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# Role of rare earth on the $Mn^{3+}$ spin reorientation in multiferroic $Ho_{1-x}Lu_xMnO_3$

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The role of rare earth ion  $R^{3+}$  in spin reorientation and magneto dielectric response is investigated by substitution of non-magnetic smaller ionic radii  $Lu^{3+}$  in multiferroic hexagonal  $HoMnO_3$ . The XRD analysis suggests that the dopant may preferably goes to  $C_{3V}$  site up to 1/3rd of the composition in order to reduce the lattice distortion. We suggest that the  $R^{3+}$  ion at  $C_3$  site could play a strong role in spin reorientation than the  $C_{3V}$  site. The observation of  $T_{SR}$  even in  $LuMnO_3$  precludes the role of rare earth magnetic moment in driving the spin reorientation. Surprisingly, the magneto dielectric response of  $HoMnO_3$  is dominated by the rare earth  $RO_8$  dipoles. The oppositely oriented  $RO_8$  dipole at the  $C_{3V}$  and  $C_3$  determines the magneto dielectric response in various magnetic phases reaffirming the site specific substitution. Thus, site specific doping could be a way to enhance the magneto electric coupling strength. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4819969>]

## I. INTRODUCTION

Multiferroics are multi-functional materials which exhibit several order parameters simultaneously, i.e., ferroelectric, ferromagnetic, and ferroelastic.<sup>1–3</sup> The inherent magneto electric coupling which might offer an additional degree of freedom in device design, entails them wide variety of technological application.<sup>4,5</sup> Even though the existence of such magneto electric coupling has been predicted long back,<sup>6,7</sup> their observation is limited,<sup>8</sup> as their origin are mutually exclusive in conventional materials.<sup>9</sup> However, the origin of ferroic properties in these new class of materials is different from that of convention ferroelectric and ferromagnetic materials.<sup>10</sup> Recent observation of magneto electric coupling in compounds such as hexagonal  $RMnO_3$ ,<sup>11–13</sup> orthorhombic  $RMnO_3$ ,<sup>14</sup>  $BiFeO_3$ ,<sup>15</sup> and  $BiMnO_3$ ,<sup>16</sup> where  $R$  is rare earth ion, provided the much needed impetus for the research in multiferroics.

Rare earth hexagonal manganites  $RMnO_3$  ( $R = Ho, Er, Tm, Yb, Lu$  and  $Y$ ) is an important class of multiferroic material due to their high ferroelectric Curie temperature ( $T_C$  around 900 K) and high polarization. However, their low antiferromagnetic ordering temperature  $T_N$  (at 70 K)<sup>17</sup> and weak magneto electric coupling<sup>18,19</sup> forbid them from practical applications. In these partially filled  $d$ -orbital hexagonal manganites, ferroelectricity can be attributed to unusual trigonal bipyramidal (5-fold) coordination of  $Mn^{3+}$ , whereas the ferromagnetism is ascribed to partially filled  $d$ -orbitals of  $Mn^{3+}$ .<sup>20</sup> The existence of anomalies in the dielectric constant and the structural parameters at the  $T_N$  confirm the magneto electric coupling of these compounds which is indeed mediated by the lattice strain arising from the magnetic ordering.<sup>21,22</sup>

$HoMnO_3$  is a well studied compound where both  $Ho^{3+}$  and  $Mn^{3+}$  are magnetic ions. Thus,  $HoMnO_3$  exhibits complex magnetic phase diagram with three magnetic transitions at 70 K, 32 K, and 5 K. The transition at 70 K is attributed to

frustrated in-plane magnetic ordering of  $Mn^{3+}$  spins (space group  $P6_3'c'm$ ). The transition at 5 K ( $T_2$ ) is attributed to antiferromagnetic ordering of  $Ho^{3+}$  moments.<sup>23</sup> Researchers in general ascribe the transition at 32 K to the  $Mn^{3+}$  spin reorientation (magnetic space group  $P6_3'cm'$ ), but its driving force is not yet conclusively determined. Few have suggested that the partial or complete ordering of  $Ho^{3+}$  drives the spin reorientation.<sup>5,24</sup> However, the rare earth ordering generally occurs at very low temperatures (much <10 K) in oxides as double exchange of  $f$ -orbital is considerably weaker. Furthermore, Zhou *et al.*<sup>25</sup> reported that the substitution of non-magnetic  $Y^{3+}$  of similar ionic radii shifts the  $T_{SR}$  to a higher temperature which contradicts the reported rare earth ordering driven spin reorientation. They also observed that the  $T_{SR}$  vanishes between 0.6 and 0.7 level of  $Y^{3+}$  concentration in the magnetic measurement. The sudden vanishing of  $T_{SR}$  between 0.6 and 0.7 can be correlated to site specific substitution and its role in spin reorientation. Our earlier studies on  $Ho_{1-x}Dy_xMnO_3$  suggest that the dopant  $Dy^{3+}$  preferred  $C_{3V}$  (occupied by 1/3rd of  $R^{3+}$ ) site which lies at the edge of cell and enhances the magneto electric coupling.<sup>26</sup> To investigate the role of rare earth and its site symmetry on spin reorientation and magneto electric coupling, we doped non-magnetic smaller ionic radii  $Lu^{3+}$  in  $HoMnO_3$  as complementary to the  $Y^{3+}$  substitution. We synthesized a series of hexagonal  $Ho_{1-x}Lu_xMnO_3$  compounds and studied their dielectric properties and magneto dielectric response. Our observations suggest that the rare earth undergoes sites specific substitution and its dopant site ( $C_{3V}$  or  $C_3$ ) could play an important role in determining the  $T_{SR}$  and the magneto electric coupling strength.

## II. EXPERIMENTAL

Series of polycrystalline  $Ho_{1-x}Lu_xMnO_3$  ( $x = 0, 1/3, 1/2, 2/3$  and 1) samples are prepared by solid state route. The parent compounds  $Ho_2O_3$ ,  $Mn_2O_3$  and  $Lu_2O_3$  are ground well and calcinated at 1350 °C for 12 h. To obtain the phase pure

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compound, the powders of  $\text{Ho}_{1-x}\text{Lu}_x\text{MnO}_3$  are re-calcined at  $1500^\circ\text{C}$  for 6 h. Powder x-ray powder diffraction (XRD) patterns are obtained for the entire set of samples by using a PANANALYTIC x-ray diffractometer and the lattice parameters are calculated using Xpert highscore plus. We have employed Magnetic Property Measurement System for the magnetic measurements. For dielectric measurements, the pellets of  $\text{Ho}_{1-x}\text{Lu}_x\text{MnO}_3$  are coated with silver electrode to form parallel plate capacitor geometry and the capacitance is measured using Agilent 4248 RLC bridge in the frequency range of 5 kHz–100 kHz. The bridge is coupled to Physical Property Measurement System in order to vary the temperature from 10 to 300 K and magnetic field from 0 to 14 T.

### III. RESULTS AND DISCUSSION

#### A. Structure and magnetic properties

The powder x-ray diffraction pattern of  $\text{Ho}_{1-x}\text{Lu}_x\text{MnO}_3$  ( $x=0, 1/3, 1/2, 2/3$  to 1) series confirm that the compounds are crystallized in the hexagonal structure with  $\text{P6}_3\text{cm}$  space group. The evolution of the lattice parameter  $a$  and the  $c/a$  ratio on  $\text{Lu}^{3+}$  substitution in  $\text{HoMnO}_3$  is shown in Figs. 1(a) and 1(b), respectively. Both  $a$  and  $c/a$  starts deviating at the composition  $x > 1/3$  from the expected linear variation as per Vegard's law which is a strong indication for the lattice distortion. In hexagonal  $\text{RMnO}_3$ , the  $\text{R}^{3+}$  ion occupies the sites, namely  $\text{C}_{3\text{V}}$  and  $\text{C}_3$ .<sup>27</sup> The  $\text{C}_{3\text{V}}$  site, where 1/3rd of the rare earth occupies, lies at the edge of the unit cell. On the other hand the  $\text{C}_3$  site, where the remaining 2/3rd of the rare earth occupies, lies well inside unit cell. Due to different symmetries, we suggest that the dopant may preferably occupy one of these sites which can explain the variation in lattice parameters with doping concentration. Upon doping, initially ( $x \leq 1/3$ ) the dopant  $\text{Lu}^{3+}$  ion replaces  $\text{Ho}^{3+}$  ion at the highly symmetric  $\text{C}_{3\text{V}}$  site which results in the linear variation of the lattice parameters with  $x$ . On further increase in  $x (> 1/3)$ , the  $\text{Lu}^{3+}$  replaces the remaining  $\text{Ho}^{3+}$  ions at less symmetric  $\text{C}_3$  site which could lead to large distortion in the lattice.

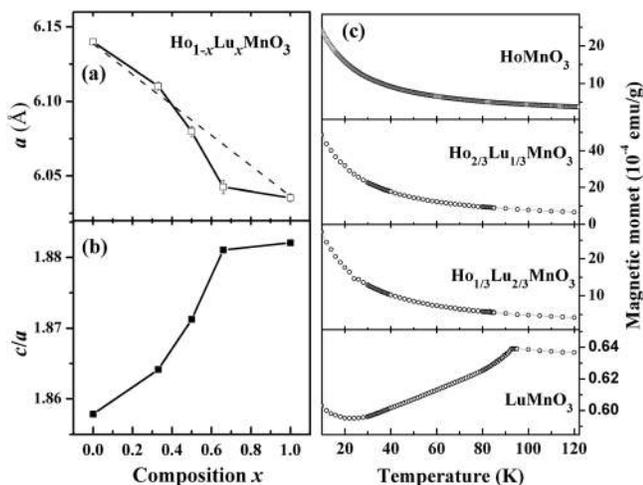


FIG. 1. (a) and (b) show the compositional variation of lattice parameter  $a$  and  $c/a$  ratio for  $\text{Ho}_{1-x}\text{Lu}_x\text{MnO}_3$ . The dashed line indicates the linear evolution based on Vegard's law. (c) The magnetic moment as a function of temperature in the ZFC case for  $\text{Ho}_{1-x}\text{Lu}_x\text{MnO}_3$ .

Though our XRD results suggest the site specific substitution, we find an indirect evidence for site specific substitution in our dielectric and magnetoelectric coupling studies.

The magnetization is measured as a function of temperature for all the samples from 10 K to 300 K. The magnetization data under zero field cooled condition are shown in Fig. 1(c) for  $x=0, 1/3, 2/3$  and 1 from 120 K to 10 K. Though we intend to study role of rare earth on the magnetic spin reorientation, the scope of the magnetic measurements to reveal any such ordering is limited due to the masking effect of high paramagnetic moment of the rare earth  $\text{Ho}^{3+}$  ion. Even the antiferromagnetic ordering (near 70 K) is masked for all the samples except for  $\text{LuMnO}_3$  as shown in Fig. 1(c). The  $T_N$  in  $\text{LuMnO}_3$  is visible because of non-magnetic nature of the  $\text{Lu}^{3+}$  ion.<sup>28</sup> However, due to the magnetoelectric nature of these compounds, the magnetic transitions are expected to manifest in the dielectric constant measurements.

#### B. Dielectric studies

Dielectric constant of the samples are measured as a function of temperature from 10 K to 300 K with applied magnetic field of 0 to 5 T at various frequencies from 5 to 100 kHz. The dielectric constant of the samples remain frequency independent indicating the intrinsic contributions from the samples. The low dielectric loss (well below 0.005 even up to 150 K) also confirm the intrinsic ferroelectric response and insulating behaviour in the temperature of our interest. At  $T_N$ , Mn undergoes a two dimensional triangular antiferromagnetic ordering, resulting in a strongly frustrated system which effectively couples the spin to lattice which in turn leads to magnetoelectric coupling.

Figure 2 shows the derivative of dielectric constant as a function of temperature for  $\text{Ho}_{1-x}\text{Lu}_x\text{MnO}_3$  series from 60 K to 100 K. The peak in the graph corresponds to the antiferromagnetic ordering temperature  $T_N$  and it is observed at 75, 79, 82, 85, and 92 K for the compositions  $x=0, 1/3, 1/2, 2/3$ , and

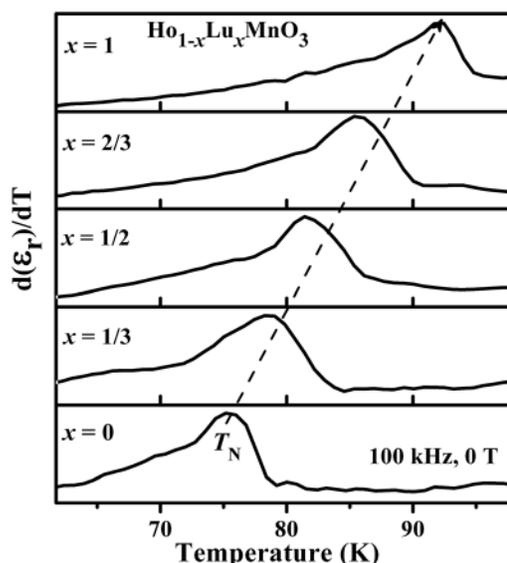


FIG. 2. Derivative of dielectric constant as a function of temperature near the  $T_N$  for  $\text{Ho}_{1-x}\text{Lu}_x\text{MnO}_3$  series. The evaluation of  $T_N$  with composition  $x$  is marked by dashed arrow.

1, respectively. The  $T_N$  increases with increase of composition  $x$  and the dashed line indicates the linear evolution of  $T_N$ . This is in accordance with smaller ionic radii of the  $\text{Lu}^{3+}$  ion which modulates the Mn-O-Mn interactions. Deviation of  $T_N$  from the linear behavior agrees with that of the deviation in  $c/a$  ratio in the intermediate compositions which indicates the inherent response arise from the structural distortion.

Upon decreasing the temperature,  $\text{Mn}^{3+}$  undergoes a spin reorientation transition of first order around 35 K which is reflected in the dielectric measurement due to strong spin-lattice coupling. The dielectric constant as a function temperature for  $\text{Ho}_{1-x}\text{Lu}_x\text{MnO}_3$  ( $x=0, 1/3, 1/2, 2/3$  and 1) in the magnetic field of 0 T and 1 T measured at 100 kHz is shown in Figs. 3(a) and 3(b), respectively.

At 0 T, the dielectric data of the polycrystalline  $\text{HoMnO}_3$  shown in Fig. 3(a) exhibit a hump at 34 K which corresponds to the spin reorientation  $T_{\text{SR1}}$  of  $\text{Mn}^{3+}$  and it agrees well with that of single crystal data.<sup>21</sup> With  $\text{Lu}^{3+}$  doping, the  $T_{\text{SR1}}$  remains at 34 K up to  $x=1/3$  and decreased to a lower value of 30 K and 28 K for  $x=1/2$  and  $x=2/3$ , respectively. However, when  $x=1$ , i.e., for  $\text{LuMnO}_3$ , we did not see the spin reorientation as reported in the literature. The evolution of  $T_{\text{SR1}}$  with composition  $x$  is marked by a dashed line in Fig. 3(a). The change in  $T_{\text{SR1}}$  with  $\text{Lu}^{3+}$  doping strongly suggests the site specific occupancy of the rare earth ion. The fact that the  $T_{\text{SR1}}$  remains same with doping up to  $x=1/3$  points out that the  $\text{Lu}^{3+}$  replaces  $\text{Ho}^{3+}$  at the  $\text{C}_{3\text{V}}$  site which could play a limited role in the spin reorientation. Upon further increase of  $x$ , the decrease of  $T_{\text{SR1}}$  gives the notion that  $\text{Lu}^{3+}$  replaces the  $\text{Ho}^{3+}$  at  $\text{C}_3$  site which could play an active role in the spin reorientation. The decrease of  $T_{\text{SR1}}$  with lower ionic radii  $\text{Lu}^{3+}$  substitution is in agreement with earlier report of  $\text{Er}^{3+}$  doped  $\text{HoMnO}_3$ .<sup>29</sup> Also the increase in intensity of  $T_{\text{SR1}}$  peak ( $x=1/2$  and  $2/3$ ) signifies the strong spin lattice coupling mediated by the strain due to lattice distortion. Interestingly, the composition  $x=1/2$  exhibits an additional hump in the dielectric constant at 45 K and it is marked as  $T_{\text{SR2}}$  in Fig. 3(a).

At 1 T, shown in the Fig. 3(b), we did not see any significant change in  $T_{\text{SR1}}$ . Surprisingly, the compounds with  $x > 1/3$  all show an additional hump around 40 K including the pure

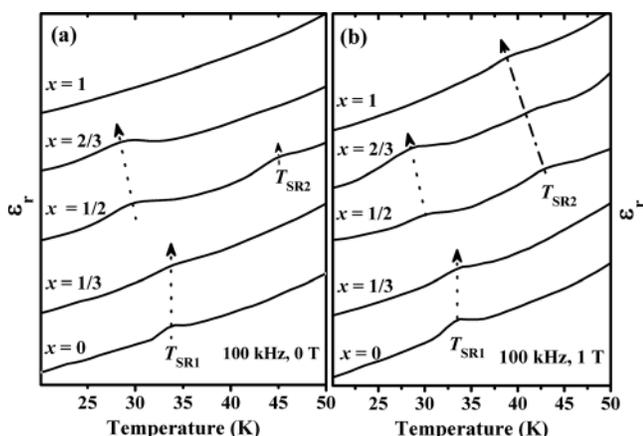


FIG. 3. Dielectric constant as a function of temperature for  $\text{Ho}_{1-x}\text{Lu}_x\text{MnO}_3$  at a magnetic field of (a) 0 T and (b) 1 T. The arrows indicate the evolution of the  $T_{\text{SR}}$  with composition  $x$ .

$\text{LuMnO}_3$ . The appearance of the hump in an applied magnetic field and its variation with dopant concentration strongly suggest it to be of magnetic origin, i.e., the spin reorientation  $T_{\text{SR2}}$ . Recent dielectric study on  $\text{Fe}^{3+}$  substituted  $\text{LuMnO}_3$  shows the signature of spin reorientation even at 0 T.<sup>30</sup> The  $T_{\text{SR2}}$  revealed in  $\text{LuMnO}_3$  at 40 K precludes rare earth magnetic moment driven spin reorientation. The change in  $T_{\text{SR2}}$  with the composition can be understood with respect to the site specific substitution of  $\text{Ho}^{3+}$  in  $\text{LuMnO}_3$ . Up to  $x > 1/3$  in  $\text{Ho}_{1-x}\text{Lu}_x\text{MnO}_3$ , the  $\text{Ho}^{3+}$  ion replaces the  $\text{Lu}^{3+}$  ion in active  $\text{C}_3$  site and hence shows increase in  $T_{\text{SR2}}$  with increase in  $\text{Ho}^{3+}$  content. The increase of  $T_{\text{SR2}}$  with higher ionic radii  $\text{Ho}^{3+}$  doping in  $\text{LuMnO}_3$  agrees with that of higher ionic  $\text{Y}^{3+}$  substitution in the  $\text{HoMnO}_3$ . When  $x \leq 1/3$ , the  $\text{Ho}^{3+}$  started replacing the remaining  $\text{Lu}^{3+}$  ion in inactive  $\text{C}_{3\text{V}}$  site. The absence of  $\text{Lu}^{3+}$  ion at  $\text{C}_3$  site accounts for the absence of  $T_{\text{SR2}}$  for  $x \leq 1/3$  compositions which corroborates the site specific substitution. The preferential site occupation of rare earth ions in  $\text{Ho}_{1-x}\text{Lu}_x\text{MnO}_3$  is given in Table I.

On further increase in magnetic field, at 3 T, similar to the single crystal,<sup>21</sup> the  $T_{\text{SR1}}$  of polycrystalline  $\text{HoMnO}_3$  sample splits in to two transitions as shown in Fig. 3(a). The split in the transition is revealed as broadening of the  $T_{\text{SR1}}$  in other compositions. Surprisingly, the  $T_{\text{SR2}}$  corresponding to  $\text{LuMnO}_3$  also shows split in the transition similar to the  $T_{\text{SR1}}$  in single crystal  $\text{HoMnO}_3$  ascertaining it to be the spin reorientation transition. At 5 T as shown in Fig. 4(b), the  $T_{\text{SR1}}$  of  $\text{HoMnO}_3$  vanishes which is in agreement with the reported single crystal data.<sup>21</sup> However, the signature of  $T_{\text{SR1}}$  for the compositions  $x=1/2$  and  $2/3$  indicates the enhancement of  $\text{P6}'\text{cm}'$  phase upon  $\text{Lu}^{3+}$  doping. On the other hand, the  $T_{\text{SR2}}$  vanishes in all the doped samples.

### C. Magneto dielectric studies

The magnetic field variation of dielectric constant at constant temperature (at 10 K) is reported to change the magnetic phase from  $\text{P6}'_3\text{cm}'$  to  $\text{P6}_3\text{c}'\text{m}$ . The site dependence of  $T_{\text{SR}}$ , where magnetic phase changes from  $\text{P6}'_3\text{cm}'$  (below  $T_{\text{SR}}$ ) to  $\text{P6}_3\text{c}'\text{m}$  (above  $T_{\text{SR}}$ ) is also expected to reveal in magnetic field induced phase transition. In order to ascertain the role of site symmetry, the dielectric constant is measured as a function of applied magnetic field at 10 K. Figure 5(a) shows the evolution of dielectric constant as a function of applied magnetic field up to  $\pm 14$  T at 10 K. The dielectric constant of  $\text{HoMnO}_3$  increases uniformly and shows a slope change around 3.5 T, where the  $\text{Mn}^{3+}$  undergoes a spin reorientation (magnetic phase  $\text{P6}_3\text{c}'\text{m}$ ). Remember that the single crystal

TABLE I. Preferential site occupation rare earth ions in  $\text{Ho}_{1-x}\text{Lu}_x\text{MnO}_3$ . P-Present, A-Absent,  $\text{C}_{3\text{V}}$ -spin reorientation inactive,  $\text{C}_3$ -spin reorientation active.

$x$	$\text{C}_{3\text{V}}$ site	$\text{C}_3$ site	$T_{\text{SR1}}$	$T_{\text{SR2}}$
0	1/3Ho	2/3Ho	P	A
1/3	1/3Lu	2/3Ho	P	A
1/2	1/3Lu	1/6Lu+1/2Ho	P	P
2/3	1/3Lu	1/3Lu+1/3Ho	P	P
1	1/3Lu	2/3Lu	A	P

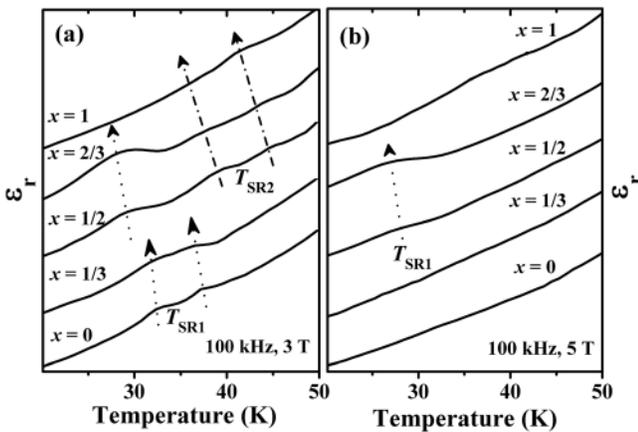


FIG. 4. Dielectric constant as a function of temperature for  $\text{Ho}_{1-x}\text{Lu}_x\text{MnO}_3$  at a magnetic field of (a) 3 T and (b) 5 T. The arrows indicate the evolution of the  $T_{\text{SR}}$  with composition  $x$ .

$\text{HoMnO}_3$  undergoes the magnetic phase changes at 3.5 T from  $\text{P6}_3'\text{cm}'$  to  $\text{P6}_3'\text{c}'\text{m}$ .<sup>21</sup> The dielectric constant reaches its maximum value around 7 T with a decreasing trend upon further increase in the magnetic field. Van Aken *et al.*<sup>31</sup> reported that the rare earth dipoles  $R1O_8$  and  $R2O_8$  corresponding to the  $C_{3V}$  and  $C_3$  sites are oriented in opposite directions as shown schematically in Fig. 5(b). At the antiferromagnetic ordering  $T_N$ , the  $R1O_8$  dipole grows at the expense of  $R2O_8$  indicating the change in character of the dipoles upon magnetic phase change.<sup>31</sup> For  $\text{HoMnO}_3$ , in the  $\text{P6}_3'\text{cm}'$  phase ( $<3.5$  T), the dominance of  $R1O_8$  dipole at  $C_{3V}$  site results in a positive magneto dielectric response. Whereas, in the  $\text{P6}_3'\text{c}'\text{m}$  phase ( $>3.5$  T), the oppositely oriented  $R2O_8$  dipoles at  $C_3$  site dominates, leading to a negative magneto dielectric response. Upon  $\text{Lu}^{3+}$  doping, for  $x=1/3$ , the dielectric constant increase with field and shows a slope change around 4 T. However above 4 T, unlike in  $\text{HoMnO}_3$  the magneto dielectric response remains positive even in  $\text{P6}_3'\text{c}'\text{m}$  phase with decreased slope compared to  $\text{P6}_3'\text{cm}'$  phase. On further

increase in composition for  $x=1/2$  and  $2/3$ , the dielectric constant shows a peak around 4.5 T and 5 T, respectively, followed by a sharp negative response in the  $\text{P6}_3'\text{c}'\text{m}$  phase.

Such variation of magneto dielectric response in the high field  $\text{P6}_3'\text{c}'\text{m}$  phase upon  $\text{Lu}^{3+}$  doping can be understood based on the  $C_{3V}$  site specific substitution. At  $x=1/3$ , the preferential substitution of  $\text{Lu}^{3+}$  at  $C_{3V}$  site enhances the role of  $R1O_8$  dipole, thus dominating over the  $R2O_8$  dipole which results in the positive magneto electric response with decreased slope. Upon further increase of  $x$ , the dopant  $\text{Lu}^{3+}$  ion replaces  $\text{Ho}^{3+}$  in  $C_3$  site (change in site occupancy of the dopant ion) thereby enhancing the  $R2O_8$  dipole over  $R1O_8$  which results in a large negative magneto dielectric response for  $x > 1/3$ . Interestingly, the critical field ( $H_{\text{SR}}$ ) at which the magnetic phase changes from  $\text{P6}_3'\text{cm}'$  to  $\text{P6}_3'\text{c}'\text{m}$ , due to the  $\text{Mn}^{3+}$  spin reorientation, increase with increase in composition  $x$ . The enhancement of  $\text{P6}_3'\text{cm}'$  for high doping concentration is in agreement with the presence of  $T_{\text{SR1}}$  even at 5 T as seen in Fig. 4(b). The magneto dielectric response of the  $\text{Ho}_{1-x}\text{Lu}_x\text{MnO}_3$  samples indirectly reaffirms the site specific substitution. In fact our earlier paper showed that the magneto dielectric response of  $\text{HoMnO}_3$  is enhanced by more than 30 times upon  $\text{Dy}^{3+}$  substitution but attains the original value of  $\text{HoMnO}_3$  when  $x \sim 1/3$  ( $C_{3V}$  site is completely replaced) indicating the site specific substitution.<sup>26</sup>

#### IV. CONCLUSION

We have investigated the role of rare earth site symmetry on the spin reorientation and magneto dielectric response of  $\text{Ho}_{1-x}\text{Lu}_x\text{MnO}_3$  by measuring the dielectric constant as a function of temperature and magnetic field. The compositional variation of lattice parameter  $a$  and the  $c/a$  ratio suggested the preferential site substitution of dopant ion. The compositional variation of spin reorientation inferred from the dielectric constant studies corroborates the site specific substitution. In addition, it also brings out the active role played by the  $C_3$  site in the spin reorientation whereas the  $C_{3V}$  site remains inactive. Surprisingly, the dielectric constant studies at high field also revealed a spin reorientation corresponds to  $\text{LuMnO}_3$  discounting the theory of rare earth magnetic moment driven spin reorientation. The magneto dielectric study on  $\text{Ho}_{1-x}\text{Lu}_x\text{MnO}_3$  indicates that the magneto dielectric response is determined by dominance of the  $RO_8$  dipoles at the  $C_3$  and  $C_{3V}$  site in various magnetic phases. In addition, the magneto dielectric response of the doped samples reaffirms the site specific rare earth ion substitution. The site specific doping can be considered as a way to enhance the magneto dielectric response.

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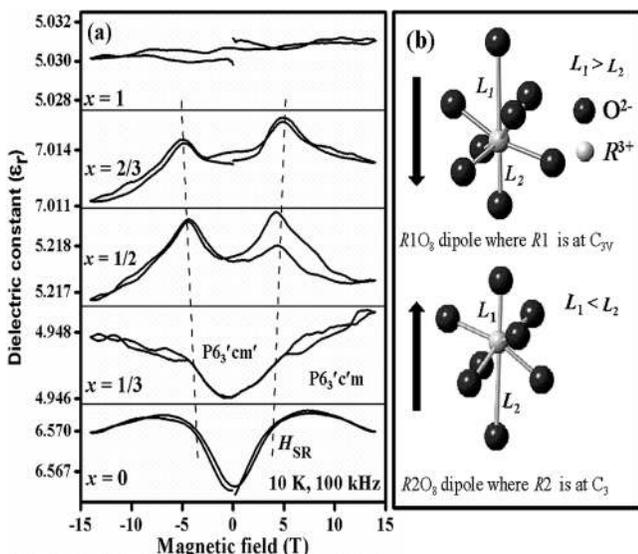


FIG. 5. (a) The variation of dielectric constant with magnetic field recorded at 10 K for  $\text{Ho}_{1-x}\text{Lu}_x\text{MnO}_3$ . (b) Schematic diagram of oppositely oriented  $RO_8$  dipoles at  $C_{3V}$  and  $C_3$  site.

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