A_{1g} mode first hardens to 212 cm⁻¹ for lowest fluence 10¹¹ ions/cm²

FIG. 3. (a) Raman spectra of pristine as well as irradiated LNO thin film for different ion fluences. (b) Pictorial representation of displacement pattern of A_{1g} and E_g modes of LNO. Variation of (c) peak position and (d) line width for A_{1g} and E_g modes with ion fluences.

and then softens with further increase in fluence with its value being 208 cm^{-1} for highest fluence $10^{12} \text{ ions/cm}^2$. The shift in peak position of A_{1g} mode shows that irradiation results in change in rhombohedral distortion by changing the octahedral tilt angle. E_g mode first softens to 415 cm^{-1} for the lowest fluence and for highest fluence it hardens to 417 cm^{-1} . The variation in frequency of these Raman modes is due to relaxation in strain after ion irradiation due to generated oxygen vacancies in the lattice and is consistent with HR-XRD results. Figure 3(d) shows the change in line width with ion fluence where for both the modes it decrease for lowest fluence followed by increase for higher fluences.

To examine the changes induced by irradiation on the temperature dependency of vibrational properties of epitaxial LNO films, we performed temperature dependent Raman spectroscopy (80K-300K) on pristine sample as well as irradiated samples (Fig. 4 (a-d)). We obtained both Raman active modes of LNO (A_{1g} and E_g) at each temperature. By using Peak analyzer in OriginPro 9.0 software, we extracted the Raman frequency and line width for both modes and plotted them as a function of temperature.

FIG. 4. Raman Spectra of (a) pristine sample⁷ and sample irradiated with (b) 10^{11} ions/cm² (c) 5×10^{11} ions/cm² and (d) 10^{12} ions/cm² in the temperature range 80 K- 300K.

Figure 5(a) and (b) depicts the change in Raman frequency of both the modes with temperature for LNO films (pristine as well as irradiated). One can clearly notice that Raman frequency of both the modes of pristine as well as irradiated samples softens with increase in temperature with larger softening for A_{1g} mode than E_g mode. This distinct extent of softening for two modes can be understood on the basis of anisotropic nature of strain in in- and out- of plane direction. This shift of A_{1g} mode towards lower frequency with increase in temperature indicates the decrement in distortion angle of $[\text{NiO}_6]^-$ octahedra. The relation between A_{1g} mode frequency of LNO and distortion angle is $23 \text{ cm}^{-1}/\text{deg}$.⁵ By using this relation, we find that with the change in temperature (80 K - 300 K), obtained Raman shift of 18.7 cm^{-1} , 17.5 cm^{-1} , 18.5 cm^{-1} , 19.6 cm^{-1} for pristine, irradiated with 10^{11} ions/cm², 5×10^{11} ions/cm², and 10^{12} ions/cm² results in decrement of distortion octahedral tilt angle by 0.813° , 0.761° , 0.805° and 0.852° , respectively.

FIG. 5. Frequency shift of (a) A_{1g} and (b) E_g modes of pristine as well as irradiated LNO plotted as a function of temperature.

The downshift in frequency of E_g mode can be explained due to its dependence on Ni-O bond length which is further sensitive to change in volume with temperature.^{4,7, 9} Oxygen vacancies induced due to ion irradiation results in variation of Ni-O bond length and hence change the frequency of this mode.

Temperature dependent phononic behavior has been studied for many oxide materials like $Ba_{1-x}Sr_xTiO_3$, PdO, TiO_2 , and CeO_2 .^{20, 35-39} At present, there are few reports available where temperature dependent phononic responses in LNO have been studied.^{4,5, 7} They analyzed the variation of Raman shift of A_{1g} mode with temperature by using Landau formulism and estimated the rhombohedral to cubic phase transition temperature. The linear approximation used to understand the mechanism related to the obtained shift in peak positions of both phononic modes with temperature can be expressed as,

$$\omega(T) = \omega_0 + \chi T \quad (2)$$

Where, ω_0 and χ represents the peak extrapolated at 0 K and first order temperature coefficient, respectively.

Figure 6 shows the change in temperature coefficient of both the modes (A_{1g} and E_g) of LNO with fluence of incident ion as determined from the linear fit using equation (2).

FIG. 6. Variation of temperature coefficient for A_{1g} and E_g modes with ion fluence.

For A_{1g} mode, temperature coefficient decrease from $-0.087 \text{ cm}^{-1}\text{K}^{-1}$ for pristine to $-0.086 \text{ cm}^{-1}\text{K}^{-1}$ and $-0.085 \text{ cm}^{-1}\text{K}^{-1}$ for $10^{11} \text{ ions/cm}^2$ and $5 \times 10^{11} \text{ ions/cm}^2$ fluences respectively, and then increased for highest fluence $10^{12} \text{ ions/cm}^2$ to a maximum value of $-0.092 \text{ cm}^{-1}\text{K}^{-1}$. For E_g mode, temperature coefficient decrease from $-0.022 \text{ cm}^{-1}\text{K}^{-1}$ for pristine to $-0.021 \text{ cm}^{-1}\text{K}^{-1}$, $-0.020 \text{ cm}^{-1}\text{K}^{-1}$, $-0.015 \text{ cm}^{-1}\text{K}^{-1}$ for $10^{11} \text{ ions/cm}^2$, $5 \times 10^{11} \text{ ions/cm}^2$ and $10^{12} \text{ ions/cm}^2$, respectively.

From Fig. 7 (a) and (b), we observed that for all the samples, with increase in temperature, line width for both modes (A_{1g} and E_g) also increases. This broadening in phonon line width with the temperature could be due to various factors like oxygen vacancies, instrumental broadening and phonon scattering processes.^{35-41, 44} But, for a given sample under study, except phonon scattering processes and oxygen vacancies defects, all listed reasons were constant with temperature and ion fluence.

Therefore, only plausible reasons behind the increase in line width with temperature is related to phonon scattering processes leading to anharmonic decay of phonons and oxygen vacancies created by different fluence of incident ion.

So, this change in line width with increase in temperatures can be approximated by considering the phonon decay processes equation:

$$t = t_0 + P \left[1 + \frac{2}{e^x - 1} \right] + Q \left[1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right] \quad (3)$$

Where t_0 represents harmonic line width at 0 K, $x = \frac{\hbar\omega}{2kT}$, $y = \frac{\hbar\omega}{3kT}$ and P, Q corresponds to three and four phonon anharmonic constants, respectively.^{44-45, 47-48}

We fitted the experimental data of line width for A_{1g} and E_g modes using equation (3) (Fig. 7 (a) and 7(b)), and observed that for the A_{1g} mode of pristine and sample irradiated with lowest ion dose $10^{11} \text{ ions/cm}^2$, P is positive while Q is negative with lower value.

FIG. 7. Variation of line width with temperature for (a) A_{1g} and (b) E_g modes of pristine as well as irradiated LNO .

Hence, three phonon processes is mainly responsible for broadening. While with increase in ion dose, contribution of three phonon decreases while four phonon contribution increases. For highest dose, P become negative and Q become positive leading to broadening only because of four phonon process. While for E_g mode of pristine sample, both anharmonic processes (three and four phonon) results in broadening in line width with increase in the temperature as both the coefficients P and Q are positive. While with increase in ion fluence, P become negative and Q remain positive. So, for irradiated samples, broadening is only due to four phonon processes while three phonon processes results in opposite behavior.

These phonon scattering processes where an optical phonon decay into two and three acoustical phonons results in decrement in optical phonon's lifetime (τ). We can calculate the lifetime of phonons by using the relation $\tau = 1/\pi c t$ where c and t are light velocity and line width of mode.⁴⁴ The lifetime of A_{1g} mode of pristine sample are calculated to be 0.53 ps and 0.29 ps at 80 K and 300 K while for sample irradiated with highest dose (10^{12} ions/cm²) these values decrease to 0.40 ps and 0.27 ps, respectively. For the E_g mode, lifetime of phonons are larger with values 0.66 ps and 0.41 ps at 80 K and 300 K for pristine and 0.58 ps and 0.37 ps for irradiated sample (10^{12} ions/cm²) respectively. The increase in temperature and ion fluences results in decrease in phonon lifetime for both the modes.

To understand the influence of ion dose on the obtained shift in Raman frequency with temperature, we quantitatively analyzed the observed Raman shift for both the modes by using a model used in our previous study.⁷ The models includes contributions from the thermal expansion, anharmonic processes and TEC mismatch induced strain effect.^{7, 35-41, 46}

The temperature dependent behavior of frequency shift of soft mode, A_{1g} can be analyzed by using the Landau model's equation:

$$\omega^2(T) = \omega_0^2 \exp\left(-n\gamma \int_0^T \alpha dT\right) + D\omega_0 \left[1 + \frac{2}{e^{\hbar\omega/2kT}-1}\right] + E\omega_0 \left[1 + \frac{3}{e^{\hbar\omega/3kT}-1} + \frac{3}{(e^{\hbar\omega/3kT}-1)^2}\right] + \beta\omega_0 \int_0^T (\alpha_{LAO} - \alpha_{LNO})dT \quad (4)$$

Where, $x = \hbar\omega/2kT$ and $y = \hbar\omega/3kT$. Here, D and E are three and four phonon anharmonic constant respectively, n represents the degeneracy whose values are 1 and 2 for A_{1g} mode and E_g mode, respectively, γ denotes Grüneisen parameter, α is TEC of LNO and β is biaxial strain coefficient with $\beta = -2\omega_0\gamma$.⁷

For E_g mode, total frequency shift can be written as,

$$\omega(T) = \omega_0 \exp\left(-n\gamma \int_0^T \alpha dT\right) + D \left[1 + \frac{2}{e^{\hbar\omega/2kT} - 1}\right] + E \left[1 + \frac{3}{e^{\hbar\omega/3kT} - 1} + \frac{3}{(e^{\hbar\omega/3kT} - 1)^2}\right] + \beta \int_0^T (\alpha_{LAO} - \alpha_{LNO}) dT \quad (5)$$

For epitaxial thin film of LNO, the experimental value of thermal expansion coefficient and Grüneisen parameter are not known. So, their product can be written as a polynomial equation,

$$\gamma\alpha = A + BT + CT^2 \quad (6)$$

where, A , B and C are constants fit parameters.⁴⁶ The more detail about the model equation can be found in our previous report.⁷ We did the best fit of our experimental data for pristine as well as irradiated samples using the model equations (4- 6) to study the shift in frequency with temperature for both the modes. Figure 8((a)-(d)) and 9((a)-(d)) shows modelling results of A_{1g} and E_g modes (pristine and irradiated samples), respectively. Pristine sample modelling results have been taken from our previous report⁷ to compare its temperature dependent phononic behaviour with irradiated samples. The modelling results are in correspondence to the experimental results. The fit parameters deduced individually for the anharmonic processes, strain effect and the thermal expansion effect are shown in TABLE I.

TABLE I. Fit parameters of A_{1g} and E_g modes for pristine as well as irradiated LNO.

Ion						
Fluence(ions/ cm ²)	Raman modes	A	B	C	D	E
Pristine ⁷	A_{1g}	$(5.53 \pm 0.75) \times 10^{-5}$	$(-5.48 \pm 1.47) \times 10^{-7}$	$(-8.80 \pm 5.24) \times 10^{-10}$	-1.30 ± 0.80	-1.65 ± 0.16
	E_g	$(0.51 \pm 0.23) \times 10^{-5}$	$(1.75 \pm 1.01) \times 10^{-7}$	$(-4.85 \pm 3.79) \times 10^{-10}$	-0.16 ± 0.09	-0.11 ± 0.07
10^{11}	A_{1g}	$(4.03 \pm 0.52) \times 10^{-5}$	$(-7.99 \pm 1.70) \times 10^{-7}$	$(3.06 \pm 0.74) \times 10^{-9}$	-1.80 ± 1.18	-1.40 ± 0.24
	E_g	$(0.51 \pm 0.68) \times 10^{-5}$	$(1.75 \pm 1.36) \times 10^{-7}$	$(-4.63 \pm 4.83) \times 10^{-10}$	0.04 ± 0.27	-0.11 ± 0.10
5×10^{11}	A_{1g}	$(1.04 \pm 0.20) \times 10^{-5}$	$(-1.21 \pm 1.04) \times 10^{-7}$	$(1.01 \pm 2.48) \times 10^{-9}$	-2.20 ± 0.63	-1.40 ± 0.13
	E_g	$(0.99 \pm 0.83) \times 10^{-5}$	$(1.23 \pm 1.66) \times 10^{-7}$	$(-3.35 \pm 0.59) \times 10^{-10}$	0.08 ± 0.34	-0.12 ± 0.13
10^{12}	A_{1g}	$(3.80 \pm 0.99) \times 10^{-5}$	$(-1.42 \pm 1.60) \times 10^{-8}$	$(-0.76 \pm 3.70) \times 10^{-9}$	-2.95 ± 0.90	-1.40 ± 0.18
	E_g	$(1.19 \pm 1.09) \times 10^{-5}$	$(0.45 \pm 2.21) \times 10^{-7}$	$(-1.65 \pm 0.78) \times 10^{-10}$	-0.06 ± 0.37	0.13 ± 0.14

FIG. 8. Modelling of frequency shift for A_{1g} mode of (a) pristine sample⁷ and sample irradiated with (b) 10^{11} ions/cm² (c) 5×10^{11} ions/cm² and (d) 10^{12} ions/cm².

From this study we deduced that the temperature dependent Raman shift for A_{1g} mode of pristine (Fig. 8(a)) as well as irradiated samples (Fig. 8(b-c)), induced mostly due to four phonon process with weak contribution from the three phonon process, thermal expansion effect and strain effect.

The SHI irradiation did not affect the dominant mechanism and our analysis suggests that the four phonon processes is the principal mechanism in all samples. However, the weightage of each contribution varies with the change in ion fluence. For all samples, the contribution of thermal expansion effect is very small and negligible throughout the whole temperature range. The contribution of four phonon process for pristine sample is largest which decrease for the irradiated samples. While, three phonon processes follows an opposite trend of four phonon processes, its contribution increases with increases in ion fluence. The contribution of strain effect is small for pristine sample which further decreases with increase in ion irradiation fluence and is minimum for sample irradiated with highest dose (10^{12} ions/cm²).

FIG. 9. Modelling of frequency shift for E_g mode of (a) pristine sample⁷ and sample irradiated with (b) 10¹¹ ions/cm² (c) 5 × 10¹¹ ions/cm² and (d) 10¹² ions/cm².

This decrease in strain component after ion irradiation is consistent with our HR-XRD results discussed earlier in this manuscript. According to which, strain is released after ion irradiation due to creation of oxygen vacancies.

For E_g mode of pristine as well as irradiated samples (Fig. 9 (a-d)), the observed temperature dependent shifts and non-linearities are originated mainly from thermal expansion with little contribution from the anharmonic processes and strain effect. With increase in ion dose, the contribution of thermal expansion increase while, the four phonon processes contribution follow an opposite trend and decrease with increase in ion dose. The contribution of strain effect and three phonon anharmonic processes are small as compared to thermal expansion effect and there is not any appreciable change in their contribution with variation in ion dose.

IV. CONCLUSIONS

We investigated the impact of 200 MeV Ag^{15+} SHI irradiations on phononic properties of epitaxial LNO and find that the A_{1g} and E_g modes broaden and soften with increase in temperature. The analysis of broadening in line-width with temperature and irradiation fluence is attributed the anharmonic interactions between phonons (three- and four-phonon scattering) leading to a decreased lifetime of optical phonons. The effect of irradiation fluence on temperature dependent Raman shift analyzed using an analytical model suggests that for pristine sample, the shift of A_{1g} mode generated mainly due to four- phonon processes, whose contribution decreased with an increase in ion fluence. Ion irradiation resulted in decrement of contribution from strain effect which is in line with our observation of relaxation of mismatch strain with irradiation from HR-XRD results. For E_g mode of the pristine sample, main contribution came from thermal expansion effect which increases with increases in ion fluence. For maximum ion fluence; Raman shift is entirely due to thermal expansion effect with negligible contribution from three phonon process while strain effect and four phonon process counteract the effect of each other.

SUPPLEMENTARY MATERIAL

Additional data including RSM and XPS measurements of pristine and irradiated films of LNO are presented in the Supplementary material.

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DATA AVAILABILITY

The data that supports the findings of this study are available with in the article.

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Supplementary Information

Influence of swift heavy ion irradiations on temperature dependent phononic behavior of epitaxial LaNiO_3 thin film

Sunidhi .¹, Vishal Sharma¹, Sunil K. Arora^{1}, Florencio Sánchez², Fouran Singh³ and Vasant Sathe⁴*

¹Centre for Nanoscience and Nanotechnology, Block-II, South Campus, Panjab University, Sector-25, Chandigarh-160014, India

²Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, Bellaterra 08193, Spain

³Materials Science Group, Inter-University Accelerator Centre, New Delhi 110067, India

⁴UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore-452001, India

*Corresponding author: aroras@pu.ac.in

Figure S1 (a-d) show the reciprocal space mapping (RSM) on pristine as well as irradiated samples of LNO.

Fig. S1. XRD Reciprocal space mapping around (103) reflection for (a) pristine LNO/LAO and irradiated with (b) 10¹¹ ions/cm², (c) 5*10¹¹ ions/cm² (d) 10¹² ions/cm².

Figure S2 (a-f) shows the XPS spectra of O 1s, La 3d and Ni 2p region for pristine as well as sample irradiated with 10¹² ions/cm². Here, the deconvolution of O 1s peaks presents three peaks O_I, O_{II} and O_{III} with the B.E. 528.39 eV, 529.94 eV and 531.77, respectively. Here, O_I is assigned to lattice oxygen, O_{II} is due to oxygen attached to hydroxyl groups while O_{III} represents the oxygen vacancies. The ratio of lattice oxygen to oxygen vacancies (O_I/ O_{III}) decreases with increase in ion irradiation from 0.349 for pristine to 0.113 for highest dose indicating the loss in lattice oxygen with ion irradiation. Spectra of La 3d with multiplet La 3d_{5/2} and La 3d_{3/2} as shown below, mainly centered around (835± 0.05) eV and (852± 0.05), eV respectively. The spectra

of Ni 2p for single layer structure mainly consists of two multiplets i.e. $2p_{3/2}$ and $2p_{1/2}$ around (850 ± 0.05) eV and (870 ± 0.05) eV, respectively. Each of these multiplet have doublets corresponding to Ni^{3+} and Ni^{2+} valence state and centered at (850.33 ± 0.05) eV and (854.28 ± 0.05) eV for Ni $2p_{3/2}$ and (871.61 ± 0.05) eV and (873.33 ± 0.05) eV for Ni $2p_{1/2}$, respectively. We calculated the stoichiometric ratio (La/Ni) for pristine as well as irradiated samples. The quantitative analysis of La3d-Ni2p spectra region before and after irradiation shows the significant decrease in La/Ni from 0.346 for pristine to 0.197 for highest dose. Even for pristine sample, the La/Ni ratio is less than value expected for stoichiometric perovskite (~ 1) which further decreases with increase in ion irradiation. This quantitative analysis of La3d-Ni2p as well O1s spectra show that oxygen vacancies exists in pristine samples also, their concentration increases further with increase in ion irradiation.

Fig. S2. XPS spectra of (a-b) O 1s, (c-d) La 3d and (e-f) Ni 2p for pristine and sample irradiated with highest dose 10^{12} ions/cm²

Moreover, when oxygen vacancies are produced in the lattice, the valence state of Ni atoms near the oxygen vacancies changes from +3 to +2 as a result of charge balance. The ratio of atomic concentration of Ni⁺² and Ni⁺³ as calculated from XPS peak fitting can be used to calculate the oxygen vacancies.¹⁰⁻¹² After irradiation, there is decrease in the ratio of Ni⁺³/Ni⁺² from 2.08 for pristine to 0.52 for highest dose 10^{12} ions/cm² (Fig. S3). This decrease indicates the formation of more oxygen vacancies after irradiation. This could be accounted due to the preferential removal of oxygen because of its lower binding energy. The irradiation experiment, the low oxygen partial pressure in the environment as well high energy Ag ion beam irradiation preferentially knocked the oxygen atoms off into interstitials and locally displaced oxygen atoms, providing a very reducing environment. This reducing environment leads to oxygen vacancies in the lattice.

Fig. S3 Variation of the ratio of atomic concentrations of Ni^{3+} and Ni^{2+} as a function of ion fluences.