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Dielectric and Raman spectroscopy measurements across structural phase transition in multiferroic $\text{HoFe}_3(\text{BO}_3)_4$ single crystal

A. Tripathy^{1, a)}, K. Gautam¹, K. Dey¹, A. Ahad², I. A. Gudim³, V. G. Sathe¹, D. K. Shukla¹

1UGC-DAE Consortium for Scientific Research, Indore (452001), India

2Department of physics, Aligarh Muslim University, Aligarh (202002), India

3L. V. Kirensky Institute of Physics, Siberian Branch of Russian Academy of Sciences, Krasnoyarsk 660036, Russia

a)Corresponding author: atripathy30692@gmail.com

Abstract. We report on findings in the $\text{HoFe}_3(\text{BO}_3)_4$ single crystal across structural phase transition by the dielectric and Raman spectroscopic measurements. In most of the compounds of $\text{RFe}_3(\text{BO}_3)_4$ (R=La-Lu) family low temperature P3121 structure is introduced through structural phase transition (from space group R32). Temperature dependent dielectric measurements on the $\text{HoFe}_3(\text{BO}_3)_4$ crystal depicts a step like feature at the structural phase transition at ~ 366 K. The Raman spectroscopy study also confirms the structural transition around this temperature. A clear signature of structural transition is reflected in the Raman spectra, mainly in the frequency range (200- 400 cm^{-1}). Appearance of new Raman modes below the transition temperature also indicates that the transition is from a high symmetry phase to a low symmetry phase.

INTRODUCTION

In last decade there has been a large interest in multiferroic materials having both magnetic and electric order parameters [1-3]. Considerable attention is given to $\text{RFe}_3(\text{BO}_3)_4$ (R=La-Lu) family because of significant spontaneous polarization, and it also shows large magnetoelectric effect [4,5]. The $\text{RFe}_3(\text{BO}_3)_4$ belongs to mineral compound $\text{CaMg}_3(\text{CO}_3)_4$ (huntite) and the crystal structure in high symmetry phase is having RO_6 triangular prism, FeO_6 octahedra connected by two types of BO_3 (B1O_3 and B2O_3) triangular planes. FeO_6 octahedra share the edges forming helicoidal chains parallel to the c-axis. The rare earth iron borates crystallizes in the space group R32 (space group no-155) of trigonal system [4]. Major of them exhibit a structural phase transition from high symmetry space group R32 to low symmetry space group P3121 and transition temperature scales with the ionic radii of rare earth elements, where as some of them preserve the high symmetry phase upto lowest temperature. These also show some intriguing magnetic properties due to presence of the magnetic ions (3d and 4f ions) and exhibit cascade of magnetic transitions at low temperature [5,6]. Due to the non-centrosymmetric crystal structure (P3121) these are also having wide applications in optics and optoelectronic devices.

Our present work focuses on studies of the change in the dielectric constant across the structural phase transition temperature and also on the vibrational behavior of the $\text{HoFe}_3(\text{BO}_3)_4$ crystal by Raman spectroscopy.

EXPERIMENTAL DETAILS

Single crystal of the $\text{HoFe}_3(\text{BO}_3)_4$ was grown by flux method using $\text{Bi}_2\text{MO}_3\text{O}_{12}$ based flux [7]. Orientation of the crystal was determined by the Laue x-ray diffraction. Temperature dependent dielectric measurement was performed on a c-axis oriented crystal using HIOKI LCR meter (IM 3536) and a CRYOCON temperature controller.

Raman studies were carried out in a back scattering configuration where incident light is along the c-axis of the sample, using LabRam HR800 system with excitation source of Ar+ laser of 473nm, 1800g/mm grating and CCD detector. The frequency resolution is better than 1cm⁻¹ for the measured frequency region of our experiment.

RESULTS AND DISCUSSIONS

In the present work we performed the temperature dependent dielectric study in the frequency range 100Hz-1MHz. Figure 1 is showing a step like feature at ~366 K in both cooling and heating cycles. This feature has been found to almost frequency independent. Previously also structural phase transition in the GdFe₃(BO₃)₄ was shown by step in the capacitance verses temperature data [7]. Overlap of the dielectric constant in heating and cooling cycles exhibit a negligible hysteresis which together with sharpness of transition hints to the good quality of the crystal.

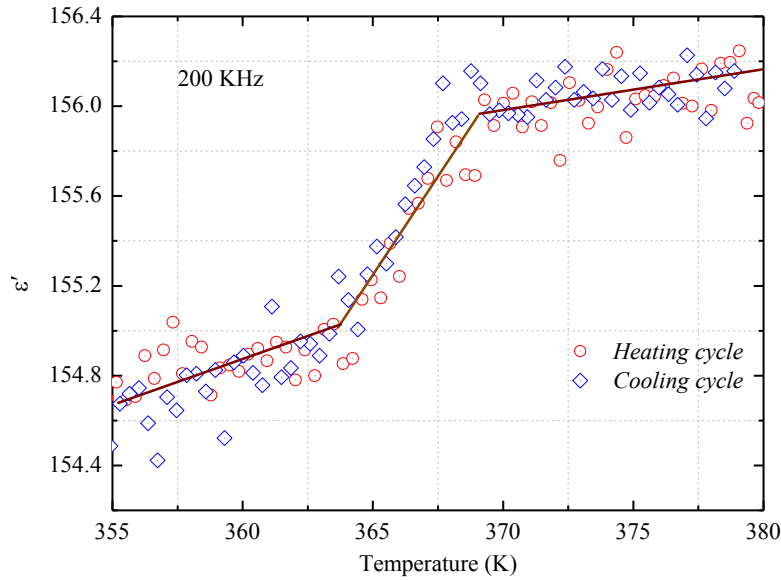


FIGURE 1. Temperature dependent dielectric permittivity at 200 KHz in both heating and cooling cycles & Solid straight lines are guide to the eye.

To investigate more on the vibrational behaviour across the structural transition we have also performed temperature dependent Raman study on HoFe₃(BO₃)₄ single crystal across 354 K to 390 K. Noticeable changes in the Raman modes across the structural transition temperature is observed mainly in the frequency range between 200 cm⁻¹ to 400 cm⁻¹. Earlier investigations through group theory analysis on RFe₃(BO₃)₄, (R=Nd,Gd,Tb,Er) have determined the external and internal modes, for both, the high temperature phase R32 (D37), and low temperature phase P3121 (D34) using all the local symmetry of atomic positions [8]. The external modes include both the translational motions of R and Fe atoms as well as the librational motions of BO₃ groups, where as internal modes are dominated by the BO₃ groups in higher frequency range.

RFe₃(BO₃)₄ compound in the P3121 phase (three formula units) is having 86 Raman active modes out of total 118 vibrational modes which are classified as $\Gamma_{\text{vib}} = 27A_1 + 32A_2 + 59E$, while in the R32 phase (one formula unit) is having 26 Raman active modes out of total 38 vibrational modes which are characterised as $\Gamma_{\text{vib}} = 7A_1 + 12A_2 + 19E$, where A₁ and E modes are Raman active [9]. Figure 2 shows the room temperature unpolarized Raman spectroscopy of the HoFe₃(BO₃)₄ single crystal. In our experimental spectra in the spectral range of 50 to 700 cm⁻¹, we have observed lesser no of Raman modes compared to calculations reported previously at room temperature [9]. This may be due to the resolution limit of the instrument or low intensity of the modes.

The Raman spectra taken in the temperature range from 354 K to 390 K show visible changes of the modes observed at ~276 cm⁻¹, ~319 cm⁻¹, ~285 cm⁻¹, ~334 cm⁻¹, and ~371 cm⁻¹ frequencies. These modes mostly possess E character. With the raising of temperature above 354 K, the intensity of ~285 cm⁻¹ and ~371 cm⁻¹ modes

start reducing (see figure 3) which finally vanished at 370 K, which indicates transformation from the lower symmetry phase (P3121) to the higher symmetry phase (R32). The extra modes present in the P3121 phase arises mainly due to the reduction in the symmetry. D. fausti et al., [8] showed the first order phase transition in $RFe_3(BO_3)_4$ for ($R=Nd,Gd,Tb,Er$) is mainly due to the active participation of the BO_3 librational vibrations. Hence the new modes ($\sim 285\text{ cm}^{-1}$ and $\sim 371\text{ cm}^{-1}$) arising in the P3121 phase are due to the displacements associated with tilting of the BO_3 triangular planes from the actual position in R32 phase [10]. With the help of theoretical calculations on $HoFe_3(BO_3)_4$ [9], we interpret that the Raman modes at the lower frequency region are mainly due to translational motions of the Ho and the Fe atom (heavier atoms) and the librational nature of BO_3 groups.

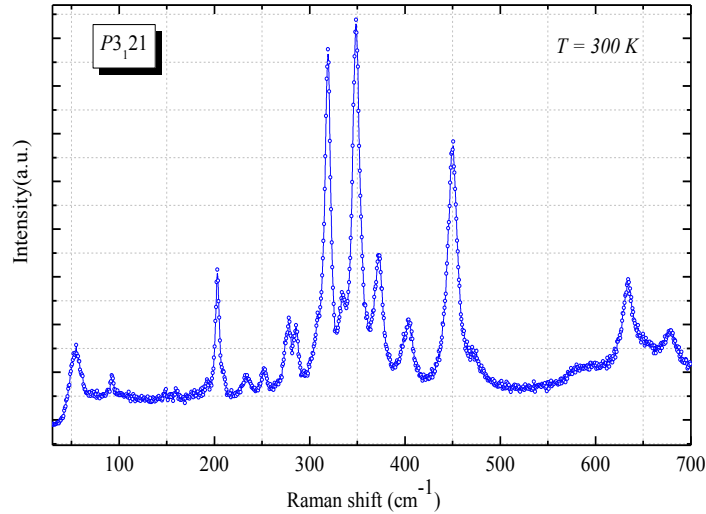


FIGURE 2. Room temperature Raman spectrum of the $HoFe_3(BO_3)_4$.

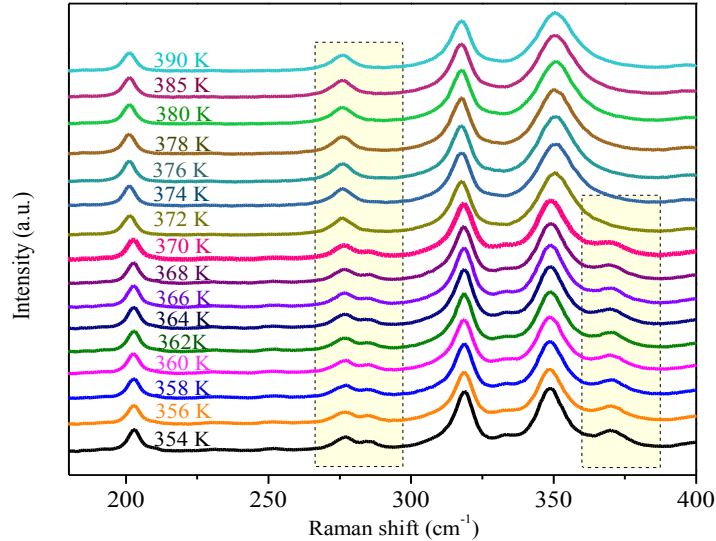


FIGURE 3. Temperature dependent Raman spectra of the $HoFe_3(BO_3)_4$ showing transition at $\sim 370\text{ K}$.

Temperature effects on a well defined $\sim 319\text{ cm}^{-1}$ mode's frequency position and corresponding line widths are plotted in figure 4 (a&b) in the temperature range of 350 K to 400 K . This mode showed a sharp step like variation (figure 4 (a)) in the Raman shift at $\sim 370\text{ K}$, though it shows a usual softening of the phonon mode with increasing temperature. In addition at the phase transition a sharp anomaly in the phonon life time of this mode indicates strong spin phonon and spin lattice coupling involved in this system near this transition temperature.

Figure 4 (c) and (d) represent the temperature dependence of the Raman shift variation of the phonon modes present at ~ 285 cm^{-1} and ~ 371 cm^{-1} , which vanish on heating at the transition temperature.

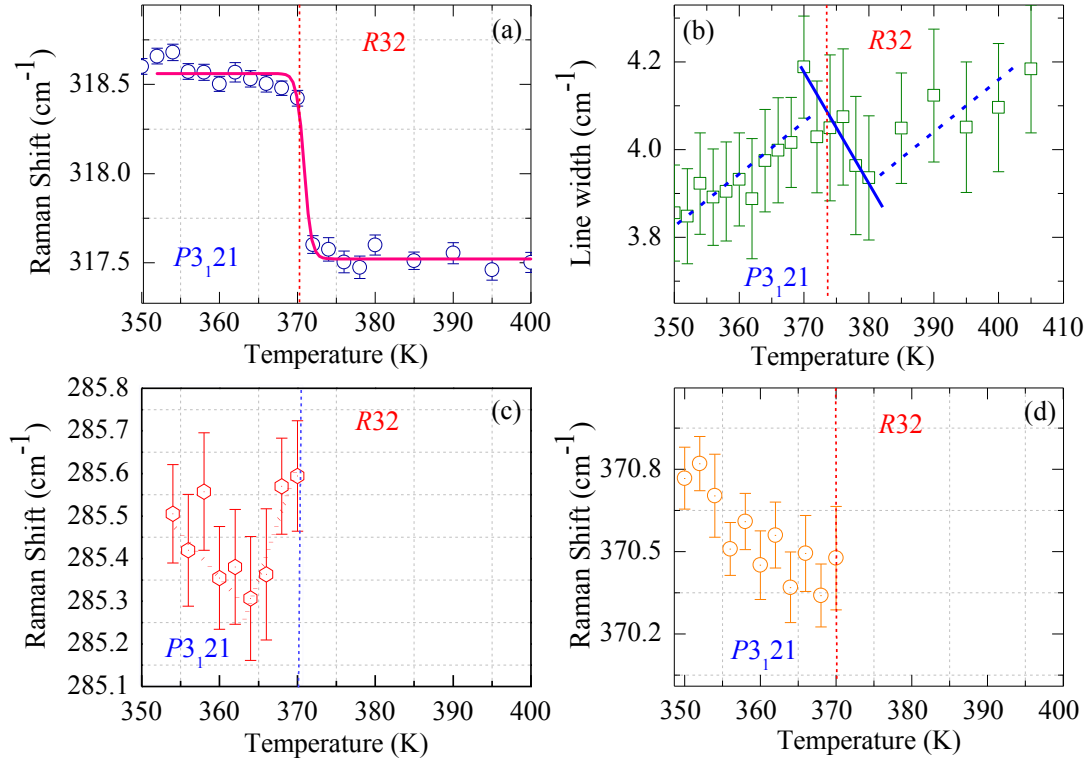


FIGURE 4. Temperature dependence of (a) the Raman shift position and (b) the line width of ~ 319 cm^{-1} mode involving Ho and Fe atom vibrations in $\text{HoFe}_3(\text{BO}_3)_4$. Temperature dependent (c) Raman shift of ~ 285 cm^{-1} mode, and (d) Raman shift of ~ 371 cm^{-1} mode across the structural phase transition.

Interestingly, an opposite behavior of the modes ~ 285 cm^{-1} and ~ 371 cm^{-1} is observed. The ~ 285 cm^{-1} mode shows an anomaly ~ 363 K (softening to hardening) while the mode at 371 cm^{-1} , show a normal behavior (softening of mode) with increase in temperature before disappearance. Though the 285 cm^{-1} mode (BO_3 group) displaces from its position in low temperature phase but the hardening may be due to the stronger bond in between B-O which resists the expansion of bond length and found deviating from the usual temperature behavior.

CONCLUSION

We have investigated the structural phase transition in the $\text{HoFe}_3(\text{BO}_3)_4$ using the temperature dependent dielectric measurement and Raman spectroscopy. With the ensembles of these observations a step like frequency independent feature in dielectric constant and sudden disappearance of the phonon modes in Raman spectra in the high temperature phase while approaching T_s , it is worth mentioning that there is a sharp first order phase transition.

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