Studies on structural and electrical properties of nanostructured RMnO$_3$ (R = Gd & Ho)

Solanki Sapana, Davit Dhruv, Zalak Joshi, Keval Gadani, K. N. Rathod, Hetal Boricha, V. G. Shrimali, R. K. Trivedi, A. D. Joshi, D. D. Pandya, P. S. Solanki, and N. A. Shah

Studies on Structural and Electrical Properties of Nanostructured RMnO₃ (R = Gd & Ho)

Solanki Sapana[1,2], Davit Dhruv[1,2], Zalak Joshi[1], Keval Gadani[1], K.N. Rathod[1], Hetal Boricha[1], V.G. Shrimali[1,3], R.K. Trivedi[4], A.D. Joshi[5], D.D. Pandya[6], P.S. Solanki[1], N.A. Shah[1,a)]

[1]*Department of Physics, Saurashtra University, Rajkot – 360 005, India*
[2]*V.V.P. Engineering College, Gujarat Technological University, Rajkot – 360 005, India*
[3]*Government Polytechnic, Gujarat Technological University, Rajkot – 360 003, India*
[4]*H. & H.B. Kotak Institute of Science, Rajkot – 360 001, India*
[5]*Department of Nanoscience and Advanced Materials, Saurashtra University, Rajkot – 360 005, India*
[6]*Human Resource Development Centre, Saurashtra University, Rajkot – 360 005, India*

a)Corresponding author: snikesh@yahoo.com

Abstract. We report the results of the studies on the structural and electrical properties of multiferroic GdMnO₃ and HoMnO₃ materials synthesized by sol-gel route. Structural analysis of the results of X-ray diffraction (XRD) measurement shows that materials are found to be crystallized in orthorhombic and hexagonal symmetry, respectively for GdMnO₃ and HoMnO₃. Frequency dependent dielectric properties of nanostructured GdMnO₃ and HoMnO₃ were carried out using LCR meter in the frequency range of 100Hz to 2MHz at room temperature. Dielectric constant decreases with increasing frequency for both the nanostructured multiferroics which can be attributed to the dipole relaxation process. AC conductivity (σ_{AC}) has been measured for both the samples and fitted theoretically by using power law equation.

INTRODUCTION

In the past few years, multiferroics with significant magnetoelectric coupling effect have been widely investigated because of its attractive physical mechanism and potential applications in data storage and sensors [1–3]. The multiferroic rare earth (R) manganites (such as RMnO₃) are a group of materials with interesting properties which have attracted interest from the fundamental and basic physics perspectives. Perovskite rare-earth manganites RMnO₃ (R= Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, etc.) compounds have been attracting a lot of attention in the last years due to strong coupling between ferroelectricity and magnetism [4]. According to the crystallographic structure, these multiferroic materials are divided into two classes. The compounds with larger rare-earth ion (R = Gd, Tb, Dy) crystallize in orthorhombic structure, whereas hexagonal structure is more stable for smaller ionic radius of R (R = Ho to Lu, Y). It is well known fact that the nanosized materials may exhibit unique electrical, magnetic, and optical properties far different from those of their bulk counterparts because of low dimensionality and quantum confinement effect [5–7]. Gadolinium manganite (GdMnO₃) belongs to the orthorhombic rare-earth manganite family that is magnetoelectric at low temperature while Holmium manganite HoMnO₃ (HMO) is promising multiferroic and magnetoelectric material which belongs to the family of rare earth hexagonal manganites. Physical properties of the HoMnO₃ ceramics can be tuned, as it exhibits both hexagonal and orthorhombic structures. Magnetic and dielectric properties of GdMnO₃ and HoMnO₃ multiferroics have been already reported [8–10]. In the present communication, we report the results of the studies on sol-gel grown nanostructured GdMnO₃ and HoMnO₃ manganites for their structural and electrical properties.

EXPERIMENTAL TECHNIQUE

GdMnO₃ and HoMnO₃ nanostructures were synthesized using simple and low cost sol-gel technique. For GdMnO₃, Gadolinium Acetate [Gd (CH₃CO₂)₃ × XH₂O] and Manganese Acetate [Mn (CH₃CO₂)₂ × 4H₂O] while for HoMnO₃, Holmium Acetate [Ho (CH₃CO₂)₃ × XH₂O], and Manganese Acetate [Mn (CH₃CO₂)₂ × 4H₂O] were taken as starting materials in appropriate stoichiometric ratio. Both the precursor solutions were prepared by dissolving the constituents (precursors / starting materials) in double distilled water (DDW) and acetic acid (AA) with desired composition. To yield 0.4M solution, the optimum ratio of DDW and AA was maintained in proportion of 1:1 in volume. Using magnetic stirrer, the solutions were stirred at 95°C until clean and transparent solutions were obtained. Obtained solutions were slowly heated at 150°C until liquid solution gets converted to brownish colored powder. Both the obtained brownish powders were calcined at 500°C for 6hrs. Finally, the materials were sintered at 1100ºC for 2hrs in air in the pellet form. XRD of GdMnO₃ and HoMnO₃ samples were recorded using PANalytical PW3040/60 X'pert PRO diffractometer having Cu Kα radiation. AC conductivity (σ_AC) and dielectric study of both samples was recorded using Agilent E4980A Precision LCR meter having frequency range of 100Hz – 2MHz.

RESULTS AND DISCUSSION

Fig.1 shows XRD profiles of GdMnO₃ and HoMnO₃ nanoparticles. The XRD patterns show that GdMnO₃ nanoparticles are crystallized in orthorhombic crystal structure with space group Pbnm while HoMnO₃ nanoparticles are having hexagonal structure with space group P6₃cm which can be confirmed with JCPDS card No. 25–0337 and 25–1059, respectively. Crystallinity of both nanoparticles can be observed by full width half maxima (FWHM) of most intense XRD peak. The crystallite sizes of both nanoparticles can be calculated using the formula, CS = 0.9λ / β cosθ, where λ is the wavelength of X-rays used, β is the value of FWHM and θ is the angle of incident. Crystalline size of GdMnO₃ and HoMnO₃ nanoparticles are found to be 37.83nm and 23.00nm, respectively.
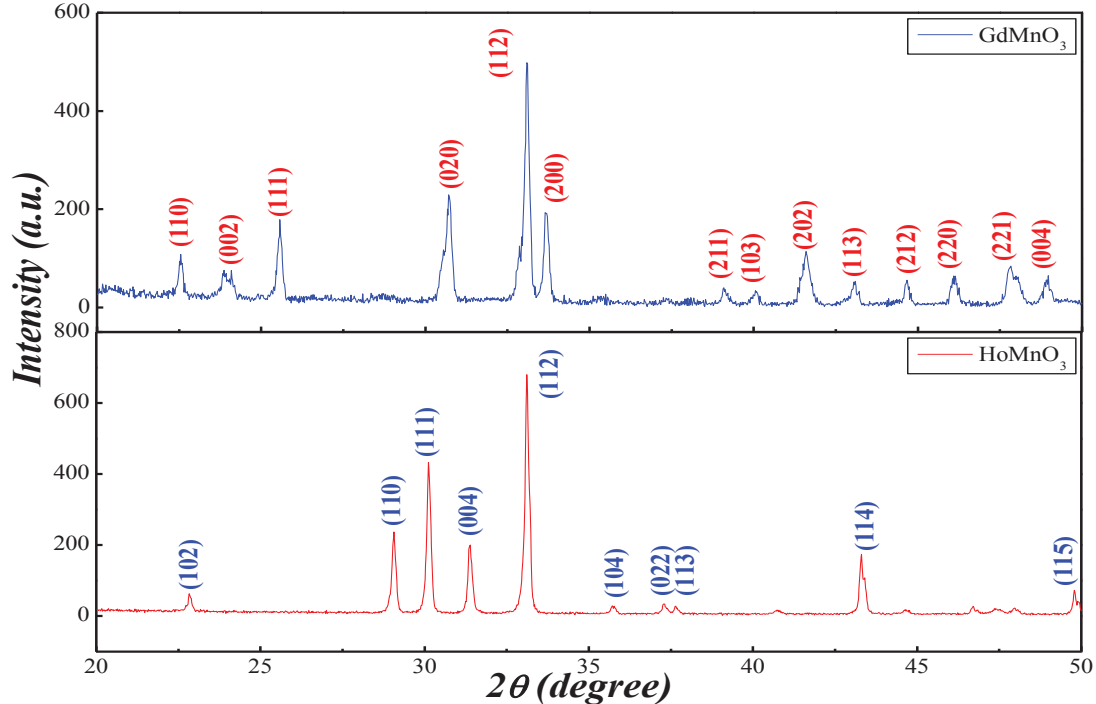

FIGURE 1. Indexed XRD patterns of GdMnO₃ and HoMnO₃.

To understand electrical properties of nanostructured GdMnO₃ and HoMnO₃, dielectric studies were carried out. Fig.2 shows (left) real part and (right) imaginary plots of the dielectric constant for both nanoparticles. The real and imaginary parts of dielectric constant explain that how much of applied energy has been stored and lost in the materials, respectively. For both GdMnO₃ and HoMnO₃, the frequency dependent real and imaginary parts decrease with increasing frequency which describes characteristics of multiferroics [11, 12]. For both materials, the dielectric

constant gets decreased with increase in frequency due to higher relaxation time [13] because dipoles can follow low field frequencies but cannot follow the frequencies of higher field [14], which results into the dielectric loss. From dielectric studies, we can observe that $HoMnO_3$ has large value of dielectric constant as compared to $GdMnO_3$. This may be due to large structural distortion (in the context of less symmetric and highly disordered hexagonal phase) in $HoMnO_3$ manganite. Also, large number of crystal boundaries (i.e. small crystal size) in $HoMnO_3$ supports the high dielectric constant in the material.
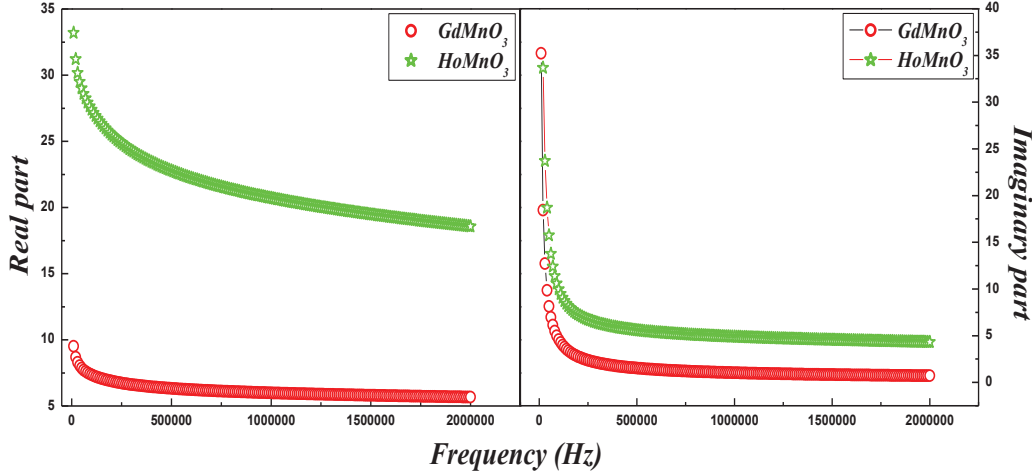

FIGURE 2. Variation in (left) real and (right) imaginary parts of dielectric constant with frequency for $GdMnO_3$ and $HoMnO_3$ nanoparticles.
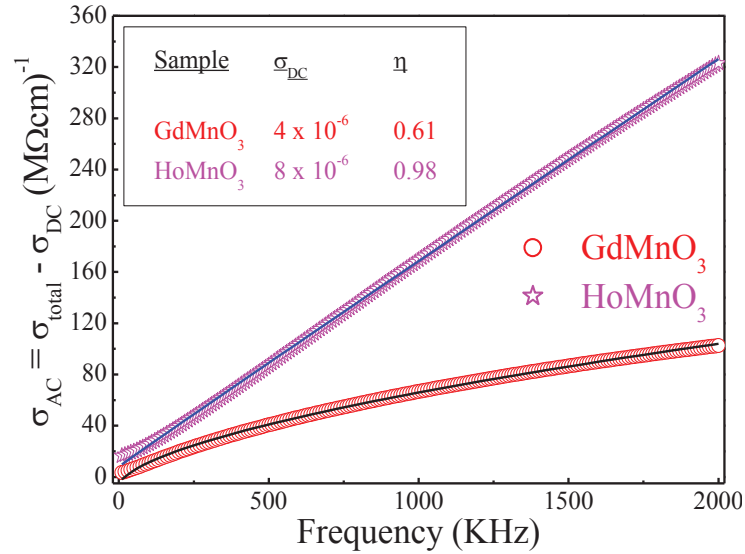

FIGURE 3. Variation in σ_{AC} with frequency and corresponding fits using power law for $GdMnO_3$ and $HoMnO_3$ nanoparticles.

Electrical conducting property of nanostructured $GdMnO_3$ and $HoMnO_3$ have been studied by measuring frequency dependent AC conductivity (σ_{AC}) in the frequency range 100Hz to 2MHz which can be calculated by total conductivity (σ_{total}) and DC conductivity (σ_{DC}) according to given relation in following equation [15, 16]: $\sigma_{AC} = \sigma_{total} - \sigma_{DC}$. Universal Power law for σ_{AC} is given by, $\sigma_{AC} = A\omega^{\eta}$ where σ_{DC} is the frequency independent contribution from DC conductivity, A is constant, ω is the angular frequency of the applied field and η is the power law exponent. Measured DC conductivity was subtracted from the measured total conductivity and the value of η was extracted from the fitting (Fig.3) for both the nanoparticles. It can be easily observed that η has a value less than 1 for both samples. The value of η is found to be ~ 0.61 and ~ 0.98 for $GdMnO_3$ and $HoMnO_3$ nanoparticles, respectively. Observed behavior of η may be analyzed by assuming that the AC conduction mechanism is the

correlated barrier hopping (CBH) type for the presently studied systems [17, 18]. According to this model, the conduction occurs via a bipolaron hopping process where two polarons simultaneously hop over the potential barrier between the two charged defect states.

CONCLUSION

In summary, it can be concluded that $GdMnO_3$ and $HoMnO_3$ nanoparticles were grown using a sol–gel method. $GdMnO_3$ is grown with orthorhombic structure while $HoMnO_3$ possesses hexagonal phase. Crystallite size of $GdMnO_3$ and $HoMnO_3$ nanoparticles has been found 37.83nm and 23.00nm, respectively. Dielectric study shows presence of relaxation phenomenon in the system. It can be observed that $HoMnO_3$ has large value of dielectric constant than of $GdMnO_3$ which has been discussed in the context of structural disorder. σ_{AC} data for both samples have been fitted using power law where the value of power exponent (η) is 0.61 and 0.98 for $GdMnO_3$ and $HoMnO_3$, respectively suggesting that correlated barrier hopping (CBH) mechanism is the key factor.

REFERENCES

1. S.W. Cheong and M. Mostovoy, *Nat. Mater.* **6**, 13–20 (2007)
2. Li Yan, Zengping Xing, Zhiguang Wang, Tao Wang, Guangyin Lei, Jiefang Li and D. Viehland, *Appl. Phys. Lett.* 94, 192902:1–3 (2009)
3. R. Ramesh and N.A. Spaldin, *Nat. Mater.* **6**, 21–29 (2007)
4. A. Midya, S.N. Das and P. Mandal, *Phys. Rev. B* **84**, 235127:1–10 (2011)
5. X.G. Liu, D.Y. Geng, P.J. Shang and Z.D. Zhang, *Appl. Phys. Lett.* **92**, 173117 (2008)
6. X.G. Liu, J.J. Jiang, D.Y. Geng, B.Q. Li, Z. Han, W. Liu and Z.D. Zhang, *Appl. Phys. Lett.* **94**, 053119:1–3 (2009)
7. X.G. Liu, Z.Q. Ou, D.Y. Geng, Z. Han, Z.G. Xie and Z.D. Zhang, *J. Phys. D Appl. Phys.* **42**, 155004:1–3 (2009)
8. T. Lottermoser, T. Lonkai, U. Amann, D. Hohlwein, J. Ihringer and M. Fiebeg, *Nature* **430**, 541–544 (2004)
9. B. Lorenz, F. Yen, M.M. Gospodinov and C.W. Chu, *Phys. Rev. B* **71**, 014438:1–9 (2005)
10. O.P. Vajk, M. Kenzelmann, J.W. Lynn, S.B. Kim and S.W. Cheong, *Phys. Rev. Lett.* **94**, 087601:1–4 (2005)
11. Sonali Saha and T.P. Sinha, *Phys. Rev. B* **65**, 134103:1–7 (2002)
12. A.B. Ravalia, M.V. Vagadia, U.D. Khachar, R.R. Doshi, P.S. Solanki, B.T. Savalia, N. A. Shah and D.G. Kuberkar *AIP Conf. Proc.* **1349**, 1143–1144 (2011)
13. V.R. Palkar, D.C. Kundaliya, S.K. Malik and S. Bhattacharya, *Phys. Rev. B* **69**, 212102:1–3 (2004)
14. M. Kumar, V.R. Palkar, K. Srinivas and S.V. Suryanarayana, *Appl. Phys. Lett.* **76**, 2764–2766 (2000)
15. A.K. Jonscher, *Nature* **267**, 673–679 (1977)
16. S.R. Elliott, *Adv. Phys.* **36**, 135–217 (1987)
17. S.R. Elliott, *Phil. Mag. B* **36**, 1291–1304 (1977)
18. S.R. Elliott, *Philos. Mag. B* **37**, 553–560 (1978)