Strong enhancement of magnetoelectric coupling in Dy3+ doped HoMnO3

J. Magesh, P. Murugavel, R. V. K. Mangalam, K. Singh, Ch. Simon et al.

Additional information on Appl. Phys. Lett.
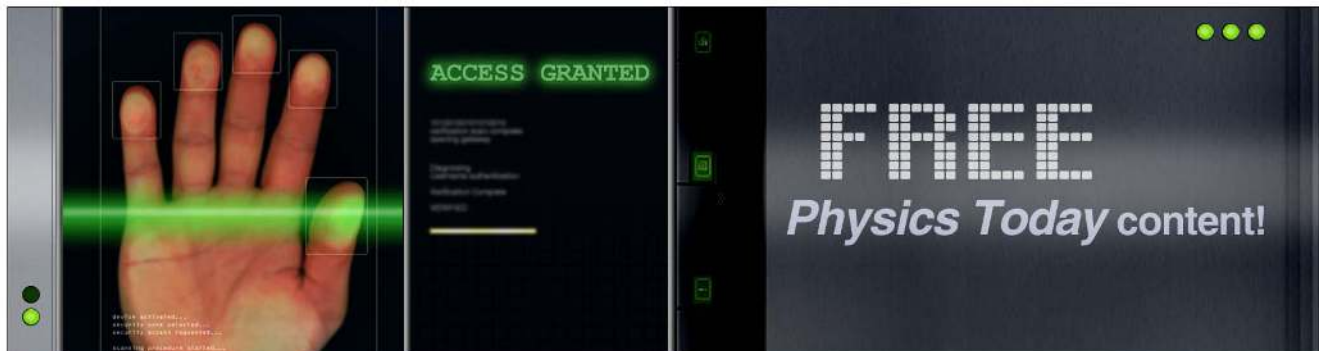
Strong enhancement of magnetoelectric coupling in Dy³⁺ doped HoMnO₃

J. Magesh,[1] P. Murugavel,[1,a)] R. V. K. Mangalam,[2] K. Singh,[2] Ch. Simon,[2] and W. Prellier[2]
[1]*Department of Physics, Indian Institute of Technology Madras, Chennai-600036, India*
[2]*Laboratoire CRISMAT, ENSICAEN/CNRS UMR 6508, 6 Blvd. Maréchal Juin, 14050 Caen, France*

The magnetoelectric effect in $Ho_{0.9}Dy_{0.1}MnO_3$ is found 31 times stronger than $HoMnO_3$ which could be due to strong lattice frustration arises out of the structural distortion on doping. The T_N observed from magnetic measurement reveals a double peak corresponding to the in-plane and inter-planar ordering leading to assignment of Γ_4 structure. The antiferromagnetic transition at T_N indeed drives dielectric transition mediated by the lattice strain whereas at the T_{SR}, lattice strain drives the spin reorientation of Mn^{3+}. In contrary to the long held belief, the magnetic structure changes from Γ_4 to Γ_1 at T_{SR} instead of Γ_4 to Γ_3. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4733367]

Multiferroics are those materials which exhibit several order parameters simultaneously, i.e., ferroelectric, ferromagnetic, and ferroelastic.[1–3] These materials offer an additional degree of freedom in device designing due to their inherent magnetoelectric coupling.[4,5] The existence of magnetoelectric coupling is evident in the dielectric measurements of rare earth hexagonal manganites $RMnO_3$ ($R = $ Y, Ho, Er, Tm, Yb, and Lu).[6–8] Even though the $RMnO_3$ has very low dielectric loss in comparison to other multiferroic materials like $BiFeO_3$ (Ref. 9) and $RCrO_3$ (Ref. 10) which is a prerequisite for applications, it suffers from the fundamental flaw that the magnetoelectric coupling is weak.[11] Based on the group theory, Bertaut *et al.*[12] predicted a weak magnetoelectric coupling when the axis of polarization is along the c direction whereas the magnetization is along the ab-plane.[13,14] However, a strong mgnetoelectric coupling can be achieved if either the magnetization has component along the c axis or polarization has a component along a or b axis. Magnetization component along the c axis occurs naturally in $RMnO_3$ where magnetic R^{3+} orders along the c axis.[15] However, the rare earth ordering occurs only below 5 K, rendering these materials inappropriate for practical applications. Such an off the axis magnetization or polarization can also be induced by structural distortions. A strong structural distortion is on the cards, as the dopant Dy^{3+} has slight higher ionic radii which crystallise in an orthorhombic phase of $RMnO_3$ at ambient pressure and temperature.[16] Thus, Dy^{3+} substitution in $HoMnO_3$ could lead to a strong lattice distortion, which in turn is expected to strengthen the magnetoelectric coupling. Furthermore, $HoMnO_3$ exhibits a complex magnetic phase diagram with three magnetic transitions at 70 K, 32 K, and 5 K. Even though the transitions at 32 K and 5 K are observed in the magnetic measurement of single crystals, the transition at 70 K do not manifest in magnetic measurement due to the masking effect of high paramagnetic moment of Ho^{3+}.[17] Indirect inference from dielectric and specific heat measurement leads to an ambiguity in the assignment of magnetic structure for various magnetic phases exhibited by $HoMnO_3$. In $HoMnO_3$, Mn^{3+} is suggested to undergo in-plane triangular frustrated antiferro-

magnetic ordering at 70 K whereas the inter-planar Mn^{3+} ordering is ignored,[18] considering it to be weak by two orders of magnitude,[19] as the inter planar Mn^{3+}-O-O-Mn^{3+} separation (6.5 Å) is almost twice than that of in plane Mn^{3+}-O-Mn^{3+} (3.5 Å) distance. But inter planar Mn^{3+}-O-O-Mn^{3+} interaction is the one which differentiates the α (ferro, Γ_1 and Γ_2) and β (antiferro, Γ_3 and Γ_4) structure. However, Lewtas *et al.*[20] reported the existence of both in-plane and inter-planar ordering in $LuMnO_3$. Based on the inelastic neutron diffraction, Fabreges *et al.*[21] suggest a change in the inter-layer coupling near the spin reorientation temperature T_{SR} at 32 K. Hence, substitution of higher ionic radii Dy^{3+} in $HoMnO_3$ could provide us an avenue both in terms of practical applications as well as to unravel the physics behind the magnetoelectric coupling in various magnetic phases. In order to study these, polycrystalline hexagonal $Ho_{0.9}Dy_{0.1}MnO_3$ is prepared by the solid state synthesis and their magnetic, dielectric, and magnetoelectric coupling response is measured. Interestingly, we observed a very strong enhancement of magneto electric coupling strength on Dy^{3+} doping along with a strong indication for the existence of inter-planar coupling between Mn^{3+} layers.

Polycrystalline $Ho_{0.9}Dy_{0.1}MnO_3$ is prepared by solid state route. Initially, the parent compounds $HoMnO_3$ and $DyMnO_3$ were synthesized from stoichiometric amount of Ho_2O_3, Mn_2O_3, and Dy_2O_3. The compounds are ground well and calcinated at 1350 °C for 12 h for several times to get uniform composition of $Ho_{0.9}Dy_{0.1}MnO_3$. Powder x-ray diffraction (XRD) patterns for the compounds are collected using a PANANALYTIC x-ray diffractometer and the lattice parameters are calculated using CELREF program. Magnetic measurements are carried out using the vibrating sample magnetometer (VSM) in the physical property measurement system (PPMS-Quantum Design). The capacitance is measured using Agilent 4248 RLC bridge in the frequency range of 5 kHz-100 kHz. The bridge is coupled to PPMS in order to vary the temperature from 10 to 300 K and magnetic field from 0 to 12 T.

An x-ray diffraction measurement confirms that the $Ho_{0.9}Dy_{0.1}MnO_3$ crystallizes in hexagonal $P6_3cm$ phase without any trace of competent orthorhombic phase. The lattice parameters a and c of $Ho_{0.9}Dy_{0.1}MnO_3$ obtained using

a)Electronic mail: muruga@iitm.ac.in.

101, 022902-1

CELREF program is found to increase to 6.147 Å and 11.424 Å from that of $HoMnO_3$ (6.134 Å and 11.406 Å) due to large ionic radii of dopant Dy^{3+}.

The temperature dependent magnetization measurement is performed from 4 K to 300 K with an applied magnetic field of 100 Oe in zero field cooled (ZFC) and field cooled (FC) conditions. Figure 1 shows the magnetization data of $Ho_{0.9}Dy_{0.1}MnO_3$ for both ZFC and FC. As such, the ZFC and FC measurements does not show any signature of antiferromagnetic ordering (T_N) at 70 K which is similar to that of single crystal $HoMnO_3$ (Ref. 22) due to high paramagnetic moment of Ho^{3+}. Though the magnetic measurement shows a dip at T_{SR} ($\sim$32 K) in the single crystal,[22] it is completely absent in case of polycrystalline samples.

Dielectric constant is measured as a function of temperature from 10 K to 300 K at various magnetic field applied parallel to the plane of the electrode. The measurement is done at various frequencies ranging from 5 kHz to 100 kHz. Below 220 K, the sample shows frequency independent dielectric behaviour emphasising the intrinsic contribution and insulating behaviour of sample. Moreover, the dielectric loss value is well below 0.05 and the dielectric constant value similar to that of single crystal indicating good quality of the sample.[22] As a representative example, the measurement done at 100 kHz in absence of magnetic field for $Ho_{0.9}Dy_{0.1}MnO_3$ is shown in Figure 1. The dielctric constant exhibits clear anomalies at 70 K and 40 K which corresponds to T_N and T_{SR}, respectively.

The difference in magnetic moment between ZFC to FC states could eliminate the contribution coming from paramagnetic moment of rare earth ion and it could throw some light on ordering of Mn^{3+} in the samples. Figure 2(b) shows the temperature variation of ZFC–FC for $Ho_{0.9}Dy_{0.1}MnO_3$. The graph reveals three transitions. One at 74 K, marked as T_{N1}, is due to in-plane Mn^{3+} antiferromagnetic ordering. It is noteworthy to mention that this transition, hitherto inferred from dielectric,[22,23] thermal conductivity,[24] and specific heat[25] measurements is confirmed unambiguously from the ZFC-FC data. The second one at 68 K, marked as T_{N2}, can be attributed to inter-planar ordering of Mn^{3+}. It is interesting that the inter-planar magnetic interaction which is two orders less in magnitude is revealed in the plot. If the inter-planar interac-
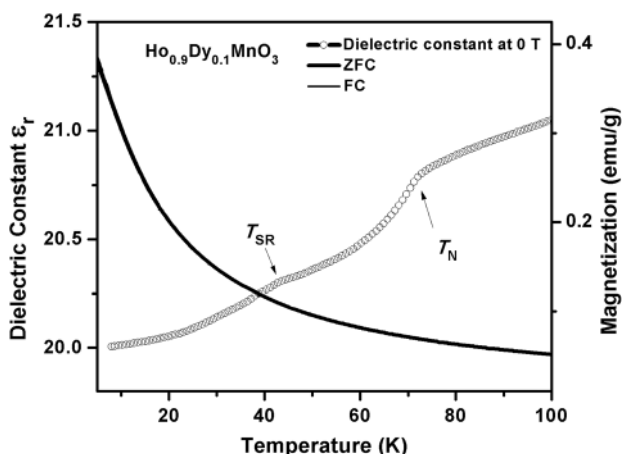

FIG. 2. (a) The difference between the ZFC and FC data as a function of temperature for $Ho_{0.9}Dy_{0.1}MnO_3$ and (b) the derivative of dielectric constant at various magnetic field near the T_N.

tion is ferromagnetic in nature (α structure), it will be reflected as a dip at 68 K rather than a hump. The observed hump which is similar in nature of T_{N1} indicates the existence of inter planar antiferromagnetic β structure (antiferro, Γ_3 and Γ_4). The origin of third transition at 61.5 K marked as T remains unclear. On contemplating about the transition at 61.5 K, the thought of secondary phase crossed our mind, but such a possibility can be excluded on the ground that the intensity decreases with increase of Dy^{3+} dopant concentration which is to be reported elsewhere. Thus, the transition T corresponds to a genuine magnetic phase of $HoMnO_3$.

Figure 2(a) shows the derivative of dielectric constant at various magnetic fields as a function of temperature for $Ho_{0.9}Dy_{0.1}MnO_3$. We observed a peak in the derivative of dielectric constant at 70 K near the T_N. The derivative clearly shows that the dielectric constant starts to change exactly at the magnetic transition and the derivative reaches a maximum at a temperature, which is 4 K less than that of the magnetic transitions. Interestingly, Lee *et al.*[26] reported lattice parameter change at T_N for $YMnO_3$ and $LuMnO_3$. This indicates that antiferromagnetic ordering of Mn^{3+} indeed drives the dielectric ordering mediated by the lattice strain.

Figure 3 shows the temperature variation of (FC–ZFC) and the derivative of dielectric constant at various magnetic fields for $Ho_{0.9}Dy_{0.1}MnO_3$ near the spin reorientation transition. The FC–ZFC data shows a broad hump at 36 K corresponding to the spin reorientation T_{SR}. Remember FC-ZFC response near the T_{SR} is opposite to that of the T_N, which indicates a ferromagnetic nature of transition (Note that in Figure 2(b), we plotted ZFC-FC variations). On considering the fact that the antiferromagnetic T_N is masked by high paramagnetic moment of Ho^{3+} even in single crystal,[22] if T_{SR} is completely antiferromagnetic, it will be masked much more effectively at low temperatures. Thus, the T_{SR} will be apparent in magnetic measurement only if it has a ferromagnetic component. Moreover, based on neutron diffraction, Lonkai *et al.*[27] and Munoz *et al.*[17] suggested a partial antiferromagnetic ordering of the Ho^{3+}. Even though a slight decrease of magnetic moment observed at T_{SR} is in favour of this

FIG. 1. Dielectric constant and magnetization as a function of temperature. Magnetization measurement is done in both ZFC and FC cases.

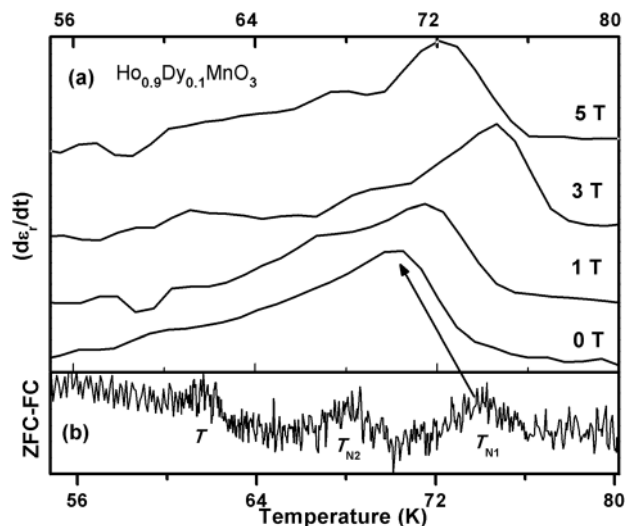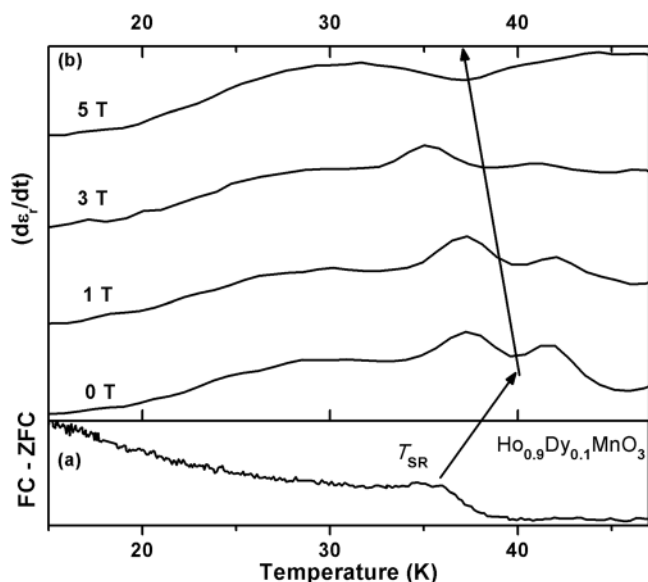FIG. 3. (a) Difference between the FC and ZFC data as a function of temperature for $Ho_{0.9}Dy_{0.1}MnO_3$ and (b) Derivative of dielectric constant at various magnetic fields near the T_{SR}.

conclusion,[22] the increase of magnetic moment in the FC case compared to that of ZFC at T_{SR} (Ref. 28) can be reinterpreted as presence of ferromagnetic inter layer (c-axis) coupling of the Mn^{3+}. On examining the T_N of $RMnO_3$ series, the higher ionic radii Y^{3+} orders in Γ_3 phase whereas the smaller ionic radii orders in Γ_4 phase which indicates that the inter layer separation plays a vital role in defining the magnetic structure. On applying the pressure, the $YMnO_3$ changes Γ_3 to mixture of $\Gamma_3 + \Gamma_4$ phase whereas the $LuMnO_3$ remain in the Γ_4 phase.[29] This leads to the observation that under pressure, the inter layer separation in $YMnO_3$ is effectively decreased thus moving on to mixture of $\Gamma_3 + \Gamma_4$ phase. On the other hand, $LuMnO_3$ which has inter layer distance smaller than that of the $YMnO_3$ remains on Γ_4 and does not lead to Γ_3. Hence, at T_{SR}, the change of magnetic phase in $HoMnO_3$ from Γ_4 to Γ_3 (inter-planar antiferromagnetic coupling) is highly improbable on decreasing the temperature as reported in the literature.[17,30–32] Furthermore, the position coordinate of Mn^{3+} (x) is $>1/3$ for $YMnO_3$ and $<1/3$ for $LuMnO_3$. At T_N, x of Γ_3 phase increases for $YMnO_3$ whereas it decreases for Γ_4 phase of $LuMnO_3$.[26] Hence the change of $x < 1/3$ to $x > 1/3$ is highly unlikely at T_{SR} thus precludes the phase change from Γ_4 to Γ_3. Consequently, the contrary nature of peak at T_{SR} to that of T_N indicates a change of inter layer coupling, i.e., transformation from β to α structure. We strongly believe that the Mn^{3+} inter layer antiferromagnetic coupling observed in $Ho_{0.9}Dy_{0.1}MnO_3$ near T_N changes into ferromagnetic near T_{SR} accompanied by in-plane spin reorientation, i.e., the magnetic structure changes from Γ_4 to Γ_1.

The spin reorientation is a first order transition, which will manifest as hump in the dielectric constant. The dielectric constant hump at the spin reorientation shown in Figure 1 is seen as a double peak in the derivative of dielectric constant at 40 K in Figure 3. In spite of a very sharp transition observed in single crystal $HoMnO_3$,[22] we observe a broad dielectric transition in $Ho_{0.9}Dy_{0.1}MnO_3$. Interestingly, the

dielectric transition precedes the magnetic transition by 4 K in this case. Based on the aforementioned observation, one can conclude that the orbital frustration of rare earth indeed drives the spin reorientation. The increase of T_{SR} on higher ionic radii Dy^{3+} doping also emphasis the role of orbital frustration in spin reorientation transition. However, the T_{SR} decrease slightly with increase of magnetic field is in agreement with the report by Zhou et al.[33]

The Figures 4(a) and 4(b) shows the variation of dielectric constant as a function of magnetic field for $HoMnO_3$ and $Ho_{0.9}Dy_{0.1}MnO_3$ at 10 K, respectively. In case of $HoMnO_3$, dielectric constant increases up to a magnetic field of ± 8 T and then decreases gradually up to a field ± 12 T. The magnetoelectric response of $HoMnO_3$ is similar to that of $YbMnO_3$.[34]

According to the phase diagram reported by Lorentz et al.,[35] at 10 K, the $HoMnO_3$ should exhibit three magnetic phases in the region of study. Regions I and II corresponding to the $P6_3'c'm$ and $P6_3'$ phase which exists up to a field of 2.5 T and 3.5 T, respectively. Region III is the high temperature phase $P6_3'cm'$. But the absence of these magnetic phases in our polycrystalline $HoMnO_3$ sample may indicate a weak magnetoelectric coupling. Abysmal % of change in the dielectric constant corroborates the weak magnetoelectric coupling in $HoMnO_3$.

The Dy^{3+} substitution in $HoMnO_3$ strongly enhances the magnetoelectric coupling behaviour due to various competing magnetic interactions. The % change of dielectric constant in an applied magnetic field which is a measure of magnetoelectric coupling increases by 31 times due to the strong lattice frustration arises from the Dy^{3+}. The % change of dielectric constant increases from 0.08% for $HoMnO_3$ to 2.5% for $Ho_{0.9}Dy_{0.1}MnO_3$. The Fig. 4(b) shows the dielectric constant of $Ho_{0.9}Dy_{0.1}MnO_3$ as a function of magnetic field

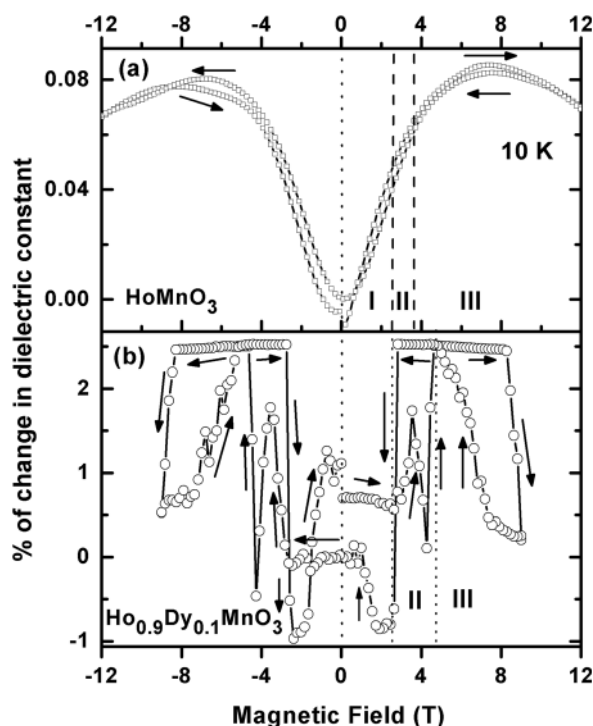

FIG. 4. Dielectric constant as a function of applied magnetic field for (a) $HoMnO_3$ and (b) $Ho_{0.9}Dy_{0.1}MnO_3$ at 10 K.

up to 9 T. The magnetoelectric response of $Ho_{0.9}Dy_{0.1}MnO_3$ can be divided into three magnetic phase regions corresponding to that $HoMnO_3$. The region I exists up to a magnetic field of 2.4 T. On the other hand, the region II which extends up to a magnetic field of 4.5 T has a contribution from the intermediate phase. Even though partial open loop behaviour is observed in region I, complete open loop behaviour is seen in regions II and III. The symmetric behaviour indicates that the overall response originates from the presence of various magnetic phases.

The Ho^{3+} occupies two different sites of site symmetry C_{3V} and C_3 in $HoMnO_3$.[36] The Ho^{3+} ion at C_{3V} site which lies at the edge of the unit cell holds the hexagonal unit cell. The C_{3V} site is occupied by $1/3^{rd}$ of the total Ho^{3+}. On the other hand, the C_3 site which lies well inside the unit cell is occupied by $2/3^{rd}$ Ho^{3+} decides the inter layer separation of Mn^{3+}. On $x = 0.1$ substitution, if the Dy^{3+} preferably occupies the C_{3V} site, then it will replaces one of the four Ho^{3+} which holds the unit cell and thereby leads to maximum distortion of hexagonal structure which in turn manifest as strong magnetoelectric coupling. The Curie-Weiss θ_{CW} temperature extrapolated from the linear region near the T_N in the dielectric measurement for $HoMnO_3$ is found to change from -771 K to -2330 K for $Ho_{0.9}Dy_{0.1}MnO_3$. The frustration factor $f (= |\theta_{CW}/T_N|)$ which is a measure of magneoelectric coupling increases from 10.2 to 33.3 on doping. The strong enhancement of frustration observed in $Ho_{0.9}Dy_{0.1}MnO_3$ is also a measure of lattice distortion, thus confirming the strain mediated coupling in these compounds. The inter-planar coupling defines magnetoelectric response as the ferroelectric polarization is along c axis. The different magnetoelectric response in various magnetic phases may be due to different nature of inter-planar magnetic interaction.

In summary, the magnetoelectric coupling in $Ho_{0.9}Dy_{0.1}MnO_3$ is enhanced by 31 times than that of pure $HoMnO_3$. The strong lattice distortion arising from higher ionic radii Dy^{3+} substitution is the key behind the strong magnetoelectric coupling. It also confirms the occurrence of inter-planar ordering near the T_N leads to assignment of magnetic strcutctre Γ_4 below 70 K (T_N). The T_N observed from the dielectric measurement is lower than that of the magnetic measurements indicates that the magnetic ordering drives the strain mediated magnetoelectric coupling which manifest in the dielectric measurement. However, the T_{SR} observed in the magnetic measurement is lower than that of the dielectric measurements concludes that the strain arises from the orbital distribution of particular site (C_3) drives the spin reorientation of Mn^{3+}. The magnetic measurement also concludes that the magnetic phase changes from Γ_4 to Γ_1 at T_{SR} rather than the Γ_3. Further study has to be done in order to reveal the role of lattice distortion in magnetoelectric coupling.

[1] N. A. Hill, J. Phys. Chem. B **104**, 6694 (2000).
[2] W. Prellier, M. P. Singh, and P. Murugavel, J. Phys.: Condens. Matter **17**, R803 (2005).
[3] D. I. Khomskii, J. Magn. Magn. Mater. **306**, 1 (2006).
[4] Y. H. Chu, L. W. Martin, M. B. Halcomb, and R. Ramesh, Mater. Today **10**, 16 (2007).
[5] Th. Lottermoser, T. Lonkai, U. Amann, D. Hohlwein, J. Ihringer, and M. Fiebig, Nature (London) **430**, 541 (2005).
[6] Z. J. Huang, Y. Cao, Y. Y. Sun, Y. Y. Xue, and C. W. Chu, Phys. Rev. B **56**, 2623 (1997).
[7] T. Katsufiji, M. Masaki, A. Machida, M. Moritomo, K. Kato, E. Nishibori, M. Takata, M. Sakata, K. Ohoyama, K. Kitazawa, and H. Takagi, Phys. Rev. B **66**, 134434 (2002).
[8] D. G. Tomuta, S. Ramakrishnan, G. J. Nieuwenhuys, and J. A. Mydosh, J. Phys.: Condens. Matter **13**, 4543 (2001).
[9] P. Murugavel, J.-H. Lee, J. Y. Jo, H. Y. Sim, J.-S. Chung, Y. Jo, and M.-H. Jung, J. Phys.: Condens. Matter **20**, 415208 (2008).
[10] Z. X. Cheng, X. L. Wang, S. X. Dou, H. Kimura, and K. Ozawa, J. Appl. Phys. **107**, 09D905 (2010).
[11] P. Murugavel, J.-H. Lee, D. Lee, T. W. Noh, Y. Jo, M.-H. Jung, Y. S. Oh, and K. H. Kim, Appl. Phys. Lett. **90**, 142902 (2007).
[12] P. Coeure, P. Guinet, J. C. Peuzin, G. Buisson, and E. F. Bertaut, in *Proceedings of International Meeting on Ferroelectricity* (1966), Vol. 1, p. 332.
[13] B. B. Van Aken, T. M. Palstra, A. Filippetti, and N. A. Spaldin, Nature Mater. **3**, 164 (2004).
[14] D. Frohlich, St. Leute, V. V Pavlov, R. V. Pisarev, and K. Khon, J. Appl. Phys. **85**, 4762 (1999).
[15] H. D. Zhou, J. Lu, R. Vasic, B. W. Vogt, J. A. Janik, S. Brooks, and C. R. Wiebe, Phys. Rev. B **75**, 132406 (2007).
[16] S. Harikrishnan, S. Rößler, C. M. N. Kumar, H. L. Bhat, U. K. Rößler, S. Wirth, F. Steglich, and S. Elizabeth, J. Phys.: Condens. Matter **21**, 096002 (2009).
[17] A. Munoz, J. A. Alonso, M. J. Martinez-Lope, M. T. Casais, J. L. Martinez, and M. T. Fernandez-Diaz, Chem. Mater. **13**, 1497 (2001).
[18] Th. Lonkai, D. G. Tomuta, J. U. Hoffmann, R. Rschneider, D. Hohlwein, and J. Ihringer, J. Appl. Phys. **93**, 8191 (2003).
[19] E. F. Bertaut and M. Mercier, Phys. Lett. **5**, 27 (1963).
[20] H. Lewtas, A. T. Boothroyd, M. Rotter, H. Müller, M. D. Le, B. Roessli, J. Gavilano, P. Bourges, and D. Prabhakaran, Phys. Rev. B **82**, 184420 (2010).
[21] X. Fabreges, S. Petit, I. Mirebeau, S. Pailhès, L. Pinsard, A. Forget, M. T. Fernandez-Diaz, and F. Porcher, Phys. Rev. Lett. **103**, 067204 (2009).
[22] B. Lorenz, A. P. Litvinchuk, M. Gospodinov, and C. W. Chu, Phys. Rev. Lett. **92**, 087204 (2004).
[23] C. D. Cruz, F. Yen, B. Lorenz, Y. Q. Wang, Y. Y. Sun, M. Gospodinov, and C. W. Chu, Phys. Rev. B **75**, 060407(R) (2005).
[24] X. M. Wang, Z. Y. Zhao, C. Fan, W. Tao, X. G. Liu, W. P. Ke, X. Zaho, and X. F. Sun, Phys. Rev. B **82**, 094405 (2010).
[25] H. D. Zhou, R. Vasic, J. Lu, J. S. Brooks, and C. R. Wiebe, J. Phys.: Condens. Matter **20**, 035211 (2008).
[26] S. Lee, A. Pirogov, M. Kang, K.-H. Jang, M. Yonemura, T. Kamiyama, S.-W. Cheong, F. Gozzo, N. Shin, H. Kimura, Y. Noda, and J.-G. Park, Nature (London) **451**, 805 (2008).
[27] Th. Lonkai, D. Hohlwein, J. Ihringe, and W. Prandl, Appl. Phys. A: Mater. Sci. Process. **74**, 843 (2002).
[28] A. Midya, P. Mandal, S. Das, S. Banerjee, L. S. S. Chandra, V. Ganesan, and S. R. Barman, Appl. Phys. Lett. **96**, 142514 (2010).
[29] D. P. Kozlenko, S. E. Kichanov, E. V. Lukin, S. Lee, J. G. Park, and B. N. Savenko, High Press. Res. **30**, 252 (2010).
[30] M. Fiebig, C. Degenhardt, and R. V. Pisarev, J. Appl. Phys. **91**, 8867 (2002).
[31] P. J. Brown and T. Chatterji, J. Phys.: Condens. Matter **18**, 10085 (2006).
[32] O. P. Vajk, M. Kenzelmann, J. W. Lynn, S. B. Kim, and S.-G. Cheong, J. Appl. Phys. **99**, 08E301 (2006).
[33] H. D. Zhou, R. Vasic, and C. R. Wiebe, and J. S. Brooks, J. Appl. Phys. **103**, 07E319 (2008).
[34] H. Sugie, N. Iwata, and K. Khon, J. Phys. Soc. Jpn. **71**, 1558 (2002).
[35] B. Lorenz, F. Yen, M. M. Gospodinov, and C. W. Chu, Phys. Rev. B. **71**, 014438 (2004).
[36] M. Divis, J. Holos, M. Lastusaari, A. P. Litvinchuk, and V. Nekvasil, J. Alloys Compd. **451**, 662–665 (2008).