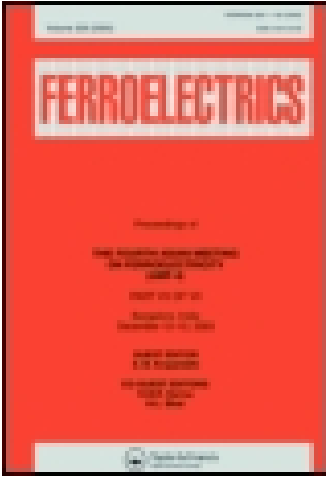


This article was downloaded by: [Cochin University of Science & Technology]

On: 31 July 2014, At: 23:49

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Ferroelectrics

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gfer20>

Multiferroic Behavior of Gd Based Manganite

S. Sagar ^a, P. A. Joy ^c & M. R. Anantharaman ^a

^a Department of Physics, Cochin University of Science and Technology, Cochin, 22, India

^b Department of Physics, Govt. Polytechnic College, Adoor, Manakkala, Pathanamthitta, Kerala, India

^c Physical Chemistry Division, National Chemical Laboratory (NCL), Pune, India

Published online: 11 Oct 2010.

To cite this article: S. Sagar, P. A. Joy & M. R. Anantharaman (2009) Multiferroic Behavior of Gd Based Manganite, *Ferroelectrics*, 392:1, 13-19, DOI: [10.1080/00150190903412408](https://doi.org/10.1080/00150190903412408)

To link to this article: <http://dx.doi.org/10.1080/00150190903412408>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Multiferroic Behavior of Gd Based Manganite

S. SAGAR,^{1,2,*} P. A. JOY,³ AND M. R. ANANTHARAMAN¹

¹Department of Physics, Cochin University of Science and Technology,
Cochin- 22, India

²Department of Physics, Govt. Polytechnic College, Adoor, Manakkala,
Pathanamthitta, Kerala, India

³Physical Chemistry Division, National Chemical Laboratory (NCL), Pune, India

Here we report the multiferroic nature of charge ordered manganite $Gd_{0.5}Sr_{0.5}MnO_3$ for the first time. The temperature variation of dielectric constant shows broad relaxor type ferroelectric transition at around 210K and magnetization measurements shows weak ferromagnetism at 50K. The dielectric peak is very close to charge ordering temperature which is an evidence of the link between electronic state and increase of dielectric response. Butterfly variation of capacitance with voltage confirms ferroelectric nature of the sample at room temperature.

Keywords Multiferroic; manganite; dielectric constant

1. Introduction

The study of ferroelectricity and magnetism has led to some of the most important technological advances [1–4]. Magnetism and ferroelectricity are involved with local spins and off-center structural distortions, respectively. These two seemingly unrelated phenomena can coexist in certain unusual materials, called multiferroics. Multiferroics, sometimes called magnetoelectrics, possess two or more switchable states such as polarization, magnetization or strain. The understanding of the physics of multiferroics is used to design smarter multiferroic materials and to control their functionality for practical applications. The ability to understand and control multiferroic behaviors may yield important applications such as electric-field-controlled ferromagnetic resonance devices, actuators, transducers, and storage devices with either magnetically modulated piezoelectricity or electrically-modulated piezomagnetism [5,6]. The magnetic transition temperature (T_N or T_C) and ferroelectric transition temperature (T_E) do not coincide. T_E is much greater than T_N or T_C in the case of $BiMnO_3$, $BiFeO_3$, $BiCrO_3$, $YCrO_3$ and hexagonal rare earth manganates $LnMnO_3$ (Ln -rare earth). In $TbMnO_3$ the ferroelectric transition temperature is less than T_C [7].

The family of rare earth manganites $Ln_{1-x}Ca_xMnO_3$ (Ln -rare earth) has attracted much attention in the last two decades due to their CMR effect [8–12]. They exhibit simultaneous phase transitions namely ferromagnetic to paramagnetic and metal to insulator. From a fundamental point of view the interplay of various factors that influence the electrical transport properties assume significance. A variety of parameters like charge, orbital coupling, magnetic ordering and lattice degrees of freedom have profound influence on the

Received March 13, 2009.

*Corresponding author. E-mail: srisagarsankar@yahoo.com

electrical and magnetic properties of these materials. The multiferroic nature of manganites $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$, $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ is recently reported and the effect is explained by using the mixing of site centered or bond centered charge ordering mechanisms [13–15]. Capacitance Voltage (C-V) characteristics are used to confirm the ferroelectric behavior of certain biferroics [7]. In this letter, we report multiferroic nature of charge ordered manganite $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ using temperature variation of dielectric constant and C-V measurements.

2. Experimental Details

The polycrystalline samples $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ were prepared using wet solid state reaction method. Stoichiometric amounts of Gd_2O_3 , SrCO_3 and MnO_2 were mixed in conc. HNO_3 . The solution was heated, boiling off the excess HNO_3 . This precursor was calcinated in air at 900°C overnight. The remaining black powder was pressed into pellets and sintered at 1200°C in air for 3 days [16]. The sample was analyzed by means of X-Ray Powder Diffractometer (Rigaku Dmax—C) using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5414\text{\AA}$). The low temperature dc conductivity (in the range 20K–300K) measurements were carried out by using source measuring unit. The dielectric permittivity studies on the Gd based manganite sample were carried out by using dielectric cell and an HP 4285 LCR meter in the frequency range 100 KHz—8 MHz from 145K to 310K. High measuring frequencies were used to avoid strong contact contribution at the sample electrode interface, which dominate at low frequencies. The dielectric cell was standardized by using Teflon. The principle of parallel plate capacitor was employed for the evaluation of permittivity. The LCR meter was interfaced with a PC using a virtual instrumentation package called LabVIEW. The capacitance voltage measurements were done for the Gd based manganites using the 4192A impedance analyzer at room temperature. The sample in the form of pellet (which was used for the dielectric measurements) was loaded in the cell. The bias dc voltage was varied from -8 to $+8$ volt and in each step the capacitance value was measured. The below room temperature magnetization (zero field cooled) measurement was done by using vibrating sample magnetometer.

3. Results and Discussion

From the XRD pattern (Fig. 1) it is clear that the sample $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ is single phasic with an orthorhombically distorted perovskite structure (spatial group Pbnm) [16,17]. The variation of resistivity with temperature is shown in Fig. 2. There is a slope change at 40K which is a signature of metal insulator phase transition. Generally in the case of manganites there is increase in resistivity with temperature at the metallic phase (i.e., with negative slope in the resistivity versus temperature diagram). But in the case of low bandwidth manganites there is no transition in the diagram in the absence of magnetic field. This is in agreement with the reported one [16]. Another slope change near 200K is indicative of charge ordering (CO) in the sample as reported by many groups in the case of similar perovskites [18,19].

The variation of dielectric permittivity with frequency at different temperatures for the sample is given in Fig. 3. The dielectric permittivity decreases with increase of frequency for the sample. The dielectric spectra reveal a quasi-Debye relaxation, which can be explained satisfactorily with the help of a two- or tri layer Maxwell-Wagner capacitor [18]. The Fig. 4 shows the temperature dependence of dielectric constant at different frequencies.

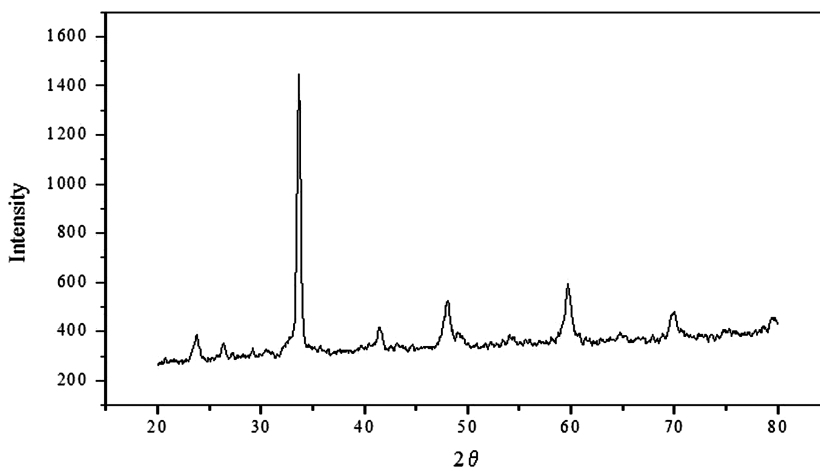


Figure 1. XRD pattern of $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ showing single phase perovskite structure.

From the figure it is clear that as temperature increases dielectric constant increases, attains a maximum value and then decreases. The dielectric peak is very close to T_{CO} , which is an evidence of the link between electronic state and increase of dielectric response [18]. The anomaly in dielectric constant at the charge ordering temperature was earlier observed in Pr-Ca manganites [20,21]. The peak height at the transition temperature was observed to decrease with increase in frequency and the dielectric constant peak shifted to lower temperature with increase in frequency, which indicates the relaxation behavior of the material [19]. The word relaxor is used because of broad peak instead of a sharp peak as in the case of conventional ferroelectric materials.

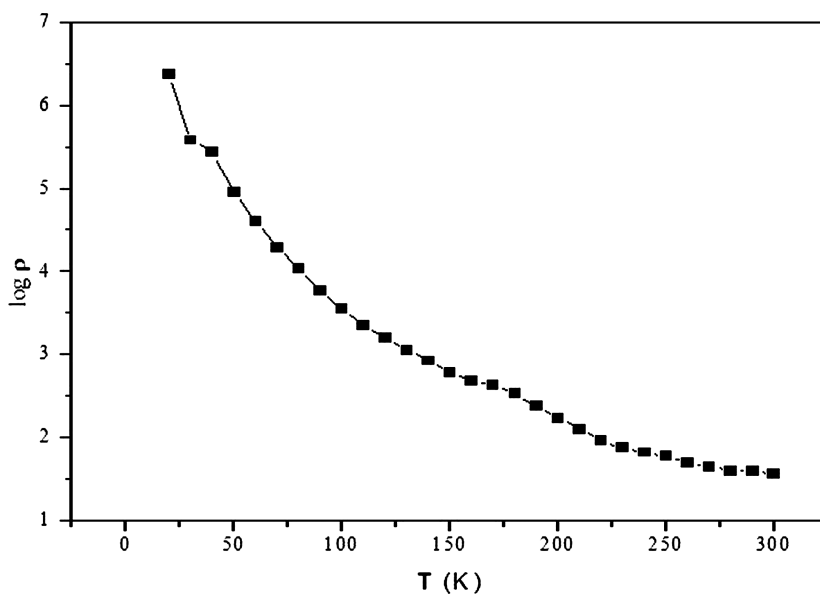


Figure 2. Thermal variation of resistivity of $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ showing metal insulator transition.

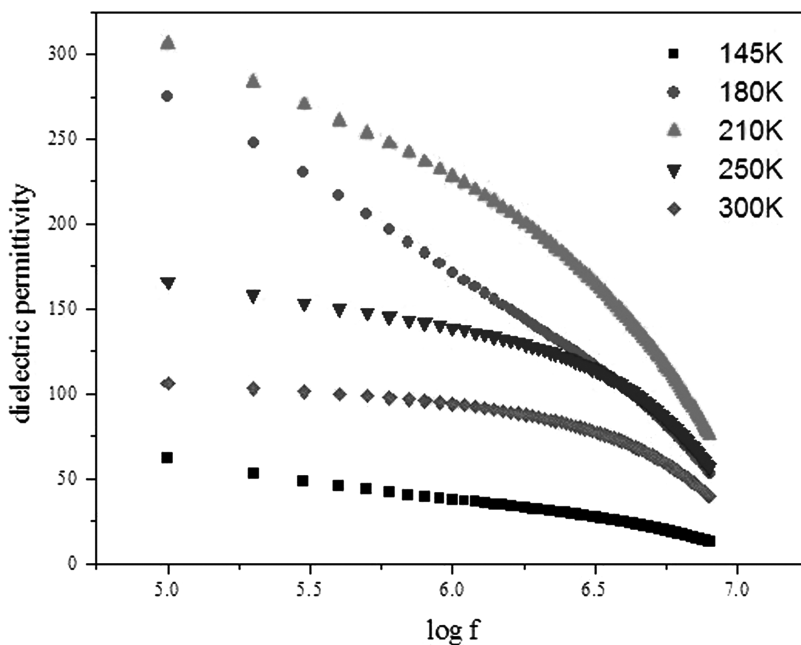


Figure 3. Frequency variation of dielectric permittivity of $Gd_{0.5}Sr_{0.5}MnO_3$. (See Color Plate I)

The ferroelectric behavior of the sample was confirmed by room temperature Capacitance Voltage measurements (Fig. 5). The butterfly nature of CV curves suggests a weak ferroelectric behavior at room temperature [7]. From the temperature variation of magnetization (zero field cooled) graph (Fig. 6) it is clear that there is an antiferromagnetic

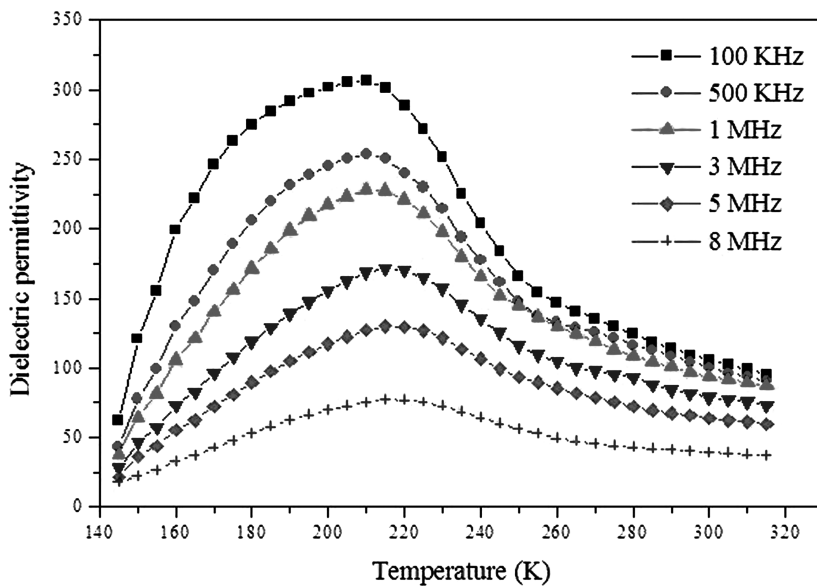


Figure 4. Temperature variation of dielectric permittivity of $Gd_{0.5}Sr_{0.5}MnO_3$. (See Color Plate II)

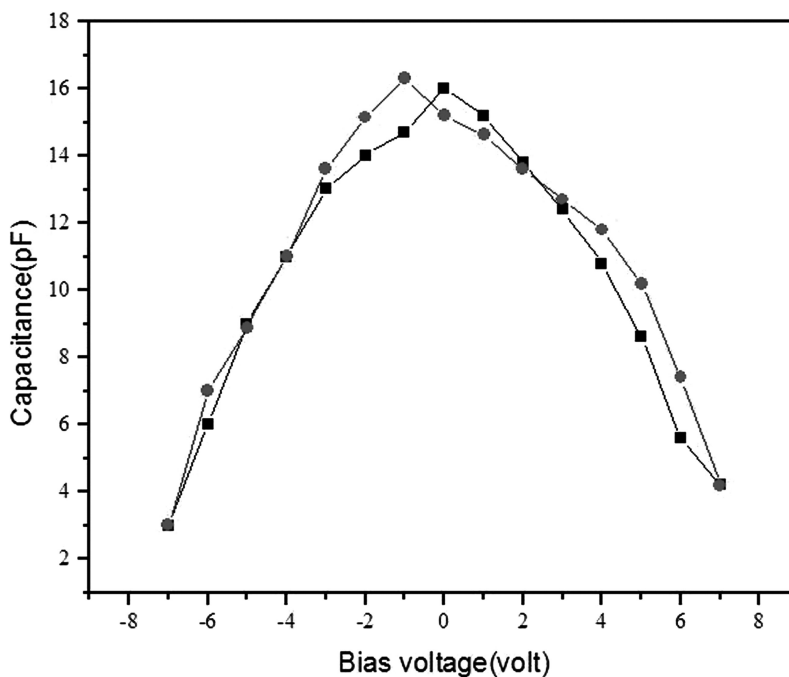


Figure 5. Capacitance Voltage (C-V) characteristics of $Gd_{0.5}Sr_{0.5}MnO_3$. (See Color Plate III)

to ferromagnetic transition ($T_N = 50K$), which is very near to metal insulator transition temperature (T_{M-I}) and ferromagnetic to paramagnetic at 70 K.

In the case of manganites the ferroelectric nature can be explained by using intermediate charge ordering state. Charge ordering is usually considered as an ordering of transition

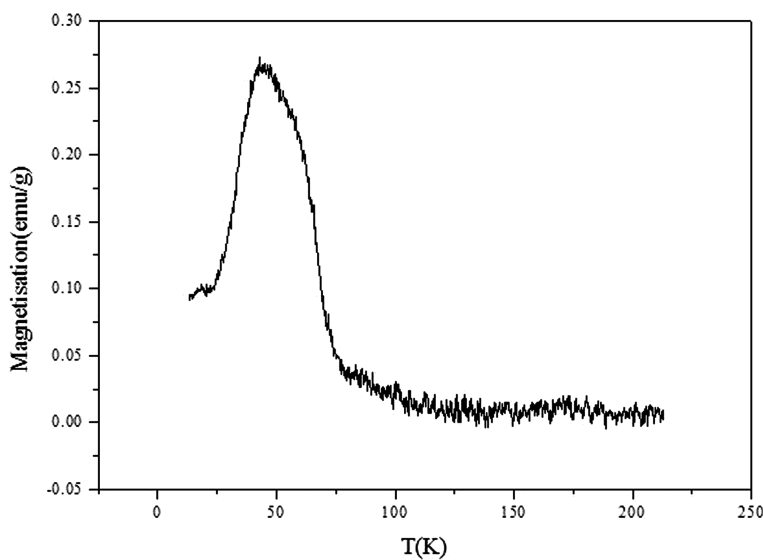


Figure 6. Temperature variation of magnetization $Gd_{0.5}Sr_{0.5}MnO_3$.

metal ions with different valencies. That charge ordering state is called Site-centered Charge Ordering (SCO). Recently another type of charge ordering is discovered called Bond-centered Charge Ordering (BCO). This state is actually an oxygen centered charge ordering state as oxygen ions are located on the TM-TM bonds in the typical perovskite crystal structure. Within such a dimer, spins are aligned ferromagnetically due to Zener double exchange mechanism. It is referred to as Zener polaron state. In SCO Mn ions have unequal valencies but in BCO they have the same valency. The superposition of these two states results into a ferroelectric intermediate state. The CE structure (SCO) has a center of inversion symmetry and consequently there are no electric dipole moments present in the ground state. This is also the case with the pure Zener polaron structure (BCO) as both the Mn ions in each dimer are equivalent. But the intermediate state has a magnetic structure in which the inversion symmetry is lost and the dimer attains a dipole moment. Thus there is a net polarization which leads to a ferro-electric ground state [14,22].

4. Conclusion

In conclusion we have performed the dielectric, conductivity, magnetization and C-V characteristic studies of the sample $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$, which is prepared by wet solid state reaction method. The dielectric spectra reveal a quasi-Debye relaxation. From the study of temperature variation of dielectric constant it is seen that the material shows relaxor ferroelectric nature (with T_E around 210 K), which is confirmed by the butterfly nature of C-V characteristic. The dielectric response shows a correlation with the charge order of the material. The ferroelectric nature of manganite sample $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ is due to the presence of an electric dipole moment in the intermediate phase between canonical magnetic CE phase and a Zener polaron state. The magnetization measurement reveals the weak ferromagnetic nature of the sample at very low temperature ($T_N = 40\text{K}$). Thus the results shown in this work indicate the multiferroic nature of the sample $\text{Gd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$.

Acknowledgment

We would like to thank the Council for Scientific and Industrial Research (CSIR), India for providing financial assistance.

References

1. N. A. Spaldin, Multiferroic materials tower up. *Physics world*. **April** 20–21 (2004).
2. A. Hill, and A. Filippetti, Why are there any magnetic ferroelectrics?. *J. Mag. Mag. Mater.* **976**, 242 (2002).
3. N. A. Hill, Why are there so few magnetic ferroelectrics?. *J. Phys. Chem. B*, **104**, 6694 (2000).
4. Alois Loidl, Hilbert von Loehneysen, and G. Michael Kalvius, Multiferroics. *J. Phys.: Condens. Matter*, **20**, 430301 (2008).
5. C. H. Ahn, K. M. Rabe, and J.-M. Triscone, Ferroelectricity at the Nanoscale: Local Polarization in Oxide Thin Films and Heterostructures. *Science* **303**, 488 (2004).
6. T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Magnetic control of ferroelectric polarization. *Nature* **426**, 55 (2003).
7. Claudy Rayan Serrao, Asish K. Kundu, S. B. Krupanidhi, V. Umesh Waghmare and C. N. R. Rao, Biferroic YCrO_3 . *Phys. Rev. B* **72**, 220101 (2005).
8. C. N. R. Rao, and A. K. Cheetham, Giant magnetoresistance in transition metal oxides. *Science* **272**, 369 (1996).

9. L. A. Pedersen, and W. F. Libby, Unseparated rare earth cobalt oxides as auto exhaust. *Catalysts. Science* **176**, 1355 (1972).
10. T. Venkatesan, M. Rajeswari, Z. W. Dong, S. B. Ogale, and R. Ramesh, Manganite-based devices: opportunities, bottlenecks and challenges. *Philos. Trans. roy. Soc. A* **356**, 1661 (1998).
11. J. M. D. Coey, M. Viret, and S. von Molnar, Mixed-valence manganites. *Advances in Physics* **48**, 248 (1999).
12. A. Goyal, M. Rajeswari, R. Shreekala, S. E. Lofland, S. M. Bhagat, T. Boettcher, C. Kwon, R. Ramesh, and T. Venkatesan, Material characteristics of perovskite manganese oxide thin films for bolometric applications. *Appl. Phys. Lett.* **71**, 2535 (1997).
13. Claudy Rayan Serrao, A. Sundaresan, and C. N. R. Rao, Multiferroic nature of charge-ordered rare earth manganites. *J. Phys.: Condens. Matter* **19**, 496217 (2007).
14. Dmitry V. Efremov, Jeroen Van Den Brink, and Daniel I. Khomskii, Bond- versus site-centred ordering and possible ferroelectricity in manganites. *Nature materials* **1236**, 853 (2004).
15. N. Biskup, A. de Andres, and J. L. Martinez, Origin of the colossal dielectric response of $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$. *Phys. Rev. B* **72**, 024115 (2005).
16. B. Garcia-Landa, J. M. De Teresa, M. R. Ibarra, C. Ritter, R. Drost, and M. R. Lees, Colossal magnetoresistance in $\text{Gd}_{1/2}\text{Sr}_{1/2}\text{MnO}_3$. *J. Appl. Phys.* **83**, 7664 (1998).
17. A. Asamitsu, Y. Moritorno, Y. Tomioka, T. Arima, and Y. Tokura, A structural phase transition induced by an external magnetic field. *Nature* **373**, 407 (1995).
18. J. Rivas, B. Rivas-Murias, A. Fondado, J. Mira, and M. A. Señarís-Rodríguez, Dielectric response of the charge-ordered two-dimensional nickelate $\text{La}_{1.5}\text{Sr}_{0.5}\text{NiO}_4$. *Appl. Phys. Lett.* **85**, 6226 (2004).
19. G. Goodman, R. C. Buchanan, and T. G. Reynolds III, Ceramic materials for electronics; Processing, properties, and applications. New York: Marcel Dekker Inc; 1991.
20. C. Jardon, F. Rivadulla, L. E. Hueso, A. Fondado, M. A. López-Quintela, J. Rivas, R. Zysler, M. T. Causa, and R. D. Sánchez, Experimental study of charge ordering transition in $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$. *J. Magn.Magn.Mater.* **196**, 475 (1999).
21. S. Mercone, A. Wahl, A. Pautrat, M. Pollet, and C. Simon, Anomaly in the dielectric response at the charge-orbital-ordering transition of $\text{Pr}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$. *Phys.Rev.B* **69**, 174433 (2004).
22. P. M. Botta, J. Mira, A. Fondado, J. Rivas, Increase of the dielectric constant near a magnetic phase transition in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. *Materials Letters* **61**, 2992 (2007).