The correlation between magnetic interactions and lattice distortions in Pr and Eu substituted NdCrO₃

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Abstract. The study reveals the comparison of Nd₀.₉Pr₀.₁CrO₃ and Nd₀.₉Eu₀.₁CrO₃ samples where the A-site is doped by Pr³⁺ having the larger ionic radius (1.126 Å°) corresponding to less chemical pressure and Eu³⁺ (1.066 Å°) having the smaller ionic radius corresponding to enhanced chemical pressure exerted on the NdCrO₃, with the help of X-ray diffraction, Raman spectroscopy, UV-visible spectroscopy, and dc magnetization measurements. The different spin configuration Pr³⁺ (J = 4) and Eu³⁺ (J = 0) altering the strong coupling between Nd³⁺ (J = 9/2) and Cr³⁺ (S = 3/2) spins result in the variation of the optical band gap, fermi energy and exchange bias.

1. Introduction
The rare earth chromites RCrO₃ (R = rare earth) consist of octahedrally coordinated B-sites occupied by Cr ions and A-sites occupied by R-ions. The complex interaction between magnetic moments of R and Cr ions gives rise to the canted antiferromagnetism. The NdCrO₃ is a multifunctional material with antiferromagnetic (AFM) ordering of Cr spins at Tᵣ = 219 K followed by a spin-reorientation transition at Tₛᵢ = 35 K. In this compound, the origin of exchange bias (EB) is mostly spin-phonon induced [1]. The RCrO₃ shows semiconductor behavior in the visible frequency range, which is related to structural distortion. In few chromites, the effect of the external pressure leads to structural distortions, which modifies band structure and resulting interesting magnetic properties [2]. In this paper, we explored the effect of chemical pressure by substituting the A-site with Pr³⁺ and Eu³⁺ ions.

2. Experimental details
Polycrystalline samples of Nd₀.₉Pr₀.₁CrO₃ and Nd₀.₉Eu₀.₁CrO₃ were prepared by standard solid-state reaction route. The structural characterization of the samples was performed using the X-ray diffractometer (Rigaku, Smart Lab) and Raman spectrometer (Horiba Jobin Yvon, LabRam HR). The absorption spectra have been investigated by using a UV-Vis spectrometer (Perkin Elmer). Magnetization measurements were performed by PPMS (Quantum Design).

3. Results and discussions
3.1. Structural properties
The structural characterization of Nd₀.₉Pr₀.₁CrO₃ and Nd₀.₉Eu₀.₁CrO₃ samples done by XRD analysis (figure 1) confirms the orthorhombic structure (Pnma space group) similar to NdCrO₃.
The substitution of Pr\(^{3+}\) ions gives the increment in the cell parameters, whereas the decrement in the overall cell parameters is obtained due to Eu\(^{3+}\) ions with the changes in CrO\(_6\) octahedral bond lengths and angles for the Nd\(_{0.9}R_{0.1}\)CrO\(_3\) sample, listed in table 1. The influence of the dopant on the average A-site ionic radius, \(r_{\text{avg}}\) accounts for this variation. The distortion of cell edges from the ideal cubic perovskite is calculated using Goldschmidt’s tolerance factor, \(t = (r_R + r_O)/\sqrt{2}(r_{Cr} + r_O)\) and the orthorhombic strain, \(s = 2(a-c)/(a+c)\). The decrease in \(t\) and increase in \(s\) values are observed for decreasing \(r_{\text{avg}}\) (table 1). The microstructural analysis revealed the good quality of the homogenous bulk samples. The Raman spectra (figure 2) shows that the modes \(B_{2g}(2), A_g(4)\) belonging to \(R\)-O\(_1\) vibration, \(B_{1g}(2), B_{2g}(3)\) related to CrO\(_6\) octahedral rotations and \(A_g(6)\) corresponds to CrO\(_6\) octahedral bending, exhibit noticeable red shift (Pr doping) and blue shift (Eu doping), possibly due to changes in average ionic radii and atomic mass. Thus, structural analysis suggests that lattice distortions are less for Nd\(_{0.9}Pr_{0.1}\)CrO\(_3\) and more for Nd\(_{0.9}Eu_{0.1}\)CrO\(_3\) system compared to NdCrO\(_3\).

**Table 1.** Average A-site ionic radius \(r_{\text{avg}}\), tolerance factor \((t)\), orthorhombic strain \((s)\), cell parameters and Cr-O2 bond lengths, and Cr-O2-Cr bond angles obtained from the Rietveld refinement of Nd\(_{0.9}R_{0.1}\)CrO\(_3\) \((R = \text{Pr, Eu})\) with parent sample.

|                  | Nd\(_{0.9}Pr_{0.1}\)CrO\(_3\) | NdCrO\(_3\) | Nd\(_{0.9}Eu_{0.1}\)CrO\(_3\) |
|------------------|-------------------------------|--------------|-------------------------------|
| \(r_{\text{avg}}\) (Å) | 1.111                         | 1.109        | 1.105                         |
| \(a\) (Å)        | 5.481                         | 5.482        | 5.484                         |
| \(b\) (Å)        | 7.690                         | 7.689        | 7.688                         |
| \(c\) (Å)        | 5.419                         | 5.418        | 5.415                         |
| \(V\) (Å\(^3\)) | 228.45                        | 228.37       | 228.30                        |
| \(t\)            | 0.884                         | 0.883        | 0.882                         |
| \(s\)            | 0.0114                        | 0.0117       | 0.0127                        |
| Cr-O2 (Å)        | 1.963                         | 1.939        | 1.901                         |
| Cr-O2-Cr (deg.)  | 156.19                        | 156.3        | 161.6                         |
3.2. Optical properties

The optical behavior of the samples is investigated by the UV–Vis diffuse reflectance spectroscopy technique. The UV–Vis spectrum of the samples are analyzed by optical absorption, i.e., Kubelka-Munk (KM) function F(R) \[3\], which can be expressed as, F(R) = (1-R)^2/2R, where R is the diffuse reflectance of the sample. From F(R) versus wavelength plot in figure 3, we see the Nd_{0.9}Pr_{0.1}CrO_3 system has a multiband electronic structure. The electronic structure of NdCrO_3 consists of a filled O 2p band and partially filled Cr 3d^3 and Nd 4f^4 orbitals. The broad absorption band located around 250-390 nm is attributed to bandgap E_g of the material due to O 2p-Cr 3d transitions. The other two intense absorption bands at about 463 nm and 593 nm corresponds to 4A_2g–4T_1g and 4A_2g–4T_2g transition. The two weak transitions at 748 nm and 804 nm corresponds to 4A_2g–2T_1g and 4A_2g–2E_g transition. These transitions are related to the octahedral crystal field splitting of Cr^{3+} d-orbitals that allow the corresponding d(Cr) → d(Cr) transitions. The optical energy band gap can be calculated from the Tauc relation F(R)h\nu = B(h\nu – E_g)^n. The value of n depends on the direct (n = 1/2) or indirect (n = 2) band gap of the material. The Tauc plot of (F(R).h\nu)^2 versus (h\nu) is used to determine the direct band gap (E_g) as shown in figure 4, which shows the samples have the bandgap E_g = 3.24 eV (Pr doping) and 3.20 eV (Eu doping) lies in the visible region. We have also utilized the Density functional theory (DFT) with the quantum ESPRESSO suite to calculate the fermi energy of the Nd_{0.9}R_{0.1}CrO_3 system. The obtained fermi energy values are E_F = 14.48 eV (Pr doping) and E_F = 14.57 eV (Eu doping). From the magneto-optical study of NdCrO_3, we know that the coupling between Nd^{3+} and Cr^{3+} spins are extremely strong \[4\], hence the substitution of different R on Nd-site can influence Cr-O overlap integral, which can also modify the structural distortion via the distortion of CrO_6 octahedra, resulting in the change in the optical bandgap and fermi energy.

3.3. Magnetic properties

The magnetization measurements (figure 5) confirm the AFM ordering of Cr^{3+} spins occurring at T_N = 226.7 K, 224.1 K, and the spin reorientation transition due to reorientation of Cr^{3+} spins at T_{SR} = 41.8 K, 39.2 K for Nd_{0.9}Pr_{0.1}CrO_3 and Nd_{0.9}Eu_{0.1}CrO_3 samples respectively. The magnetic behavior below T_N varies significantly due to different alignment of Cr sublattice, |Nd+Pr| and |Nd+Eu| sublattice that weakens the reorientation of Cr^{3+} spins in Nd_{0.9}Pr_{0.1}CrO_3 but leaves the Nd_{0.9}Eu_{0.1}CrO_3 system slightly affected. The negative exchange bias (figure 6)
having the exchange bias field of $H_{EB} = -258$ Oe and -209 Oe with the coercive field $H_C = 1528$ Oe and 583 Oe at 5 K ($T < T_{SR}$) is obtained for Nd$_{0.9}$Pr$_{0.1}$CrO$_3$ and Nd$_{0.9}$Eu$_{0.1}$CrO$_3$ samples. The value of (EB) field increases at 100 K ($T < T_N$) such that $H_{EB} = -748$ Oe and -1280 Oe with $H_C = 405$ Oe and 1049 Oe is observed for Nd$_{0.9}$Pr$_{0.1}$CrO$_3$ and Nd$_{0.9}$Eu$_{0.1}$CrO$_3$ samples, respectively. The high EB field at 100 K for Nd$_{0.9}$Eu$_{0.1}$CrO$_3$ is obtained due to high chemical pressure acting on competing AFM interaction between the weak ferromagnetic component of Cr$^{3+}$ moments and the paramagnetic moment of Nd$^{3+}$/R$^{3+}$ ions. However, the value of EB field for the parent compound [5] is significantly higher than both these substituted compounds. It is possible that coupling between the A-site and the B-site has been sufficiently modified, leading to the decrease in EB effect.

4. Conclusions
The single-phase Nd$_{0.9}R_{0.1}$CrO$_3$ $(R = Pr, Eu)$ samples were formed by the solid-state reaction method. The structural analysis confirmed the increase in structural distortion with the variation of $R$-ion. The change in optical band gap and fermi energy via the Cr-O overlap integral is observed. The coupling between Nd$^{3+}$/R$^{3+}$ and Cr$^{3+}$ spins was altered, resulting in the change in $T_N$ and $T_{SR}$ values and the negative exchange bias effect. Our results clearly demonstrate that the magnetic interaction between Nd/R and Cr moments varies with the average A-site ionic radius due to different chemical pressure in Nd$_{0.9}R_{0.1}$CrO$_3$ $(R = Pr, Eu)$ system.

5. Acknowledgments
The authors would like to acknowledge the FIST program of Department of Science and Technology, India, for partial support of this work [Ref. No. SR/FST/PSII-037/2016] and CIF IIT Guwahati for providing its facilities.

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