Anomalous magnetic behavior and complex magnetic structure of proximate LaCrO$_3$–LaFeO$_3$ system

Brajesh Tiwari 1 , Ambesh Dixit 2 and M S Ramachandra Rao 3

1 Department of Physics, Institute of Infrastructure Technology Research and Management, Ahmedabad 380026, India
2 Department of Physics & Center for Solar Energy, Indian Institute of Technology Jodhpur, Karwad 342037, India
3 Department of Physics, Indian Institute of Technology Madras, Chennai 600036, India

E-mail: brajeshtiwari@iitram.ac.in

Keywords: magnetism, proximity effect, ternary magnetic oxides, Raman Spectra, transition temperature, ferrimagnetism, antiferromagnetism

Abstract
We investigated complex magnetic properties of multifunctional LaCrO$_3$–LaFeO$_3$ system. The magnetic measurements substantiate the presence of competing complex magnetic ordering against temperature, showing paramagnetic to ferrimagnetic transition at $\sim 300$ K, followed by antiferromagnetic (AFM) transition near $\sim 250$ K superimposed on ferrimagnetic phase. The onset of weak ferrimagnetic ordering is attributed to the competing complex interaction between two AFM LaCrO$_3$–LaFeO$_3$ sublattices. The low-temperature AFM ordering is also substantiated by temperature-dependent Raman measurements, where the intensity ratio of 700 cm$^{-1}$ Raman active mode showed a clear enhancement with lowering the temperature. The non-saturating nature of magnetic moments in LaCrO$_3$–LaFeO$_3$ suggests the predominating AFM ordering in conjunction with ferrimagnetic ordering between 250 K–300 K up to 5 T magnetic field. A complex magnetic structure of LaCrO$_3$–LaFeO$_3$ is constructed, emphasizing the metastable magnetic phase near room temperature and low-temperature antiferromagnetic state.

Introduction
The multifunctional materials, especially complex oxide materials, are not only attracting attention due to their potential but also providing a rich understanding of the fundamentals, which allows designing novel materials with desired functional properties. LaTMO$_3$ (TM = Transition Metal) is one such family of complex oxide materials, having a perovskite structure with TM magnetic ions. Direct or indirect cross-coupling among spin, orbital, lattice and charge degrees of freedom provide an avenue for potential application and fundamental study in these materials. The canted spin structure of TM ions also exhibits competing magnetic interaction and thus, giving rise to the intricate magnetic structures. LaCrO$_3$ and LaFeO$_3$ oxide systems exhibit antiferromagnetic transitions at $\sim 290$ K and 740 K respectively [1–5] and more interestingly, also exhibit weak ferromagnetisms near room temperature [6–9]. The search of more than one ferroic ordering in oxide systems is always attracting attention for their potential in a new class of electronic devices such as four state memories, voltage-controlled magnetic switches and sensors, electric field controlled spintronic devices. The recent studies provide evidences about the room temperature magnetoelastic coupling in LaCrO$_3$ [6] and probably the ferroelectric ordering in LaFeO$_3$ perovskite systems [5]. In spite of magnetic and magnetodielectric properties, these oxide systems exhibit enhanced oxygen ionic conductivity and their electronic conductivity can be tailored by manipulating the suitable dopant at different cation sites. For example, the calcium doping at La site in LaCrO$_3$ makes it highly conducting and is a potential candidate for high-temperature solid oxide fuel cell electrode material. The distorted TMO$_6$ octahedra in LaTMO$_3$ systems is the driving cause for the complex physical properties such as variation of transition temperature, strong electron–phonon coupling, weak ferromagnetism, electrical conductivity by manipulating the exchange and hopping strengths [10–12]. The order and amplitude of such changes in physical properties are associated with the degree of distortion. The divalent doped lanthanum
manganite system shows charge–ordering, which is closely related to antiferromagnetic phase, while charge delocalization, i.e. metallic state, coincides with ferromagnetism. The screened potential energy becomes large in certain TM oxide materials, due to the various external factors (doping, temperature, pressure, etc.), causing electron localization and thus, inhibiting the electrical conduction. This is known as Mott—transition in such transition metal-based perovskite systems [13, 14]. In addition, the hole-doped La$_2$CuO$_4$ antiferromagnetic becomes a high-temperature superconductor because of the strong electron–electron correlation. These systems provide a wide avenue to understand the underlying physics and related mechanism governing such functional properties and their possible tunability. The double perovskite materials with and without transition metals are gaining attention for designing multifunctional material systems [15–18]. Way back in the 1960’s, Goodenough-Kanamuri predicted that double perovskite La$_2$CrFeO$_6$ should have a ferromagnetic ground state with Tc close to room temperature [19–21]. Since then a lot more efforts are made experimentally and theoretically with varying conclusions. Some concluded ferromagnetic ground state [20] while others ferromagnetic [21]. This prompted us to explore La$_2$CrFeO$_6$ double perovskite while synthesizing LaCrO$_3$-LaFeO$_3$ system. This system is usually showing intermediate properties of both perovskites, however, some unique magnetic and optical phonon properties are also noticed due to close proximity of these two predominantly antiferromagnetic compounds. It is a fundamental challenge in materials’ design to control and understand the change in materials behavior in close proximity to other materials under varying external conditions. In the present work, we investigated the effect of spin ordering on the magnetic and electronic properties of closely proximated LaCrO$_3$-LaFeO$_3$ system.

## Experimental details

Samples were synthesized by solid state reaction route from oxide precursors, La$_2$O$_3$, Cr$_2$O$_3$ and Fe$_2$O$_3$ (from Alpha Aesar with 99.9% purity). To remove moister La$_2$O$_3$ was pre-heated at 800 °C and ground thoroughly in a stoichiometric ratio; 2:1:1: La$_2$O$_3$:Cr$_2$O$_3$:Fe$_2$O$_3$ to homogenize the pre-synthesized materials. This homogeneous material was heated at 950 °C for 48 h with intermediate grinding to ensure the homogeneity of a solid solution. For structural and phase identification, powder x-ray diffraction (XRD) data of the samples were recorded using a PANalytical X’Pert Pro x-ray diffractometer with Cu Kα (1.5406 Å) radiation in the range of 20°–90° in steps of 0.017°. DC magnetic measurements were performed using a vibrating sample magnetometer (Model 6 000, Quantum Design, USA) in the temperature range of 100–350 K. Magnetization measurements were performed as a function of temperature in zero-field cooled (ZFC) and field cooled (FC) modes. Various magnetization isotherms were recorded at different temperatures up to an applied magnetic field of 50 kOe in the vicinity of magnetic transitions. Raman spectra were recorded for LaCrO$_3$, LaFeO$_3$ and proximate LaCrO$_3$-LaFeO$_3$ at room temperature with the help of 532 nm green laser source (Nd:YAG) using confocal Raman microscope (WITec Alpha300 R) in backscattering geometry. However temperature-dependent Raman spectra were also recorded for LaCrO$_3$-LaFeO$_3$ system down to 100 K in order to understand the spin-phonon coupling if any, following the magnetic behavior. For this a Jobin-Yvon Horiba Triax 550 spectrometer with a liquid-nitrogen cooled CCD detector while 514.5 nm argon ion laser source is used for excitation. The scattered light collected with a microscope objective that focused on the entrance slit of the spectrometer with a 1200 line/mm diffraction grating.

## Results and discussion

The phase identification of synthesized materials was confirmed using x-ray diffraction and the respective diffractograms are shown in figure 1 in conjunction with LaCrO$_3$ and LaFeO$_3$ perovskite structure to understand the phase evolution of LaCrO$_3$-LaFeO$_3$ system. The XRD patterns, figure 1 (lower and middle panel), confirm the phase purity of pristine LaCrO$_3$ and LaFeO$_3$ bulk materials and results are consistent with the reported literature [6, 7, 22]. Observed peak positions are in agreement ICDD card No 330701 and representative (h k l) planes are marked for LaCrO$_3$ system. LaCrO$_3$ and LaFeO$_3$ both systems crystallize in a distorted orthorhombic perovskite system with almost similar lattice parameters [2, 22]. It is important to note that for LaCrO$_3$, the highest intensity peak (121) is observed at 32.686° and for LaFeO$_3$ at 32.299° whereas for LaCrO$_3$-LaFeO$_3$ composite the observed peaks at 32.329° and 32.686°, correspond to LaFeO$_3$ and LaCrO$_3$ systems, respectively. The difference observed in the peak shift is not very significant and thus, inconclusive in studied resolution of x-ray diffraction measurements. The structure consists of corner shared tilted TMO$_6$ (TM = Cr, Fe) octahedra. The structural and magnetic details as reported earlier suggest that the tilted octahedral may induce non-collinearity in the spin structure, giving rise to the weak ferromagnetism in these systems [2, 6]. The XRD diffractogram, figure 1 (upper panel), can be visualized as the superimposed XRD...
spectrum of these pristine materials. These closely spaced doublets confirm the formation of mixed-phase LaCrO$_3$-LaFeO$_3$ system without any additional impurities.

The room temperature Raman spectrographs of these systems are shown in figure 2 and analyzed to understand the microscopic phase evaluation for LaCrO$_3$-LaFeO$_3$ system. The factor group analysis of orthorhombic (Pnma space group) suggests that there are 24 ($\Gamma = 7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}$) Raman active modes in this distorted perovskite LaCrO$_3$ and detail of mode assignments are given in references [6, 23, 25]. The identical crystallographic structure of LaCrO$_3$ and LaFeO$_3$, space group Pnma, gives rise to the similar vibrational modes for both systems with a small deviation for different atomic masses of Cr and Fe atoms. Thus, it was difficult to separate out the vibrational contribution of one from other, as evident in XRD graphs, figure 1, as well as from Raman spectra, figure 2. The temperature-dependent Raman spectra are shown in figure 2, where some of the Raman active modes in proximate LaCrO$_3$-LaFeO$_3$ system show peculiar temperature dependence as compared to pristine systems. After careful analysis of first and second-order optical phonon B$_{2g}(1)$ modes, it is observed that intensity ratio (I$_1$/I$_2$) of these modes shows a sharp increase near the second magnetic transition, as shown in figure 2(b). This increase in the intensity of first-order B$_{2g}(1)$ mode as compared to second-order mode near magnetic anomaly indicates a spin-dependence of optical phonon mode in Raman scattering that can be a manifestation of electron transfer with lattice vibrations and/or anisotropic exchange interactions.

LaCrO$_3$ and LaFeO$_3$ materials are known antiferromagnetic with Neel temperature 290 K and 710 K, respectively [6, 9, 24]. The tilted Cr/Fe-O$_6$ octahedra lead to the canted TM electron spins and thus, causing weak ferromagnetism in these systems. In conjunction with the observed weak ferromagnetism in these systems, the near room temperature magnetodielectric coupling has also been reported in both systems. Considering the complex magnetic interactions in pristine systems, DC magnetization as a function of temperature from 350 K to 100 K has been recorded under zero-field cooled (ZFC) and field cooled (FC) condition at 1 000 Oe for LaCrO$_3$-LaFeO$_3$ system. The measured temperature-dependent magnetic moment is shown in figure 3. The observed sudden rise in magnetization near 290 K in this sample is due to the antiferromagnetic ordering of LaCrO$_3$, superimposed with weak ferromagnetism because of spin canting. The proximate presence of LaFeO$_3$ tries to reorient the magnetic spin structure of LaCrO$_3$ sublattice along the weak ferromagnetic structure of LaFeO$_3$, causing relatively larger ferromagnetic component below 290 K. This ferromagnetic state of LaCrO$_3$-LaFeO$_3$ system preserves down to 250 K, after that the antiferromagnetic ordering of LaCrO$_3$ starts dominating. This LaCrO$_3$ antiferromagnetic dominance, leads to another antiferromagnetic transition for LaCrO$_3$-LaFeO$_3$ system. Thus, two magnetic transitions are observed clearly at 290 K (weak ferromagnetic) and 250 K (antiferromagnetic) in LaCrO$_3$-LaFeO$_3$ system. Further, to understand the dynamic nature of these magnetic transitions, we carried out temperature-dependent AC magnetic measurements at 100, 300, 1 000, 3 000 and 10 000 Hz frequencies in the temperature the same range and plots are shown in figure 3. The first magnetic transition around 290 K is coinciding to that of LaCrO$_3$ long-range antiferromagnetic Neel temperature, superimposed with the weak ferromagnetic ordering of both pristine LaCrO$_3$ and LaFeO$_3$ systems [4]. The onset of an additional magnetic transition at ~250 K may be the consequence of competing spin interaction between close proximity of magnetic Cr and Fe sublattices. To our surprise even transition at 250 K is also frequency independent, suggesting a long-range spin ordering in LaCrO$_3$-LaFeO$_3$ system. The observed
Figure 2. (a) Raman Spectra of LaCrO$_3$, LaFeO$_3$ and LaCrO$_3$-LaFeO$_3$ at room temperature recorded using 532 nm laser source. (b) Temperature-dependent Raman spectra of LaCrO$_3$-LaFeO$_3$ using nm laser source. (c) Intensity ratio of first order and second order Raman peak as a function of temperature suggesting suppression of second order peak upon magnetic ordering.
frequency independence magnetic transitions also rule out the possibility of any clustering/spin glassy impurities in the synthesized LaCrO$_3$-LaFeO$_3$ system. The simultaneous presence of two AFM transitions in this system may be the consequence of the proximity of Fe and Cr magnetic ions and complex magnetic interaction between them. The XRD results confirm the synthesis of LaCrO$_3$-LaFeO$_3$ mixed-phase system and observed complex magnetic properties suggest the presence of competing magnetic interaction between different Cr and Fe ion sites in LaCrO$_3$-LaFeO$_3$ system. The magnetization isotherms are measured near these transition temperatures to probe the nature of magnetic ordering in conjunction with the measured temperature-dependent magnetization measurements. The measured magnetic isotherms are shown in figure 4 for temperatures 200, 250, 280 and 315 K. The weak ferromagnetic component at 315 K is lower than that of 280 K, suggesting that at a higher temperature, only LaFeO$_3$ weak ferromagnetic component is contributing in this system. However, at lower temperatures, the contribution of LaCrO$_3$ weak ferromagnetic component is also added, as can be observed in figure 4. In contrast to the observed weak ferromagnetism, the magnetization curves are not saturating up to 50 kOe magnetic field suggesting the dominance of antiferromagnetic state in LaCrO$_3$—LaFeO$_3$ system. The magnified magnetization curves are shown in figure 4 (lower panel), showing nearly temperature-insensitive weak remanence $\sim 3 \times 10^{-3}$ emu g$^{-1}$. However, the respective coercive field is much larger $\sim 1$ kOe for LaCrO$_3$—LaFeO$_3$ system, suggesting the robust metastable ferromagnetic state.

The magnetic phase diagram against temperature is constructed for LaCrO$_3$-LaFeO$_3$ system and is shown in figure 5. The high-temperature phase (>740 K) is paramagnetic, changing into the antiferromagnetic phase dominated by LaFeO$_3$ in the proximate LaCrO$_3$-LaFeO$_3$ system. This antiferromagnetic phase is superimposed with the weak ferromagnetic phase because of the canted iron spins in FeO$_6$ octahedron in LaFeO$_3$ sublattice, as marked in figure 5. Further reducing the temperature below 290 K, this changes into a metastable ferromagnetic state.
phase at the onset of LaCrO$_3$ antiferromagnetic transition. This phase persists until 250 K, where the system shows another antiferromagnetic phase with weak ferromagnetism simultaneously.

**Conclusion**

We studied the complex magnetic behavior of proximate LaCrO$_3$-LaFeO$_3$ system with different magnetic phases and intertwining of optical phonons with magnetic ordering. These studies may lead to the materials
engineering to design complex magnetic structured materials with competing magnetic phases at or above room temperatures in mixed-phase systems. The observed spin-lattice coupling from temperature-dependent Raman spectra shows a possibility of inducing magnetodielectric coupling in such mixed-phase systems. Further investigations are required to understand the microscopic origin of observed complex magnetic structure and spin-lattice coupling proximate LaCrO$_3$-LaFeO$_3$ system for possible tunability of spin-lattice functional properties.

Acknowledgments

Author Brajesh Tiwari acknowledges Professor Shiva Prasad for technical discussions for the manuscript. Ambesh Dixit acknowledges UGC-DAE Consortium for Scientific Research, Gov of India, through project number CRS-M-221 for this work.

ORCID iDs

Brajesh Tiwari https://orcid.org/0000-0002-2318-4709
Ambesh Dixit https://orcid.org/0000-0003-2285-0754
M S Ramachandra Rao https://orcid.org/0000-0002-7806-2151

References

[1] Solovyev I V, Hamada N and Terakura K 1997 Non-collinear magnetism in distorted perovskite compounds Phys. B Condens. Matter 237–238 44–5
[2] Tiwari B, Dixit A, Naik R, Lawes G and Rao M S R 2015 Magnetostuctural and magnetocaloric properties of bulk LaCrO$_3$ system Mater. Res. Express 0226103
[3] Hamada N, Sawada H, Terakura K and Solovyev I 1997 Electronic band structure and lattice distortion in perovskite transition-metal oxides Phys. B Condens. Matter 237–238 11–1
[4] Takahashi Y, Shimano R, Kaneko Y, Murakawa H and Tokura Y 2011 Magnetoelastic resonance with electromagnons in a perovskite helimagnet Nat. Phys. 8 121–5
[5] Acharya S, Mondal J, Ghosh S, Roy S K and Chakraborti P K 2010 Multiferroic behavior of lanthanum orthoferrite (LaFeO$_3$) Mater. Lett. 64 415–8
[6] Tiwari B, Dixit A, Naik R, Lawes C and Ramachandra Rao M S 2013 Dielectric and optical phonon anomalies near antiferromagnetic ordering in LaCrO$_3$; a possible near room temperature magnetoelectric system Appl. Phys. Lett. 103 2011–4
[7] Zhou J S, Alonso J A, Muoñz A, Fernández-Diaz M T and Goodenough J B 2011 Magnetic structure of LaCrO$_3$ perovskite under high pressure from in situ neutron diffraction Phys. Rev. Lett. 106 1–4
[8] Li P, Hu X, Zhang L, Dai H and Zhang L 2011 Sol-gel nanocasting synthesis of patterned hierarchical LaFeO$_3$ fibers with enhanced catalytic CO oxidation activity Nanoscale 3 974–6
[9] Iglesias M et al 2005 Ab initio electronic structure of rare earth orthoferrites J. Magn. Magn. Mater. 290–291 396–9
[10] Ederer C, Harris T and Kováčik R 2011 Mechanism of ferroelectric instabilities in non-d$^+$[0] perovskites: LaCrO$_3$, [3] versus CaMnO$_3$ [3] Phys. Rev. B 83 054110
[11] Lee J H and Rabe K M 2011 Large spin-phonon coupling and magnetically induced phonon anisotropy in SrMnO$_3$ perovskites (M = V, Cr,Mn,Fe,Co) Phys. Rev. B - Condens. Matter Mater. Phys. 84 1–6
[12] Weingart C, Spaldin N and Bousquet E 2012 Non-collinear magnetism and single-ion anisotropy in multiferroic perovskites Phys. Rev. B 86 094413
[13] Mott N F 1968 Metal-insulator transition Rev. Mod. Phys. 40 677–83
[14] Park H, Millis A and Maranetni C 2012 Site-selective mott transition in rare-earth-element nickelates Phys. Rev. Lett. 109 1–5
[15] Goodenough J B 1958 An interpretation of the magnetic properties of the perovskite-type mixed crystals La1−xSrxCaO3−x J. Phys. Chem. Solids 6 287–97
[16] Ghimire M P, Wu L and Hu X 2014 Possible Half Metallic Antiferromagnetism in a Double Perovskite Material with Strong spin–orbit Couplings PHYSICAL REVIEW B 93 134421
[17] Gray B, Lee H N, Liu J, Chakhalian J and Freeland J W 2010 Local electronic and magnetic studies of an artificial La$_2$Fe$_2$O$_6$ double perovskite Appl. Phys. Lett. 97 013105
[18] Chakraverty S et al 2011 Ferrimagnetism and spontaneous ordering of transition-metals in La$_2$CrFeO$_6$ double perovskite films PHYSICAL REVIEW B 83 064436
[19] Miura K and Terakura K 2001 Electronic and magnetic properties of La$_2$Fe$_2$O$_6$: Superexchange interaction for a d$^5$-d$^3$ system Phys. Rev. B 63 104402
[20] Pickett W E 1998 Ferromagnetic Superlattices Science (80-. ) 281 1571a
[21] Gray B, Lee H N, Liu J, Chakhalian J and Freeland J W 2010 Local Electronic and Magnetic Studies of an Artificial La$_2$Fe$_2$O$_6$ Double Perovskite 013105 14–7
[22] Cristóbal A A, Botta P M, Becoff P G and López J M Porto 2009 Mechanosynthesis and magnetic properties of nanocrystalline LaFe$_2$O$_4$ using different iron oxides Mater. Res. Bull. 44 1036–40
[23] Iliev M et al 2006 Distortion-dependent Raman spectra and mode mixing in RMnO$_3$ perovskites (R = La,Pr,Nd,Sm,Eu,Gd, Tb,Dy,Ho,Y) Phys. Rev. B 73 3–8
[24] Chen C, Xu K B, Cui Y M and Wang C C 2012 Polaronic relaxation in LaFeO$_3$ Mater. Lett. 89 153–5
[25] Iliev M et al 2006 Raman spectroscopy of low-temperature (Pnma) and high-temperature (R3$'$c) phases of LaCrO$_3$ Phys. Rev. B 74 (n) 1–7