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First-Principles Study of Electronic and Dielectric Properties in Lanthanum Manganate

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Abstract **- First-principles calculations based on Density Functional Theory have been done on Lanthanum manganate. Its orthorhombic unit cell has been simulated. Electronic density of states has been computed and it shows that the material shows the nature of semiconducting material with a band gap of 1.38eV. Dielectric constant and Polarizability of the material have been computed. The value of dielectric constant comes out to be 47.3, 13.3 and 15.2 along X, Y and Z axes respectively with an average value of 25.3. The polarizability values are found to be 55.1(Å)^3, 47.2(Å)^3 and 48.5 (Å)^3 along X, Y and Z axes respectively with an average value of 50.3(Å)^3. Phonon modes at gamma point in the material range from 0 cm^{-1} to 885 cm^{-1}.**
Keywords: **Lanthanum Manganate, Dielectric Constant, Electronic Density of States, First-Principles Calculations, Polarizability, Phonon Modes**

I. INTRODUCTION

Lanthanum manganate is an inorganic compound with the formula $LaMnO_3$. It is usually abbreviated as LMO. It has been noticed that the Lanthanum manganate is formed in the perovskite structure, consisting of oxygen octahedra with a central Mn atom. It is observed that the cubic perovskite structure is distorted into an orthorhombic structure by a strong Jahn–Teller distortion of the oxygen octahedral [1]. It has been found that the Lanthanum manganite is an electrical insulator and an A-type antiferromagnet. Lanthanum manganite is the parent compound of several important alloys, which are termed as rare-earth manganites or colossal magnetoresistance oxides. These families include lanthanum strontium manganite, lanthanum calcium manganite and others.

It has been seen that in lanthanum manganate, both the La and the Mn are in the +3 oxidation state. Substitution of some of the La atoms by divalent atoms such as Sr or Ca induces a similar amount of tetravalent Mn+4 atoms. Such substitution, or doping can induce various electronic effects, which form the basis of a rich and complex electron correlation phenomena that yield diverse electronic phase diagrams in these alloys [2].

The orthorhombic perovskites $RMnO_3$ (R = La, Y , Pr, Nd, Eu, Gd) have recently attracted the scientific community as it is found that a partial substitution of R by Ca, Sr, Ba, Na, or Pb causes the phase transition and the occurrence of colossal magnetoresistance near the temperature of spin ordering of Mn ions [3–8]. These properties make these compounds promising for the magnetic sensors and the read head technology [9]. The parent compound RMnO3 exhibits rich and interesting physical properties because of the strong interplay between lattice distortions, transport properties, and magnetic ordering.

It has been found that any little modification in the structure and composition of a material will bring in sufficient changes in the properties of the material [10, 11]. Thus it is important to study the structure of the materials and look at the parameters which can be altered to get a better material for technological applications. First-principles calculation based on Density Functional Theory [12] has been proved to be an effective tool in the study of structural, electronic and dielectric properties of organic materials [13, 14]. Lanthanum manganate crystals have attracted the scientific community in various aspects [1 – 9]. With this in view, structure of Lanthanum manganate crystal [$LaMnO_3$] has been simulated using First-principles calculations based on Density Functional Theory and computation of Electronic density of states, Dielectric constant and Polarizability have been done and the results have been reported in the present paper.

II. COMPUTATIONAL DETAILS

Several codes are available for the theoretical structure simulation [15]. The density functional theory approach has emerged as a well established computational method. It has been widely employed to arrive at the conformations of a large number of molecular systems. The practical applicability and sophistication of DFT is strongly sensitive to the good choice of exchange–correlation function along with the appropriate basis set.

Quantum espresso is an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modelling. It is based on density-functional theory, plane waves, and pseudopotentials. Author has used plane wave self consistent field (PWSCF) [16] implementation of density functional theory (DFT), with a Local density approximation (LDA) [17] to exchange correlation energy of electrons and ultrasoft

pseudopotentials [18], to represent interaction between ionic cores and valence electrons. Kohn-Sham wave functions were represented with a plane wave basis with an energy cutoff of 30 Ry and charge density cutoff of 180 Ry. Integration over Brillouin zone was sampled with a Monkhorst-Pack scheme [19] with appropriate k point mesh and occupation numbers were smeared using Methfessel-Paxton scheme [20] with broadening of 0.03 Ry. The structure was relaxed to minimize energy.

III. RESULTS AND DISCUSSION

In the present study, the orthorhombic unit cell of Lanthanum manganate was first simulated using "Avogadro" [21] taking the X-ray diffraction data published by J. Rodriguez-Carvajal *et al.*, [22]. Later, atomic positions of the simulated structure have been used in the plane wave self consistent field calculations.

The structure was relaxed and the values of the unit cell parameters are; a=5.5817Å b=5.5834Å c=7.8896Å, $\alpha=\beta=\gamma=90^{o}$. "scf"" calculation was done using the program 'pw.x' of Quantum espresso. Completely relaxed structure of the unit cell was visualized using the program "XcrysDen" [23] and the structure of Lanthanum manganate as seen along Z-axis has been shown in Fig.1. Molecular surface of Lanthanum manganate crystal as seen along Z-axis has been shown in Fig. 2.

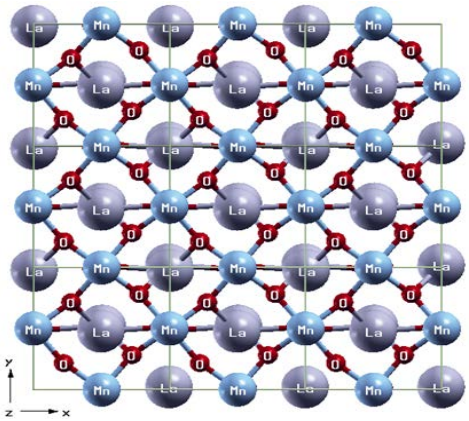

Fig.1 Structure of Lanthanum manganate crystal as seen along Z-axis

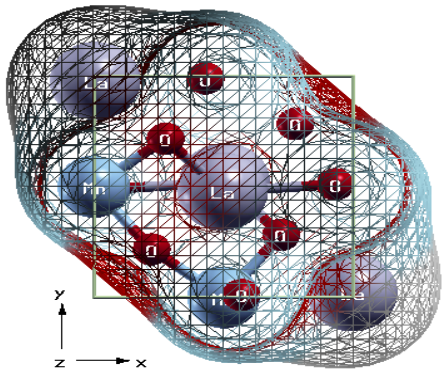

Fig. 2 Molecular surface of Lanthanum manganate crystal as seen along Z-axis

A. EDOS Calculation: Electron Density of States (EDOS) has been computed in Lanthanum manganate using Electronic structure calculation code of Quantum espresso. EDOS in Lanthanum manganate shows the nature of a semiconducting material with a band gap of 1.38eV which matches well with the value reported earlier [24].

B. Dielectric Constant, Polarizability and Phonon Modes: Dielectric constant has been computed in case of Lanthanum manganate. The value of dielectric constant in Lanthanum manganate comes out to be 47.3, 13.3 and 15.2 along X, Y and Z axes respectively with an average value of 25.3. Polarizability of Magnesium phosphide has also been estimated and it comes out to be 55.1(Å)^3, 47.2(Å)^3 and 48.5 (Å)^3 along X, Y and Z axes respectively with an average value of 50.3(Å)^3. Phonon modes at gamma point have also been calculated in the material and they range from 0 cm^{-1} to 885 cm^{-1}.

IV. CONCLUSION

The EDOS calculation shows that the Lanthanum manganate shows the nature of semiconducting material with a band gap of 1.38 eV. The value of dielectric constant comes out to be 47.3, 13.3 and 15.2 along X, Y and Z axes respectively with an average value of 25.3. The polarizability values are found to be 55.1(Å)^3, 47.2(Å)^3 and 48.5 (Å)^3 along X, Y and Z axes respectively with an average value of 50.3(Å)^3. Phonon modes at gamma point in the material range from 0 cm^{-1} to 885 cm^{-1}.

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REFERENCES

[1] S. Satpathy, Zoran S. Popovic, and Filip R. Vukajlovic, "Electronic Structure of the Perovskite Oxides: $La_{1-x}Ca_xMnO_3$", *Physical Review Letters*. Vol.76, pp960--963. doi:10.1103/PhysRevLett.76.960, 1996.

[2] Dagotto, E. "Nanoscale Phase Separation and Colossal Magnetoresistance", *Springer Series in Solid-State Sciences*, 2003.

[3] R.Von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, "Giant negative magnetoresistance in perovskitelike La2/3Ba1/ 3MnOx ferromagnetic films", *Phys. Rev. Lett.* Vol.71, pp. 2331-2333, 1993.

[4] P. Schiffer, A. P. Ramirez, W. Bao, and S. W. Cheong, "Low Temperature Magnetoresistance and the Magnetic Phase Diagram of La1−xCaxMnO3", *Phys. Rev. Lett.* Vol.75, No.18, pp. 3336-3339, 1995.

[5] C. N. R. Rao, "Novel materials, materials design and synthetic strategies: recent advances and new directions", *J. Mater. Chem.* Vol. 9, No.1, pp. 1-14, 1999.

[6] S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, "Thousand fold change in resistivity in magnetoresistive la-ca-mn-o films", *Science* Vol.264, pp. 413-415, 1994.

[7] K. Petrov, L. Krusin-Elbaum, J. Z. Sun, O. Field, and P. R. Duncombe, "Enhanced magnetoresistance in sintered granular

manganite/insulator systems", *Appl. Phys. Lett*. Vol.75, pp. 995-997, 1999.

[8] J. Z. Sun, L. Krusin-Elbaum, A. Gupta, G. Xiao, P. R. Duncombe, and S. S. P. Parkin, "Magnetotransport in doped manganate perovskites", *IBM J. Res. Dev*. Vol.42, pp. 89-102, 1998.

[9] S. S. P. Parkin, "Giant Magnetoresistance in Magnetic Nanostructures", *Annu. Rev. Mater. Sci*. 25, pp. 357-388, 1995.

[10] H. R. Sreepad, K. P. S. S. Hembram and U.V. Waghmare, "First-principles Study of Electronic and Dielectric Properties of Polyoxymethylene", *AIP Conference Proceedings*, Vol. 1349, pp. 871-872, 2011.

[11] H. R. Sreepad, "First-principles study of fluorination of azobenzene", *Molecular Crystals and Liquid Crystals*, Vol. 634, pp. 91- 96, 2016.

[12] M. C. Payne, M.P. Teter, D.C. Allan, T.A. Arias and J.D. Joannopoulas, "Iterative minimization techniques for *ab initio* total-energy calculations: molecular dynamics and conjugate gradients", *Reviews of Modern Physics*, Vol. 64, No. 4, pp.1045-1097, 1992.

[13] H. R. Sreepad, H. R. Ravi, Khaleel Ahmed and U.V. Waghmare, "Radiation induced changes in electronic and dielectric properties of polyoxymethylene" *AIP Conference Proceedings*, Vol.1447, No. 1, pp.793-794, 2013.

[14] H. R. Sreepad, "Structure simulation and study of electronic and dielectric properties of two derivatives of benzamide", *Molecular Crystal sand Liquid Crystals*, Vol. 625, No.1, pp.195-201. 2016.

[15] [Online] Available: http://en.wikipedia.org/wiki/ Molecular_ modelling.

[16] S. Baroni, S. A. DalCorso, P. DeGironcoli and Gianozzi, [Online] Available: http://www.pwscf.org

[17] J. P. Perdew and A. Zunger, "Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems", *Physical Review B*, Vol. 23, pp. 5048-5079, 1981.

[18] D. Vanderbilt, "Soft self-consistent pseudo potentials in generalized eigenvalue formalism", *Physical Review B*, Vol. 41, pp.7892–7895, 1990.

[19] H. J. Monkhorst and J. D. Pack, "Special Points for Brillouin-Zone Integrations," *Physical Review B*, Vol. 13, No. 12, pp. 5188-5192, 1976.

[20] M. A. Methfessel and Paxton, "High-precision sampling for Brillouin-zone integration in metals", *Physical Review B*, Vol. 40, pp. 3616-3621, 1989.

[21] [Online] Available: http://avogadro.openmolecules.net/wiki/

[22] J. Rodriguez-Carvajal, M. Hennion, F. Moussa, A. H. Moudden, L. Pinsard, A. Revcolevschi, "Neutron-diffraction of the Jahn-Teller transition in stoichiometric $LaMnO_3$", *Physical Review B - Condensed Matter*, Vol. 57, pp. 3189-3192, 1998

[23] A. Kokalj, "Computer graphics and graphical user interfaces as tools in simulations of matter at the atomic scale," *Computational Materials Science*, Vol. 28, pp. 155-168, [Online] Available: http://www.xcrysden.org/ 2003

[24] Taka-hisa Arima, and Yoshinori Tokura. "Optical Study of Electronic Structure in Perovskite-Type RMO_3 (*R*=La, Y; *M*=Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu)", *J. Phys. Soc. Jpn.* Vol. 64, pp. 2488-2501, 1995.