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Citation: *Appl. Phys. Lett.* **103**, 152906 (2013); doi: 10.1063/1.4824919

View online: <http://dx.doi.org/10.1063/1.4824919>

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# Dielectric and optical phonon anomalies near antiferromagnetic ordering in LaCrO<sub>3</sub>: A possible near room temperature magnetodielectric system

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(Received 27 July 2013; accepted 28 September 2013; published online 10 October 2013)

We report on anomalies in the dielectric and optical phonon spectra in bulk orthorhombic distorted perovskite LaCrO<sub>3</sub> near an antiferromagnetic transition at 290 K. These anomalies were tracked using temperature dependent (200 K–320 K) dielectric and Raman spectroscopy. We observed a blue-shift for the B<sub>3g</sub>(3) optical phonon mode coincident with the onset of antiferromagnetic ordering of LaCrO<sub>3</sub> in conjunction with a broad dielectric anomaly near the Néel temperature. The dielectric and optical phonon anomalies are discussed in the context of the observed antiferromagnetic transition in temperature dependent magnetic studies. © 2013 AIP Publishing LLC.

[<http://dx.doi.org/10.1063/1.4824919>]

The coupling among charge, lattice, and magnetic (spin and orbital) degrees of freedom in transition metal oxides is a widely investigated phenomenon and has been studied theoretically and experimentally in materials exhibiting colossal magnetoresistance, high temperature superconductivity, half-metallicity, and recently multiferroicity.<sup>1–4</sup> It is therefore essential to understand the coupling between magnetic and dielectric properties and how these relate with the underlying physical phenomenon. Furthermore, spin degrees of freedom in conjunction with lattice ordering may provide new class of multifunctional materials. Coupled magnetic and dielectric properties of materials may be utilized for devices such as magnetic sensors, tunable filters, and spin-charge transducers. LaCrO<sub>3</sub> is a GdFeO<sub>3</sub>-type distorted perovskite system that crystallizes in an orthorhombic structure with space group Pnma ( $D_{2h}^{16}$ ),  $Z = 4$ .<sup>5,6</sup> This material exhibits a phase transition from the high temperature paramagnetic to the low temperature antiferromagnetic phase with a Néel temperature  $T_N \sim 290$  K.<sup>6</sup> This magnetic transition particularly at room temperature makes LaCrO<sub>3</sub> interesting material system to study magnetodielectric properties as it may find several device applications. The orthorhombic Pnma LaCrO<sub>3</sub> system, with 4 formula units per unit cell ( $4 \times \text{LaCrO}_3$ ) exhibits 24 Raman active phonon modes. Factor group analysis at the  $\Gamma$  point suggests  $\Gamma_{\text{Raman}} = 7 A_g + 5 B_{1g} + 7 B_{2g} + 5 B_{3g}$ , enumerating the 24 Raman active modes for LaCrO<sub>3</sub>. The first-order Raman-active phonons modes (at the  $\Gamma$  point) below  $600 \text{ cm}^{-1}$  have been studied in detail by Iliev *et al.*<sup>7</sup> in the low-temperature orthorhombic phase Pnma (<528 K) and high-temperature rhombohedral phase  $R\bar{3}c$  (>528 K). The specific vibrational modes are assigned according to their symmetry properties by Iliev *et al.*<sup>7</sup> However, the cross correlations among different properties such as phonon, spin, and dielectric response in this material remain unclear. In this report, we will discuss the effects of the magnetic transition on the phonon spectra and dielectric

response and determine the phonon modes most strongly coupled to the antiferromagnetic phase transition based on temperature dependent Raman spectroscopic studies.

LaCrO<sub>3</sub> ceramic samples were prepared by conventional solid state reactions. The stoichiometric ratio of high purity of binary oxides La<sub>2</sub>O<sub>3</sub> (99.99% Alfa Aesar) and Cr<sub>2</sub>O<sub>3</sub> (99.997% Alfa Aesar) powders were mixed and ground, followed by two thermal treatments at 850 °C for 48 h in conjunction with intermediate grindings. A light green colour for the LaCrO<sub>3</sub> powder was observed after the final heat treatment.<sup>8</sup> The phase purity of this material was confirmed using room temperature powder X-ray diffraction (PXRD) experiments with Cu K <sub>$\alpha$</sub>  (1.5406 Å) radiation, and the measured PXRD pattern confirms the orthorhombic Pnma structure of LaCrO<sub>3</sub>. Temperature and field dependent magnetic measurements were carried out using the standard options available in Quantum Design Physical Property Measurement System (PPMS). We carried out temperature dependent Raman spectroscopic measurement using a Jobin-Yvon Horiba Triax 550 spectrometer, assisted with a liquid-nitrogen cooled CCD detector, an Olympus model BX42 microscope, and 514.5 nm argon ion laser. The scattered light was collected with the same microscope objective and focused on the entrance slit of the spectrometer with a 1200 line/mm diffraction grating. Dielectric measurements were carried out on cold pressed pellets in parallel plate geometry, with top and bottom electrodes fashioned from silver epoxy using an Agilent LCR meter.

The PXRD data for LaCrO<sub>3</sub> are shown in Fig. 1 and are consistent with the expected orthorhombic Pnma structure.<sup>6,7</sup> These XRD data were refined to Pnma space group using GSAS software,<sup>9</sup> and a good fit was observed with  $R$  factors,  $wRp = 8.9\%$ ,  $Rp = 4.3\%$ , and  $\chi^2 = 1.27$ . The refined lattice constants and volume of the unit cell are  $a = 5.479(1) \text{ \AA}$ ,  $b = 7.759(2) \text{ \AA}$ , and  $c = 5.516(1) \text{ \AA}$  and  $V = 234.9 \text{ \AA}^3$ , respectively, which are consistent with previous reports.<sup>6,7</sup> The observed bond angle Cr-O1-Cr ( $\sim 160^\circ$ ) has a crucial role in dielectric and magnetic behavior of orthorhombically distorted perovskite LaCrO<sub>3</sub>. We carried out temperature and frequency dependent ac magnetic measurements, which are

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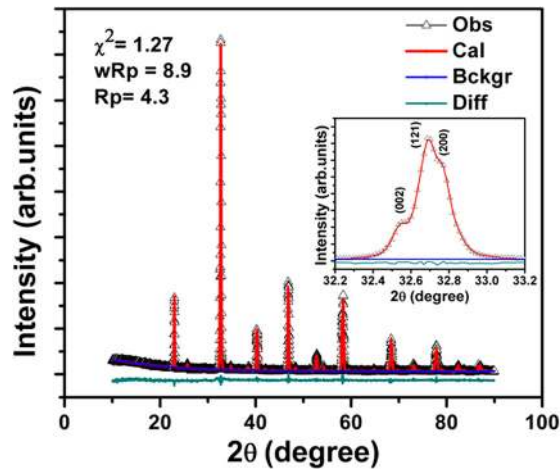


FIG. 1. Rietveld refined powder XRD pattern of  $\text{LaCrO}_3$  sample using GSAS. Difference (Diff) between observed (Obs) and calculated (Calc) pattern is shown. Inset: the magnified view of peaks around  $32.59^\circ$  which clearly orthorhombic splitting of peaks.

plotted in Fig. 2. The plots show the magnetic susceptibility ( $\chi'$ ) versus temperature at frequencies of 0.1, 0.3, 1.0, 3.0, and 10.0 kHz. Bulk  $\text{LaCrO}_3$  shows an antiferromagnetic phase transition near  $T_N = 290$  K from high temperature paramagnetic phase. The imaginary part of magnetic susceptibility ( $\chi''$ ) has no anomaly in the observed temperature range (not shown here). The frequency independent antiferromagnetic transition in  $\text{LaCrO}_3$  confirms a long range magnetic ordering and eliminates the possibility of magnetic clusters or impurities, which typically show a frequency dependent response.<sup>10</sup> Additionally, the sharp increase in magnetization near the Néel temperature is characteristic of weak ferromagnetism,<sup>11</sup> which may exist in a canted antiferromagnetic material as is also the case for  $\text{LaCrO}_3$ . The weak ferromagnetism observed in  $\text{LaCrO}_3$  is consistent with our *ab initio* studies, where non-collinear spin arrangements in conjunction with spin-orbit coupling have been observed, leading to non-zero total magnetization ( $0.34 \mu_B$  per  $\text{Cr}^{3+}$ ), substantiating the experimental studies.<sup>12</sup>

In an ideal cubic perovskite structure, with  $\text{Pm}\bar{3}\text{m}$  space group and multiplicity  $Z = 1$ , all atoms are at centrosymmetric sites, so there are no Raman active modes for this structure. However, as for  $\text{GdFeO}_3$ -type distorted perovskite

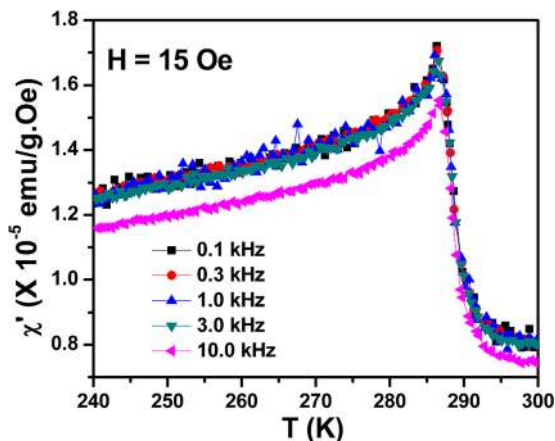


FIG. 2. Temperature dependence of ac magnetic susceptibility  $\chi'$ , at different listed frequencies recorded using applied magnetic field of 15 Oe.

structures,  $\text{LaCrO}_3$  with  $\text{Pnma}$  space group and multiplicity  $Z = 4$  shows four nonequivalent atomic positions: La ( $x, 0.25, z$ ), Cr ( $0.5, 0, 0$ ), O1 ( $x, 0.25, z$ ), O2( $x, y, z$ ). Among these only Cr is at a centrosymmetric site. The Raman spectra recorded at different temperatures between 200 K and 320 K are shown in Fig. 3(a). The Raman active phonons are identified and are in agreement with the reported values.<sup>7</sup> The Raman spectra at different temperatures have been shifted vertically for clarity. We observed 11 Raman active modes for bulk  $\text{LaCrO}_3$  powder samples; these are almost temperature independent except the  $B_{3g}(3)$  mode. For clarity, the Raman spectra for  $B_{3g}(3)$  optical mode is plotted in Fig. 3(b). This optical phonon mode exhibits a clear blue shift of approximately  $4 \text{ cm}^{-1}$  near the antiferromagnetic ordering temperature.

Superexchange through the Cr-O1-Cr chains is responsible for the magnetic ordering in  $\text{LaCrO}_3$  system. Therefore, the vibrational motions of Cr and O and more specifically the Cr-O1-Cr groups may be affected upon the onset of magnetic ordering in this system.<sup>13</sup> Cr-O1-Cr undergoes out of phase scissoring, associated with the  $B_{3g}(3)$  optical phonon mode.<sup>7</sup> This observed anomaly in  $B_{3g}(3)$  phonon mode near magnetic ordering may be associated with spin-phonon coupling mediated by spin-orbit coupling in  $\text{LaCrO}_3$  system. We propose that the increased energy of the  $B_{3g}(3)$  optical phonon mode is mainly associated with changes in the dynamical response of Cr-O1-Cr atomic arrangements in the antiferromagnetic phase. The changes in the optical phonons are most directly

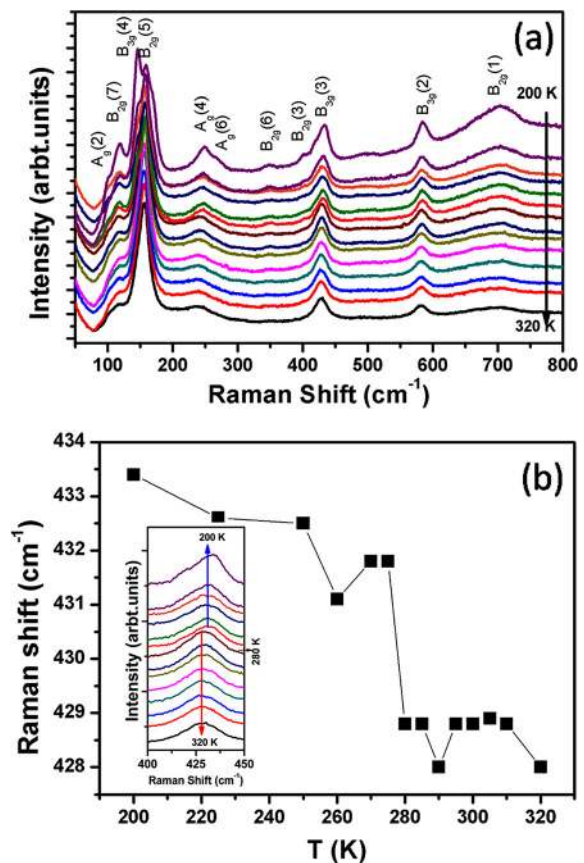


FIG. 3. (a) Raman spectra for  $\text{LaCrO}_3$  ceramic sample recorded at different temperatures in the range 200 K–320 K and (b) the temperature dependent Raman shift variation of  $B_{3g}(3)$  optical phonon mode while inset shows the magnified view this peak.

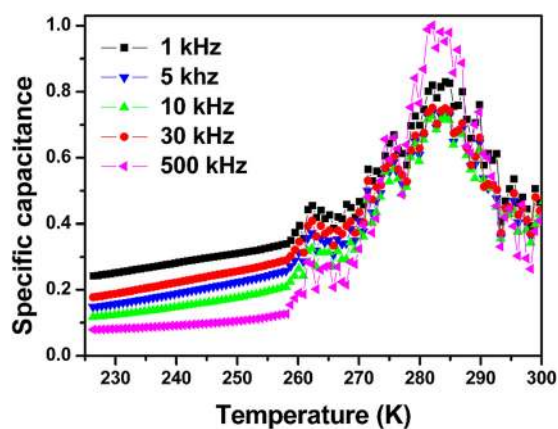


FIG. 4. Specific capacitance  $(= (C - C_{\max}(500 \text{ kHz})) / C_{\max}(500 \text{ kHz}))$  as a function of temperature close to magnetic phase transition ( $T_N \sim 290 \text{ K}$ ) for different frequencies.

associated with changes in the polarizability, which can come from a change in the effective spring constant on magnetic ordering as discussed earlier.<sup>13</sup> Coupling between the lattice and magnetic degrees of freedom can also produce changes in the dielectric constant associated with long range magnetic ordering. Such magnetodielectric coupling has been observed in a wide range of insulating magnetic materials including  $\text{EuTiO}_3$  (Ref. 14) and  $\text{SeCuO}_3$  (Refs. 13 and 15) as well as multiferroic systems such as the orthorhombic manganites  $\text{RMnO}_3$  (Ref. 16) and  $\text{Ni}_3\text{V}_2\text{O}_8$  (Ref. 17) at the onset of ferroelectric order.

To investigate possible magnetodielectric coupling in  $\text{LaCrO}_3$ , we carried out temperature dependent dielectric constant measurements in the temperature range from 225 K to 300 K at different frequencies. Plots of the specific capacitance  $(= (C - C_{\max}(500 \text{ kHz})) / C_{\max}(500 \text{ kHz}))$  or relative dielectric constant as a function of temperature are shown in Fig. 4. We observed a clear dielectric anomaly near the antiferromagnetic transition temperature  $\sim 290 \text{ K}$ . However, it is important to note that we are using the term “magnetodielectric” to refer instead to the intrinsic coupling between the dielectric response and magnetic structure, which does not depend on any external field. There are particular advantages identifying magnetodielectric coupling by looking at changes in the dielectric response at a magnetic transition in zero magnetic field. One of the most significant is that potential Maxwell-Wagner effects that can plague conventional magnetodielectric measurements are absent in these studies. Additionally, these measurements do not require only temperature control, but not an external field, which may be beneficial for certain studies that can be difficult to integrate with a magnetic field (e.g., certain optical studies). More interestingly, we do not observe any significant dielectric relaxation. This confirms the presence of long range ordering in bulk  $\text{LaCrO}_3$ , consistent with our magnetic measurements. The shift in the dielectric constant on magnetic ordering can be attributed to variations in the optical phonon frequencies arising from changes in the mean spin interaction energy on magnetic ordering, which affects the

dielectric response through the Lyddane-Sachs-Teller relation.<sup>15,18</sup> In this context, the observation of a dielectric anomaly in  $\text{LaCrO}_3$  is completely consistent with the observed shift in the  $B_{3g}(3)$  optical phonon. We observed a broad dielectric anomaly at  $T_N \sim 290 \text{ K}$  which is frequency independent (up to 500 kHz). Thus, the observed long range magnetic ordering coupled with the onset of dielectric anomaly near antiferromagnetic ordering temperature suggests the possibilities of near room temperature magnetodielectric coupling in this system. It is worth noting that the shape of dielectric anomaly upon antiferromagnetic ordering suggests possibility of ferroelectricity in  $\text{LaCrO}_3$  which is permissible as an antiferromagnetic transition which doubles the unit cell leading to noncentrosymmetric point group.<sup>19</sup>

In summary, we have synthesized phase pure ceramic  $\text{LaCrO}_3$  samples and investigated the coupling among the structural, magnetic, and dielectric properties in this system. These studies indicate the onset of long-range antiferromagnetic order below 290 K. The observed blue shift in  $B_{3g}(3)$  optical phonon mode suggests strong phonon-spin coupling in  $\text{LaCrO}_3$ . The associated dielectric anomaly at the magnetic transition in  $\text{LaCrO}_3$  confirms the spin-lattice coupling in this system and provides a possibility for exploiting  $\text{LaCrO}_3$  as a novel near room temperature magnetodielectric material. Magnetodielectric coupling in  $\text{LaCrO}_3$  at room temperature may find several device applications.

This work was supported by the DST, India through grant SR/NM/NAT-02/2005 and NSF, USA through grant DMR-0644823 and also support by the Jane and Frank Warchol Foundation as travel grant.

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