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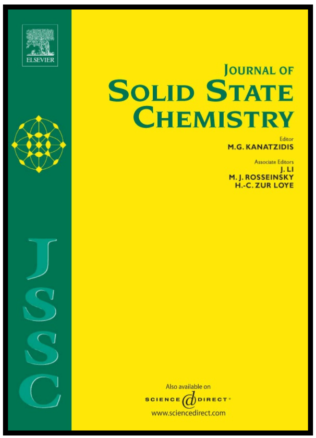

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Crystal and Magnetic Structure of Novel Brownmillerite, $Ca_2Fe_{0.875}Cr_{0.125}GaO_5$: An Approach towards Natural GMR Layers in Bulk Metal Oxides

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We present an in-depth study on the structure and magnetic properties of a novel layered oxide, $Ca_2Fe_{0.875}Cr_{0.125}GaO_5$. Structural studies from laboratory X-ray diffraction, synchrotron powder X-ray diffraction and neutron powder diffraction reveal that the compound crystallizes in an orthorhombic Brownmillerite phase with *Pnma* space group having Fe/Cr – octahedral layers and Ga – tetrahedral layers with around 9.0 % of Fe occupying tetrahedral sites. The temperature evolution of Neutron powder diffraction confirms the absence of any structural changes in the range 300 to 6 K. Magnetic characterizations show antiferromagnetic ordering at room temperature and the co-existence of antiferromagnetic and ferromagnetic phases at low temperature. The magnetic structure derived from neutron powder diffraction is a *G*-type antiferromagnetic. The ordered magnetic moments at 6 K on the octahedral and tetrahedral sites are 3.15 (2) μ_B/cation and 0.93 (4) μ_B/cation, respectively oriented in the *ac*-plane.

Graphical Abstract legend

Rietveld refined X-ray diffraction pattern at 300 K and magnetic structure obtained from Neutron diffraction at 6 K for $Ca_2Fe_{0.875}Cr_{0.125}GaO_5$

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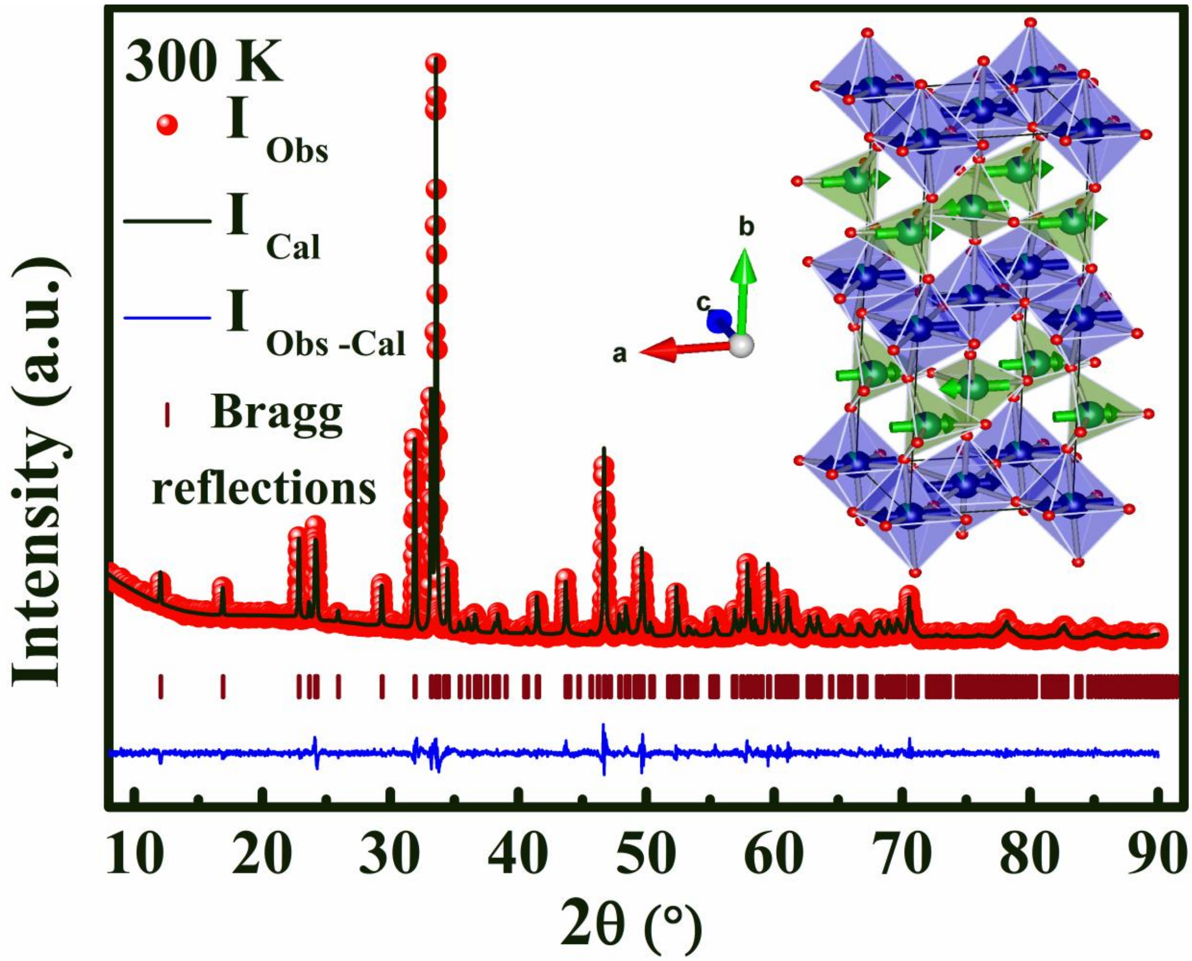

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1. Introduction

Anion-deficient oxide materials have drawn a great deal of attention for their unusual structural, magnetic, magneto-transport and redox/catalytic properties. Among them, the naturally occurring anion-deficient perovskite related layered system such as Brownmillerite type oxide ($A_2B_2O_5$/$A_2BB'O_5$; where A= alkaline-earth metals; B/B'= group III or transition metals) is the most popular one. Brownmillerite structure possesses ordering of oxygen vacancies along crystallographic [110] direction of a cubic perovskite unit cell which gives rise to an alternate stacking sequence of BO_6 octahedral and $B'O_4$ tetrahedral layers along the [010] direction[1]. Brownmillerites come under the homologous series $A_nB_nO_{3n-1}$ where n is an integer number and (n-1) gives the number of perovskite like layers sandwiched between two tetrahedral layers within the structural unit cell. Most of the Brownmillerites crystallize in orthorhombic structure with unit cell dimension, $\sqrt{2}a_p \times$

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$4a_p \times \sqrt{2}\, a_p$ Å^3, where $a_p \sim 3.8$ Å, represents the dimension of a primitive cubic perovskite unit cell. B'O_4 are linked to each other sharing their vertices and they form chains along *a*-axis. The chains of B'O_4 tetrahedra within Brownmillerite structure encounter a cooperative twist distortion which yields "L" (where tetrahedra are oriented clockwise) and "R" (where terahedra are oriented anticlockwise) chains[2]. These chains are mirror reflections of each other, and mutual interchange of them will alter neither the coordination geometry of A, B/B' cations nor the interatomic distances[3,4]. Hence both the chains are energetically equivalent with equal probability of occurrence within the structure. Brownmillerite adopts different space group depending on the tetrahedral chain ordering within the structure. If only one type of chain either "L" or "R" is present, then the structure belongs to the non-centrosymmetric *I2mb* space group. If the arrangement of the "L" and "R" chains is random then it adopts centro-symmetric *Imma* space group. The structure belongs to *Pnma* space group if it is comprised of a regular alternation of "L" and "R" chains[5]. For example, Ca_2FeAlO_5[6] and $Ca_2Cr_2O_5$[11] crystallize in *I2mb*, $Sr_2Al_{1.07}Mn_{0.93}O_5$[7] crystallizes in *Imma*, and $Ca_2Fe_2O_5$[8] crystallizes in *Pnma* space group.

Brownmillerite $Ca_2Fe_2O_5$ adopts orthorhombic *Pnma* space group[8] and it is a G-type antiferromagnet[9] having Néel temperature, T_N = 725 K[10]. $Ca_2Cr_2O_5$, on the other hand, crystallizes in orthorhombic *I2mb* space group[11]. Unusual tetrahedral coordination for Cr^{3+} ions leads to local distortion in the structure which produces a significant impact on magnetism. Cr^{3+} ions order antiferromagnetically at around 220 K with ordered moment of 1.7 (1) μ_B at 10 K. The magnetic moments lie in the bc-plane and are tilted by 51 (4)° with respect to the *b*-axis. $Ca_2Cr_{0.5}Fe_{1.5}O_5$, crystallizes in orthorhombic space group *Pnma* and has T_N = 455 K[10]. The magnetic structure was found to be a *G*-type antiferromagnet at 2.1 K with magnetic moments lying along *a*-axis without any canting and the ordered magnetic moments were obtained as 3.23 (4) and 3.95 (5) μ_B respectively at octahedral and tetrahedral sites. Even though ferromagnetism is expected from superexchange interaction between $Fe^{3+}(d^5)$ and $Cr^{3+}(d^3)$ cations according to Goodenough-Kanamori-Anderson (GKA) rule[12,13], it was not observed in $Ca_2Cr_{0.5}Fe_{1.5}O_5$. Magnetic properties of Ca_2FeGaO_5 were studied by R. W. Grant *et al.*[14] using Mössbauer spectroscopy. The magnetic structure was found to be antiferromagnetic having T_N around 315 K[15]. $Ca_2Cr_{0.5}Ga_{1.5}O_5$ was found to crystallize in *Pnma* space group with the tetrahedral site exclusively occupied by Ga^{3+}. It lacks long range magnetic ordering because of lower concentration of chromium, but it possesses good redox behaviour[16].

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The B-site cations play an important role in structural, magnetic and transport properties of Brownmillerites. To the best of our knowledge, no report has come up with Brownmillerites having Fe, Cr and Ga as B-site cations. In $Ca_2Fe_2O_5$, full replacement of Fe by Cr gives rise to non-centrosymmetric structure because of unusual tetrahedral coordination of Cr^{3+}. Also partial replacement of Fe by Al gives non-centrosymmetric structure with *Ibm2* space group[17]. Hence it will be interesting to see if the replacement of Fe by Cr and Ga gives a new non-centrosymmetric compound. According to earlier reports[16], Ga^{3+} prefers tetrahedral site, and if we could develop a Brownmillerite oxide in which the tetrahedral site exclusively occupied by non-magnetic Ga^{3+} cation and octahedral site occupied randomly by the Fe^{3+}/Cr^{3+} cations, then a

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pseudo-two dimensional material can be derived. There is growing interest in two dimensional layered materials since they have potential to act as a candidate for low field sensors, read heads, data storage devices, etc.[18]. Interestingly, if we could develop Brownmillerite type oxides with an array of alternating magnetic and non- magnetic layers along the stack of octahedral and tetrahedral layers, then it would lead to natural GMR layers which could bring fabulous innovations in the field of functional oxides. Development of natural GMR layer had been approached earlier in bi-layered manganite Brownmillerite. However, in the present work, we initiated a novel approach which involves the development of natural GMR layers in single layered Brownmillerite oxides. In this aspect we synthesized a novel single layered Brownmillerite compound $Ca_2Fe_{1-x}Cr_xGaO_5$ (x = 0.125, 0.167, 0.25). Further we focused on the systematic exploration and thorough analysis of structural and magnetic measurements to provide an in-depth idea about the crystal structure and magnetic features of $Ca_2Fe_{0.875}Cr_{0.125}GaO_5$.

2. Experimental details

Polycrystalline powder samples of compositions $Ca_2Fe_{1-x}Cr_xGaO_5$ (x = 0.125, 0.167, 0.25) were synthesized through conventional solid state reaction route. Stoichiometric proportions of high purity $CaCO_3$ (99.999 %), Fe_3O_4 (99.995 %), Cr_2O_3 (99.9 %) and Ga_2O_3 (99.99 %) were mixed thoroughly and then fired at 1073 K in air. The calcined powders were then annealed at 1173 K, 1273 K and 1373 K for 24 h in the air with intermediate grinding. Thereafter the powders were pressed into pellets of 10 mm diameter and 1 mm thickness by applying 5 tonnes of pressure in a hydraulic press and sintered at 1373 K for 6 h in air. For all the heat treatment the rate of raising and lower the temperature was identical which is equal to 5 K/min. To check the phase purity of the sample, laboratory X-ray diffraction patterns were collected at room temperature after each heat treatment. Since all the compositions exhibit same crystal structure the $Ca_2Fe_{0.875}Cr_{0.125}GaO_5$ was taken as the representative composition for detailed analysis.

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Room temperature powder laboratory X-ray diffraction (Lab XRD) patterns were collected using Rigaku Smartlab diffractometer [Cu Kα (λ = 1.5406 Å)] with a step size of 0.02˚ in $10^\circ \leqq 2\theta \leqq 90^\circ$ angular range. Synchrotron powder XRD (SXRD) patterns were collected in the temperature range 300 K to 35 K using Angle Dispersive X-ray diffraction beam-line (BL-12) (λ = 0.8074) at Indus-2, synchrotron source at RRCAT. Image plate area detector was used, and full Debye rings were integrated. Wavelength and the sample to detector distance were accurately determined using diffraction pattern of LaB_6 NIST standard. Neutron powder diffraction (NPD) data were recorded on the PD2 diffractometer [λ = 1.2443 Å] at Dhruva reactor, Bhabha Atomic Research Centre, Mumbai in the temperature range between 6 K and 300 K at the interval of 25 K and in the angular range $5^\circ \leqq 2\theta \leqq 130^\circ$. The Rietveld analysis of all the diffractograms was performed using FullProf Suite[19]. Magnetization data were collected using MPMS VSM based SQUID magnetometer (Quantum Design).

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3. Results and discussion

The Rietveld refinement of room temperature Lab XRD pattern of polycrystalline $Ca_2Fe_{0.875}Cr_{0.125}GaO_5$ reveals a single phase orthorhombic Brownmillerite structure with *Pnma* (62) space group. The lattice parameters and the goodness of fit parameters were obtained as a = 5.3917 (2) Å, b = 14.6635 (5) Å, c = 5.6026(2) Å, R_P = 2.06 %, R_{WP} = 2.82 % and χ^2 = 3.01. However, only after considering B-site cation disorder a better structural refinement and fitting parameters were obtained for SXRD (a = 5.3944 (4) Å, b = 14.6698 (1) Å, c = 5.6059 (4) Å)) and NPD patterns (lattice parameters given in Table-1). The obtained lattice parameters from SXRD and NPD are comparable with the values in the literature[8]. Thus the structural analysis confirmed that the compound has orthorhombic *Pnma* structure with 9.0 % of Ga^{3+} entering into the octahedral site and the corresponding amount of Fe^{3+} is occupying the tetrahedral site. The observed, calculated and difference patterns obtained after the refinement of $Ca_2Fe_{0.875}Cr_{0.125}GaO_5$ at 300 K for SXRD and NPD patterns are shown in Fig. 1(a) and (b) respectively. SXRD data shows preferred orientation for (002) reflection around 2θ = 16.56˚ (Fig. 1(a)). This may be because the measurements were done in transmission mode. For refining the NPD data, the lattice parameters and atomic positions obtained after the refinement of SXRD data were taken as the initial parameters. Then the instrument zero parameter, lattice parameters, atomic positions and thermal parameters were refined systematically. The diagrammatic representation of the crystal structure is shown in Fig. 2. Temperature variation of NPD experiment was carried out in the range of 300 – 6 K and the Rietveld refinement of the NPD patterns validates same crystal symmetry in this temperature range and hence confirms the absence any structural phase transition below 300 K. However, thermal evaluation of lattice parameters (Fig. 3) shows a change in slope around 50 K which may be due to some iso-structural first order transition where the crystal symmetry remains unchanged. The slight decrease in cell parameters (a, b, c) and volume indicates normal contraction of the unit cell with decreasing temperature. The detailed structural parameters obtained from the refinement of NPD data at 300 and 6 K are given in the Table-1. The typical bond lengths and bond angles obtained from the refinement of NPD data at 300 and 6 K are also listed in the Table-1. Bond lengths and bond angles are comparable with the previous reports on single layer Brownmillerites[7]. Another important structural observation is that the equatorial environment for the octahedral (Four Fe1-O1) is not square as a result of non-equivalent pairs of equatorial bonds (two Fe1-O1: 1.974 (1) Å and Two Fe1-O1: 1.939 (2) Å at 6 K). The Bond Valence Sum (BVS) calculation was done to determine the valence state of Ca, Fe/Cr and Ga ions and the obtained values are compared in the Table-1. The BVS values for Cr/Fe/Ga are close to 3.0, which is same as the oxidation number according to the structural refinement which further confirms lack of B-site cation ordering as there is no cationic charge difference. According to Crystal Field Stabilization Energy (CFSE) of d^3 electronic configuration, Cr^{3+} ion has a strong octahedral site preference, however, Fe^{3+} (d^5) and Ga^{3+} (d^{10}) have almost equal tendency for both sites[20]. Thus in the present compound Cr^{3+} occupy the octahedral sites only, but there will be mixing of Fe^{3+} and Ga^{3+} in both the sites, as confirmed by the structural refinement.

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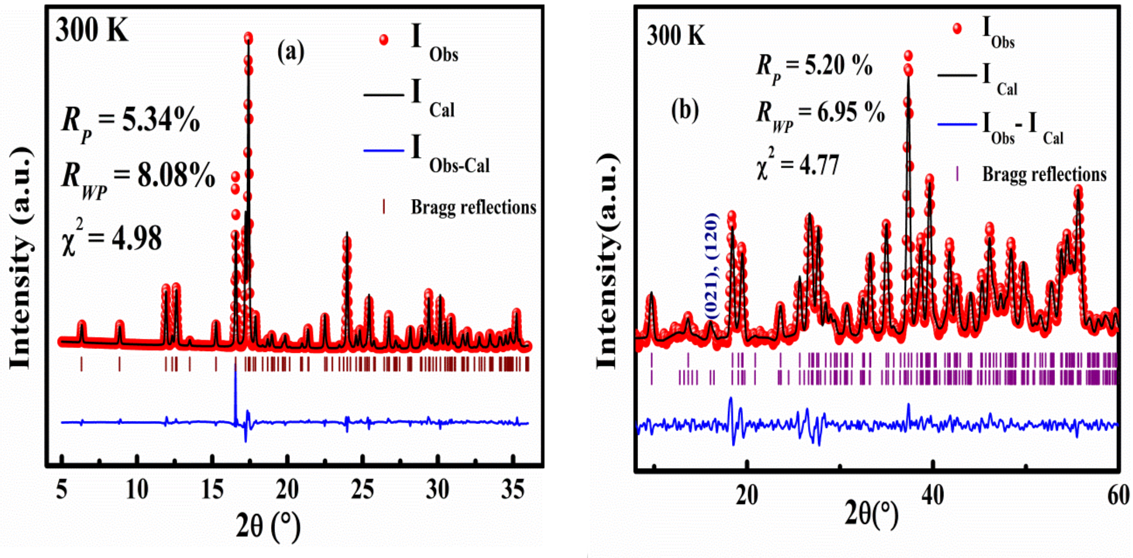
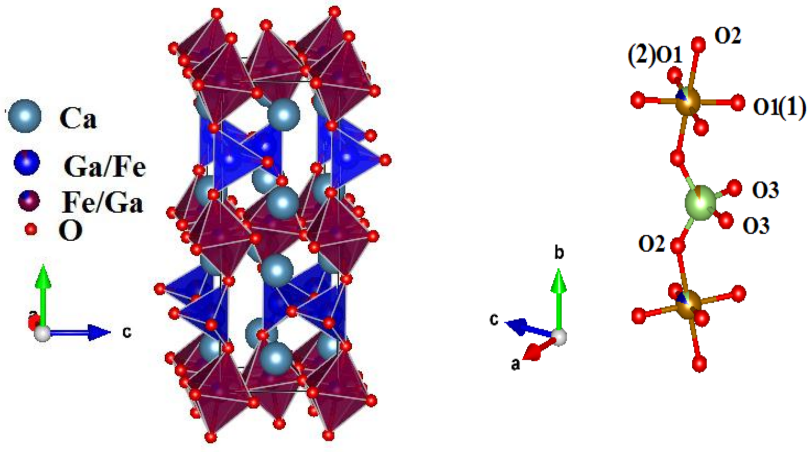


Fig. 1 Rietveld refinement plot (observed (I_{Obs}), calculated (I_{cal}) and difference ($I_{obs\text{-}cal}$) profiles) for (a) SXRD and (b) NPD collected at room temperature [(021), (120) reflections correspond to magnetic ordering)].



(a) (b)

Fig. 2 (a) Crystal Structure obtained from the refinement of the NPD data at room temperature and (b) nomenclature of the Oxygen atoms

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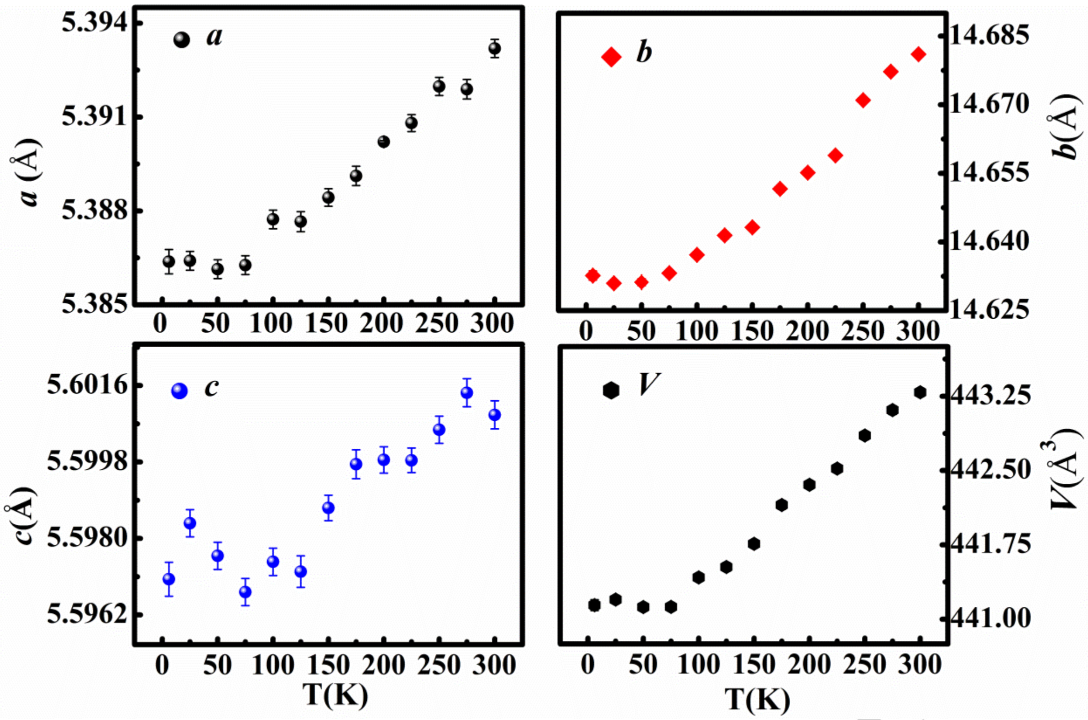

Fig. 3 Temperature dependence of unit cell parameters (*a*, *b*, *c*) and unit cell volume (V)

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Table 1:

Atom positions (x, y, z), isotropic thermal parameters (B_{iso}), typical bond lengths and bond angles, Bond Valence Sum (BVS) and magnetic moment obtained after the refinement of NPD data collected at 300 and 6 K.

Refined parameters		300K	6K
Space Group		*Pnma*	*Pnma*
a (Å)		5.3931(2)	5.3866(4)
b (Å)		14.6810(7)	14.6325(1)
c (Å)		5.6009(4)	5.5972(4)
V (Å^3)		443.287(2)	441.177(6)
Ca (8d)	**x**	0.4821(1)	0.4821(1)
	y	0.1079(2)	0.1083(2)
	z	0.2437(9)	0.0268(9)
B_{iso}(Å^2)		0.76(9)	0.53(8)
Occupancy		1.0	1.0
Fe1/Cr/Ga2 (4a)	(0 0 0)		
B_{iso}(Å^2)		0.69(7)/0.69(7)/0.32(8)	0.43(6)/0.43(6)/0.14(8)
Occupancy		0.79/0.12/0.09	0.79/0.12/0.09
Fe2/Ga1 (4b)	**x**	0.4467(8)	0.4496(7)
	y	0.25	0.25
	z	0.5694(7)	0.5691(7)
B_{iso}(Å^2)		0.69(7)/0.32(8)	0.43(6)/0.14(8)
Occupancy		0.09/0.91	0.09/0.91
O1 (8d)	**x**	0.2581(1)	0.2641(2)
	y	0.9846(2)	0.9846(2)
	z	0.2393(9)	0.2401(9)
B_{iso}(Å^2)		0.75(4)	0.43(4)
Occupancy		1.0	1.0
O2 (8d)	**x**	0.0229(9)	0.0229(9)
	y	0.1411(2)	0.1411(2)
	z	0.0717(6)	0.0717(6)
B_{iso}(Å^2)		0.75(4)	0.43(4)
Occupancy		1.0	1.0
O3 (4c)	**x**	0.6039(2)	0.6039(2)
	y	0.25	0.2
	z	0.8750(2)	0.8750(2)
B_{iso}(Å^2)		0.75(4)	0.43(4)
Occupancy		1.0	1.0
<Ca – O1> (Å)		2.524(8)	2.523(4)
<Ca – O2> (Å)		2.609(7)	2.603(3)
<Ca – O3> (Å)		2.343(5)	2.327(4)
<Fe1 – O1> (Å)		1.959(6)	1.959(6)
<Fe1 – O2> (Å)		2.117(3)	2.115(1)
<Ga1 – O2> (Å)		1.826(4)	1.818(1)
<Ga1 – O3> (Å)		1.890(8)	1.900(4)
Fe1/Cr – O2 – Fe2(deg.)		139.7(1)	139.2(1)
Fe1/Cr – O1 – Fe1/Cr (deg.)		165.7(2)	165.4(2)
Oxidation State of cations from BVS calculation		Ca: 1.9 Fe/Cr: 3.1 Ga: 2.8	Ca: 2.0 Fe/Cr: 3.1 Ga: 2.8
M (μ_B/cation) (Octahedral Site)		0.87(3)	3.15(2)
M (μ_B/cation) (Tetrahedral Site)		0.45(9)	0.93(4)

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Temperature variation of magnetization (M vs T) data were collected in the zero field cooled (ZFC), field cooled cooling (FCC) and field cooled warming (FCW) protocols in the temperature range 5 to 350 K in presence of 100 Oe, 500 Oe, 3 kOe, 5 kOe and 10 kOe fields. The M vs T curves obtained in 100 Oe field is shown in Fig. 4(a) in which ZFC and FC curves diverge around 325 K. The thermomagnetic irreversibility between ZFC and FC may attribute to the presence of competing magnetic interactions arising from the disordered distribution of magnetic ions in the octahedral sites. The presence of thermal hysteresis in the temperature range 90 – 290 K (at 100 Oe) also points to the existence of multiple magnetic interactions. Similar thermal hysteresis was also observed for magnetically phase separated half doped manganite[21] and in other perovskites having inhomogeneous magnetic state[22,23]. Broad humps observed in the FCC and FCW curves, in the temperature range ~ 75 - 300 K, may arise because of short-range AFM interactions within the octahedral layers alone[24]. Even though ZFC, FCC as well as FCW curves merge into a single curve at a higher applied field (at 10 kOe; shown in Fig. 4(b)), the peak around 225 K persists. M vs T curve under 5 kOe in the temperature range 300 – 900 K is shown in Fig. 5(a) which shows a magnetic transition at 582 K.

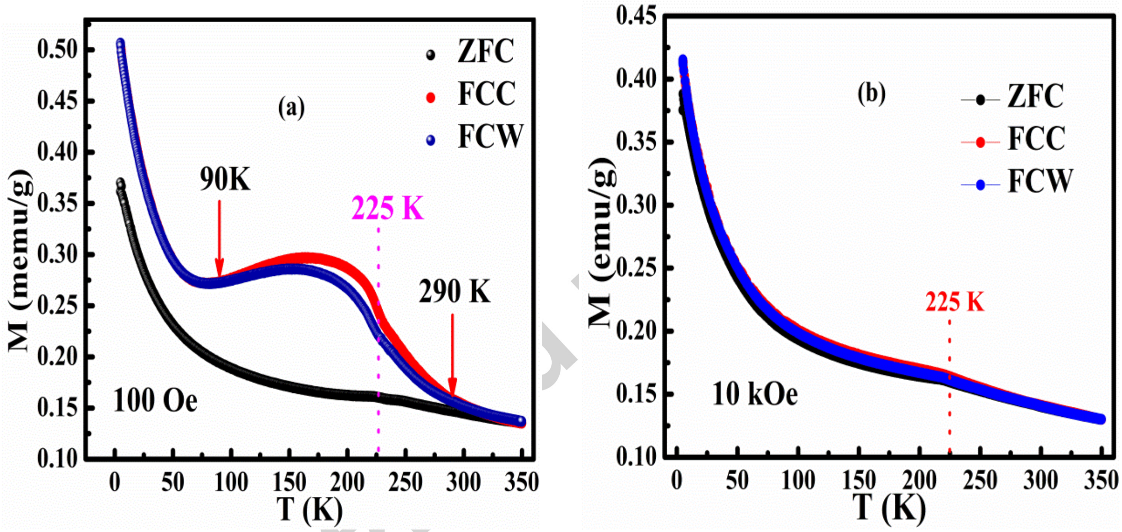

Fig. 4 (a) M vs T curve in 100 Oe and (b) M vs T curve in 10 kOe.

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Further, inverse magnetic susceptibility in the higher temperature range 750 to 900 K was fitted to Curie–Weiss (CW) law (shown in Fig. 5(b)). The negative value of paramagnetic Curie temperature (θ_p = - 8.6 K), calculated from the fit, suggests the presence of predominant antiferromagnetic interactions in the compound. The possible AFM interactions in the present compound are (i) Fe^{3+}-O-Fe^{3+} as in $Ca_2Fe_2O_5$ and (ii) Cr^{3+}-O-Cr^{3+} as in $Ca_2Cr_2O_5$, where the former exhibits T_N at 725 K[10] and the latter shows T_N at 220 K[11]. In the present compound, the majority of the octahedral sites are occupied by Fe^{3+} ions. Thus the dominant magnetic contribution will be arising from Fe^{3+}-O-Fe^{3+} AFM superexchange, generating a higher transition temperature. However, the presence of Cr^{3+} ions in the octahedral layers may give rise to short range AFM Cr^{3+}-O-Cr^{3+} clusters also. Thus the transitions at 582 K and 225 K can be assigned to the AFM transitions from Fe^{3+}-O-Fe^{3+} and

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Cr^{3+}-O-Cr^{3+} interactions, respectively. At lower temperature (below 50 K), there is a sharp increase in the ZFC and FC curves might be arising either from short range FM ordering due to FM Fe^{3+}-O-Cr^{3+} clusters or due to AFM spin canting at lower temperatures. Thus the M vs T data point to competing magnetic interactions in the layers due to the coexistence of AFM–FM interactions as a result of disordered B site cation distribution (Fe/Cr/Ga).

The effective paramagnetic moment obtained is 4.42 μ_B / f. u. which is less than the theoretically calculated value of effective paramagnetic moment, $\mu_{eff}\ (Th)$ = 5.7 μ_B / f. u. [$\mu_{eff}\ (Th)$ has been calculated using the formula, $\mu_{eff}\ (Th) = \sqrt{0.875 \times (\mu_{eff}\ (Fe^{3+}))^2 + 0.125 \times (\mu_{eff}\ (Cr^{3+}))^2}\ \ \mu_B$, where $\mu_{eff}\ (Fe^{3+}/Cr^{3+}) = g \times \sqrt{s(s+1)}$ and $g = 2$, $and\ s = \frac{5}{2}\ for\ Fe^{3+}\ and\ \frac{3}{2}\ for\ Cr^{3+}$]. Since the present compound is magnetically disordered, the antiferromagnetic to paramagnetic magnetic transition is not very sharp. As a result a pure paramagnetic state might not have attained immediately above 750 K. Thus the reduction of effective moment may be due to the presence of some magnetic (AFM) clusters in the temperature range taken for Curie-Weiss fitting.

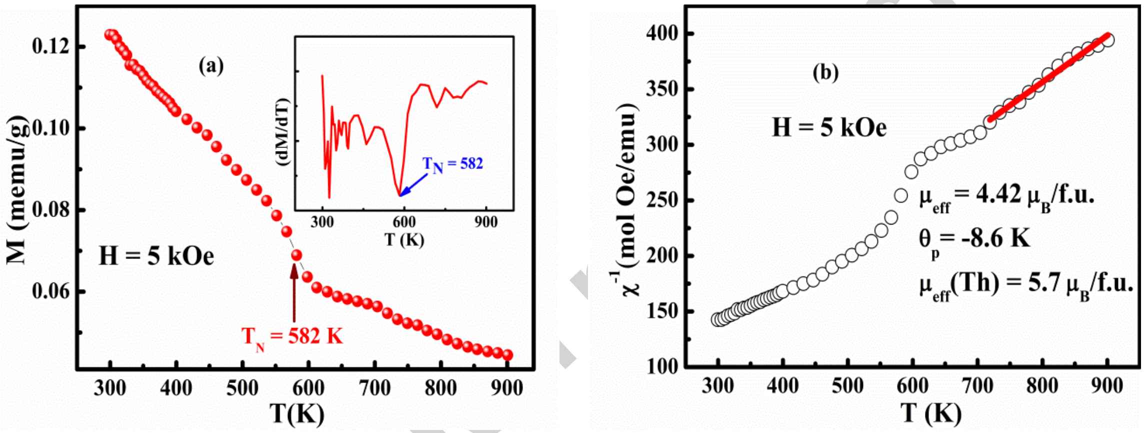

Fig. 5 (a) High temperature M vs T data collected under 5 kOe (Inset: dM/dT vs T curve) and (b) inverse susceptibility Vs T curve with Curie-Weiss fit.

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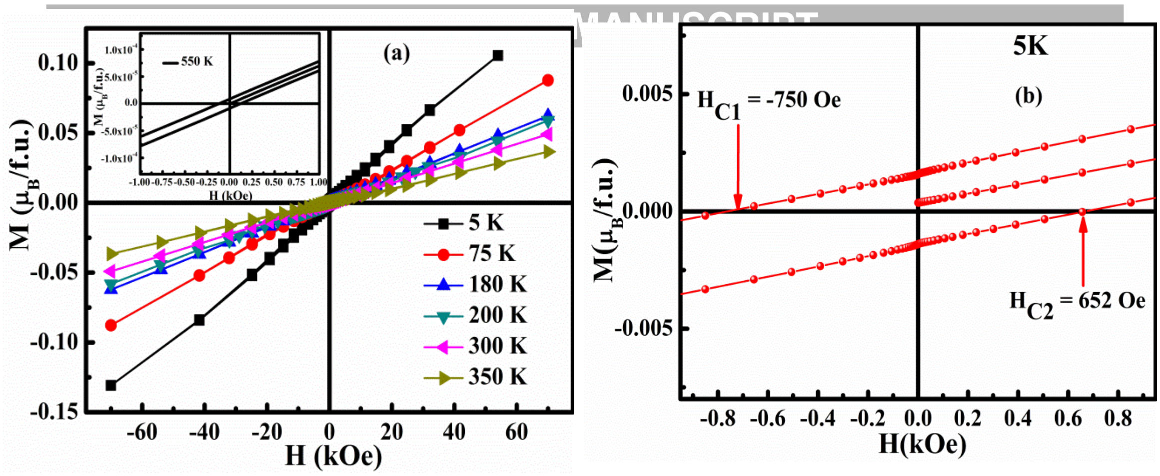

Fig. 6 (a) M vs H curves collected at different temperature in ± 70 kOe (Inset: Zoomed M vs H curve at 550 K) and (b) Zoomed M vs H curve at 5 K.

The field variations of magnetization (M vs H) for various temperatures were collected between -70 kOe and + 70 kOe applied field and are shown in Fig. 6(a). At 5 K, the M vs H curve shows a rapid increase in magnetization at lower magnetic fields with a detectable hysteresis loop (coercive field around 700 Oe). The presence of hysteresis loop can be attributed either to the short range Fe^{3+}-O-Cr^{3+} FM clusters or due to canted AFM ordering arising from Dzyaloshinskii-Moriya interaction[25,26]. Additionally, there is a shifting of hysteresis loop at 5 K along the field axis (shown in Fig. 6(b)), may conjecture the presence of competing magnetic interactions. The M(H) curves are not paramagnetic even up to 550 K, this corroborates the thermomagnetic characterization.

For the better understanding of magnetism and to explore the magnetic structure, NPD data were collected in the temperature range 300 to 6 K at an interval of 25 K. The diffractograms for some typical temperatures and the Rietveld refined diffractogram for 6 K are shown in Fig. 7 and Fig. 8 respectively. NPD patterns clearly show the enhancement in the intensity of the superlattice reflections (indicated by * in Fig. 7) as the temperature is lowered below 300 K. These reflections correspond to the magnetic ordering. The magnetic reflections persist up to 300 K. Thus the NPD data validates the magnetization data and confirms the presence of magnetic ordering in the compound at room temperature. On decreasing temperature the Bragg reflections around 2 θ = 16˚ [(021), (120)] corresponding to the magnetic ordering gain in intensity which points out that the strength of long range ordering increases towards lower temperatures. The reflections were indexed using propagation vector k = 0 in *P-1* space group. The basis vectors for the irreducible representations with moments on Fe1 and Fe2 were obtained using Sarah[27] program. The magnetic structure obtained is a G-type antiferromagnetic at 6 K (shown in Fig. 9).

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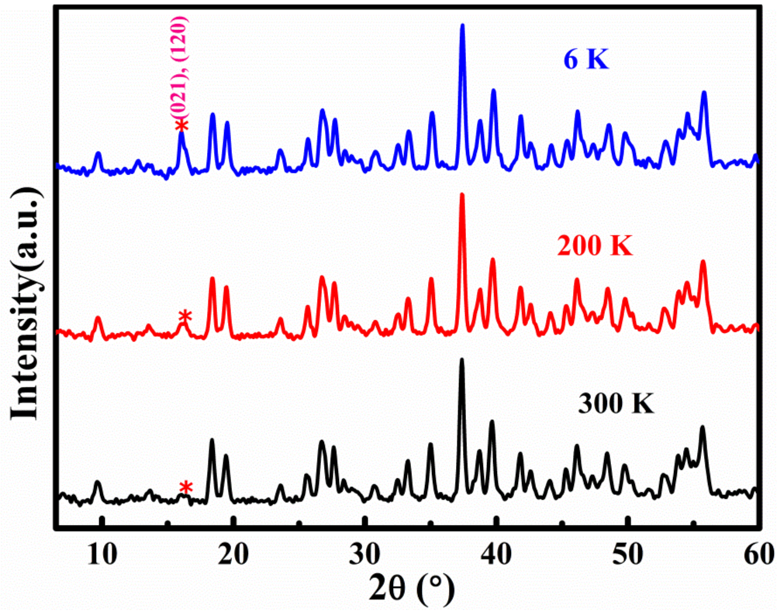

Fig. 7 NPD patterns at different temperatures for $Ca_2Fe_{0.875}Cr_{0.125}GaO_5$

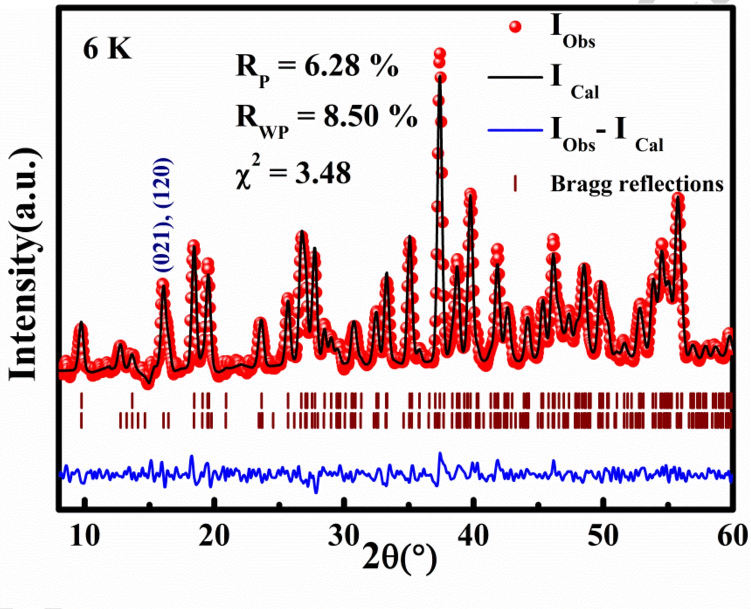

Fig. 8 Rietveld refinement plot (observed (I_{Obs}), calculated (I_{cal}) and difference ($I_{obs-cal}$) profiles) of NPD collected at 6 K.

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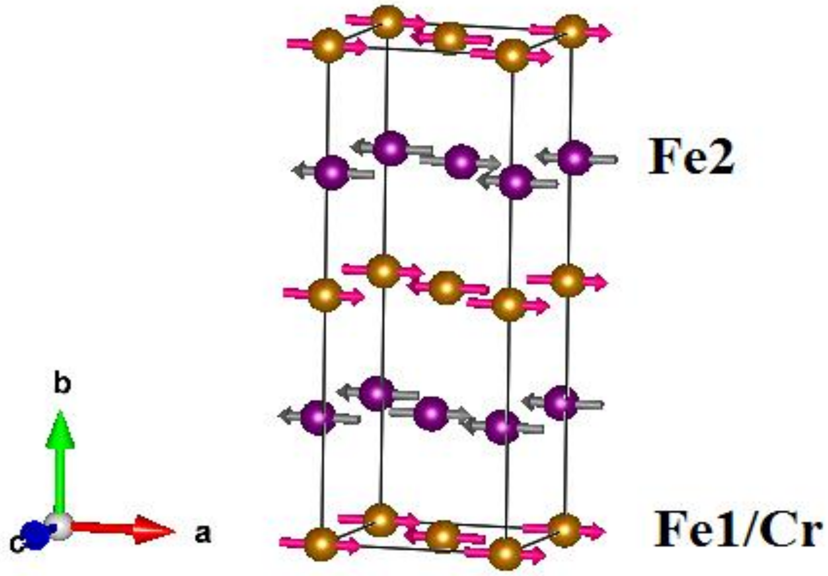

Fig. 9 Magnetic structure of $Ca_2Fe_{0.875}Cr_{0.125}GaO_5$ at 6 K

The magnetic structure shows that there are two Fe^{3+} sub-lattices: octahedral layers correspond to the Fe1 sub-lattice which is occupied by a random distribution of Fe^{3+} and Cr^{3+} ions, and the Fe2 sub-lattice within tetrahedral layers, which are predominantly occupied by Ga^{3+} ions. These two layers are individually antiferromagnetically ordered and are also coupled antiferromagnetically to each other. The magnetic moments are aligned along crystallographic *a*-direction. The ordered magnetic moments obtained at 6 K in the octahedral and tetrahedral sites are 3.15 (2) μ_B/cation (Fe/Cr) and 0.93 (4) μ_B/cation (Fe) respectively. Even though the tetrahedral sites are occupied by Fe^{3+} ions, the observed moment is very low. That is because of lower concentration (only 9.0 %) of Fe^{3+} in tetrahedral sites[28], if we ignore the Fe^{3+} ion in the tetrahedral sites the goodness of fit deteriorated significantly. Temperature evolution of ordered magnetic moments of octahedral sites and tetrahedral sites obtained from the refinement of NPD data is depicted in Fig.10. The presence of magnetic moments at 300 K in both sites (octahedral as well as tetrahedral) confirms the AFM ordering at room temperature. The G-type antiferromagnetic structure obtained from the NPD data at 6 K is very similar to the magnetic structure of parent material, $Ca_2Fe_2O_5$[9] and also to other single layered Brownmillerites such as $SrCaMnGaO_5$[29], Sr_2MnGaO_5 and Ca_2MnAlO_5[30].

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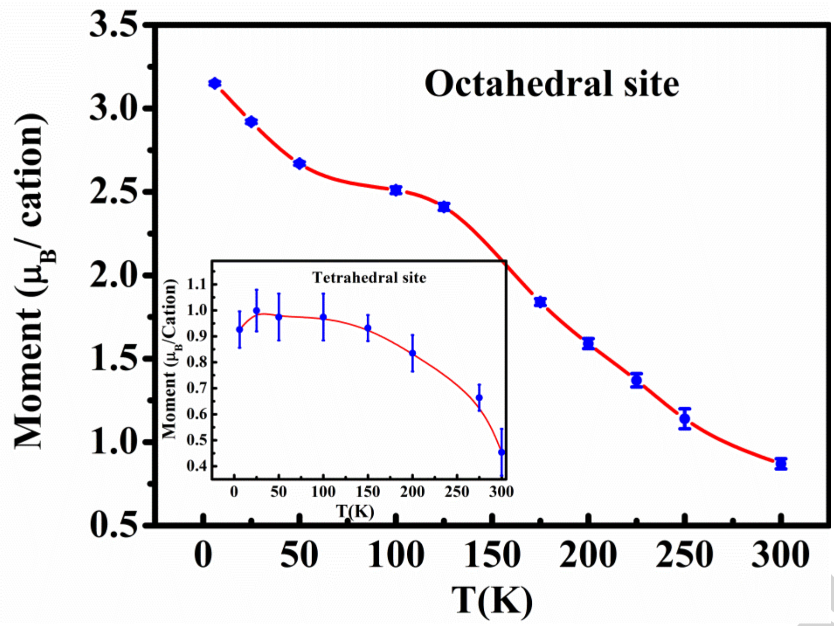

Fig. 10 Temperature variation of ordered magnetic moment at octahedral site (inset: moment at tetrahedral site)

The ZFC and FC thermomagnetic analysis as well as magnetic isotherms show the co-existence of AFM-FM phases within the layers even though the compound as a whole is AFM. NPD data confirms AFM ordering even at 300 K, but the evidence for the coexistence of AFM-FM magnetic phases and/or any spin canting is not at all observed probably because the FM component of the spins is too weak. The observed magnetism in the present compound can be explained on the basis of superexchange interactions[12]. The compound possesses a layered crystal structure, and the bond angle (~ 166˚) (intra-layer) in the octahedral layers (ac plane) alone are favourable for linear super exchange interaction since all other bond angles (inter layer as well as tetrahedral intra-layer (~ 139˚)) possess a large distortion from linear superexchange pathways (Table-1). Hence the dominant contribution to the magnetization comes from octahedral sites. The magnetization data as well as NPD data support long range three dimensional AFM ordering even at 300 K. Since the majority of octahedral sites are occupied by Fe^{3+} ions (~ 79 %, Fe rich region), the major contribution in the magnetization will be from Fe^{3+}-O-Fe^{3+} AFM superexchange interactions. The strength of Fe^{3+}-O-Fe^{3+} interaction in the octahedral site gets diluted due to the mixing of other metal ions (~ 12 % Cr^{3+} and ~ 9.0 % Ga^{3+}), resulting in much lower T_N (~ 582 K) compared to that of the parent compound $Ca_2Fe_2O_5$ (T_N = 725 K). Since this is a B-site disordered system, we cannot exclude the possibility of minor AFM superexchange Cr^{3+}-O-Cr^{3+} arising from Cr^{3+} rich regions (~ 12 % Cr^{3+}), which might be responsible for the transition at 225 K[11]. Finally, the presence of minor hysteresis in the M vs H curve at 5 K and the upturn in the thermomagnetic curves below 50 K supports the existence of FM correlation at lower temperatures which might be associated either to weak FM superexchnage interaction from Cr^{3+}-O-Fe^{3+} or to AFM spin canting which is common in the case of Fe/Cr based perovskites[24,31-32]. Thus we conclude that the compound possesses co-existence of major AFM phase arising from Fe^{3+}-O-Fe^{3+} along with weak AFM Cr^{3+}-O-Cr^{3+} and FM Cr^{3+}-O-Fe^{3+} interactions.

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4. Conclusion

The crystal and magnetic structures of a novel Brownmillerite compound, $Ca_2Fe_{0.875}Cr_{0.125}GaO_5$, were determined. The structural analysis confirmed that the compound crystallizes into a single phase orthorhombic structure with a space group *Pnma* having a mixing of 9.0 % Fe and Ga ions in both octahedral and tetrahedral sites. The temperature evolution of NPD confirms the absence of any structural changes in the temperature range 300 to 6 K. However, the increase in intensity of a low angle peak as the temperature is lowered indicates magnetic ordering. The compound possesses a *G*-type antiferromagnetic structure which involves both intra-as well as inter-layer AFM coupling of nearest neighbour spins. The ordered magnetic moments at 6 K are 3.15 (2) μ_B/cation and 0.93 (4) μ_B/cation in the octahedral and tetrahedral sites respectively. The magnetic characterizations showed the existence of weak FM correlations even though the compound as a whole is antiferromagnetic. The absence of any FM features in NPD derived magnetic structure points to weak FM correlation in the present compound.

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Highlights

- Crystal and magnetic structure of $Ca_2Fe_{0.0875}Cr_{0.125}GaO_5$ was studied thoroughly
- Compound possesses orthorhombic *Pnma* space group
- ~ 9 % of Fe/Ga disorder between the Fe/Cr – octahedral and Ga –tetrahedral layers
- Magnetic structure is found to be G-type antiferromagnetic

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