Acoustic phonon anomalies in Ca doped $SrTiO_3$ quantum ferroelectrics as studied by Brillouin Scattering

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Temperature dependence of longitudinal acoustic (LA) and transverse acoustic (TA) phonon behavior in a 3% Ca doped $SrTiO_3$ crystal have been studied in the temperature range 500 – 90 K using Brillouin light scattering spectroscopy. The frequencies of both LA and TA phonons show a minimum and their widths shows a maximum at about 275 K. The observed anomalies in both phonon modes are associated with the structural phase transition from cubic to tetragonal phase. The observed acoustic anomalies are attributed to the bilinear coupling between strain and order parameter. The temperature dependence of the relaxation time of the order parameter calculated using the Landau-Khalatnikov relaxation mechanism exhibits a critical slowing down towards the transition temperature, T_{tr} = 275 K.

1. Introduction

$SrTiO_3$, (STO) is a prototype of the quantum paraelectric system, has been extensively studied by various experimental techniques.[1-3] STO undergoes an antiferrodistortive phase transition at 110 K and begin to exhibit quantum paraelectric behavior below 40 K. STO, when doped with Ca, shows a relaxor like dielectric response with the formation of so called polar nano regions(PNRs) whose size increases on cooling. Ca doped STO is called quantum ferroelectrics as the system exhibit ferroelectric behaviour.[4] The formation of these local polarization regions appears to be due to the off center of Ca ion. Extensive optical and dielectric studies in this system suggest an inhomogeneous low temperature polar phase with two different length scales.[2,3] Recent x-ray and neutron diffraction studies in pure STO indicate that the antiferrodistortive phase transition is associated with change in structure from cubic to tetragonal symmetry.[5] For pure STO the transition temperature is 100 K, while for 4% Ca doped STO, it is 200 K. For STO, the elastic anomaly was reported at 100 K.[6] The cubic – tetragonal phase transitions in this system have been studied by Raman spectroscopy. Raman scattering studies of phase transition in Ca doped STO reveal softening of the triply degenerate F_{1u} in the cubic phase.[5] The study of acoustic phonon anomaly across the phase transition reveals more details about the mechanism of the phase transition. Brillouin light scattering is a sensitive experimental technique that brings about more detailed features of the ferroelectric/ferroelastic phase transitions. In this work, we report anomalous behavior of LA phonons in the ferroelastic phase transition of a 3% Ca doped STO crystal.

2. Experimental

Single crystals of 3% Ca doped STO were grown by flame fusion technique. Micro-Brillouin light scattering measurements were performed on (100) surface of a 3% Ca doped STO (CST) crystal in back scattering geometry using the combination of an optical microscope and a high contrast 3+3 pass Sandercock tandem Fabry-Perot interferometer. Phonon modes were excited with a 532 nm single longitudinal mode diode pumped solid-state laser. The light was focused with a 20x microscope objective on to the sample. Measurements were carried out in the FSR of 100 GHz in the temperature range of 500 – 90 K using a Linkam (FTIR 600) heating/cooling stage.

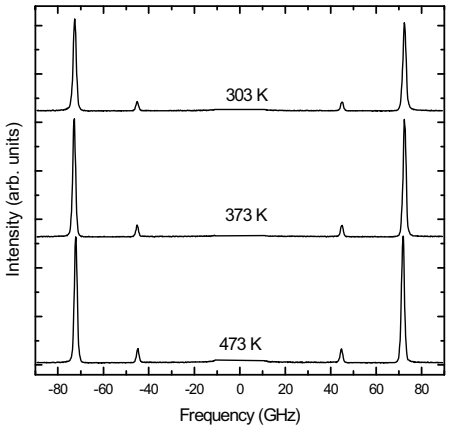

Fig. 1 Brillouin spectra at selected temperatures of a 3% Ca doped STO crystal.

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3. Results and discussion

The Brillouin spectra of CST at some selected temperatures are shown in **Fig. 1**. A LA phonon peak around 75 GHz and a TA mode at 45 GHz can be seen. **Figure 2** shows the temperature dependence of the frequency of LA phonon and its width. The frequency of the LA phonon exhibits a sharp minimum followed by a sharp maximum in width at T_{tr} = 275 K. The anomalous behavior of LA phonon is due the structural phase transition from cubic to tetragonal phase at 275 K.

In the present work, the width of the LA phonon shows a typical λ type behavior in the vicinity of T_{tr}. TA phonon mode also exhibits similar behavior. However, due to the large scattering of the data in the width of TA phonon mode, the temperature dependence of TA mode will not be discussed further.

It can be seen through Landau theory that the coupling between the strain and the order parameter leads to the softening of acoustic phonon. The predominant coupling mechanisms are (i). bilinear coupling between the strain and the order parameter and (ii). coupling linear in strain and quadratic in order parameter.[7] Both type of coupling produces a spontaneous deformation below the phase transition temperature.[7] In the present study, the softening behaviour of LA above and below T_{tr} suggests the bilinear coupling between the strain and order parameter. The λ type peak of the width maximum is reminiscent of Landau-Khalatnikov (LK) relaxation process of the order parameter. The phase transition is a ferroelastic type as there is no dielectric anomaly observed at T_{tr}.[6]

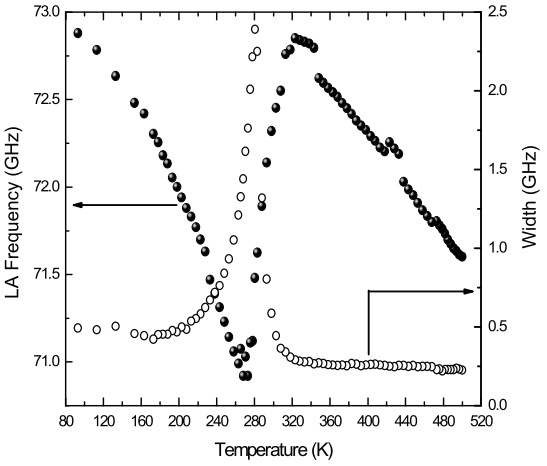

Fig. 2 Temperature dependence of LA phonon frequency and width of a 3% Ca doped STO crystal.

The relaxation rate of the order parameter was calculated on the basis LK formalism, and is displayed in **Fig. 3**. It can be seen clearly that the order parameter fluctuations exhibit a critical slowing down on approaching the transition temperature T_{tr}.

4. Conclusion

Brillouin light scattering studies in a 3% Ca doped STO crystal shows acoustic phonon anomalies across the cubic – tetragonal phase transition at T_{tr} = 275 K. The relaxation time of the order parameter exhibits critical slowing down towards the transition temperature.

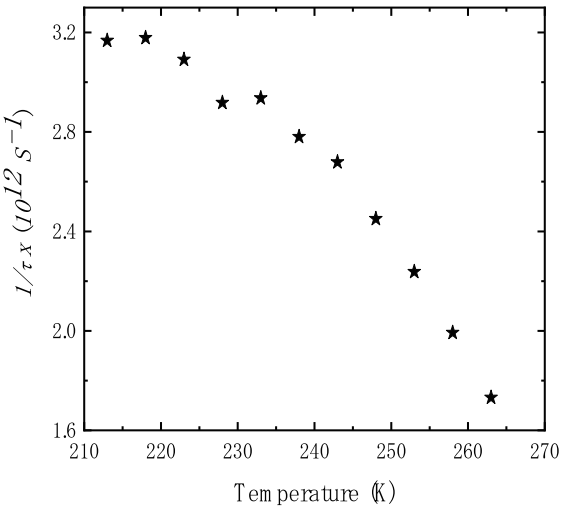

Fig. 3.Temperature dependence of the relaxation rate $1/\tau$ of a 3% Ca doped STO crystal.

Acknowledgement

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