



Structural and Frequency dependent Electrical Behaviour of Nanocomposite of La doped BiFeO₃:SrAlO₃

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ABSTRACT

La doped BiFeO₃:SrAlO₃ samples were synthesized by sol-gel method. Composite was made to synthesise nano powder in order to improve electrical, optical and thermal properties. Goldschmidt tolerance factor for SrAlO₃ is 0.9 which confirms this assembly to be a promising Perovskite. Investigations were carried out on samples where formation of false perovskite is verified by X-ray diffraction technique. The dielectric loss ($\tan \delta$) and conductivity (σ) were measured at room temperature as a function of the frequency (100 Hz – 25kHz). Structural and Electrical properties of this nanocomposite make them potential candidate in the field of thermoelectric energy devices.

Keywords: *Sol-gel, Nano-Perovskites, AC Conductivity, thermoelectric energy devices*

1. Introduction

Magnetoelectric multiferroics have generated a lot of practical and academic interest recently [1, 2]. The development of a low-power, electrically-controlled magnetic memory, a novel type of logic with four states (two polarisation "up and down" levels and two magnetic moment stages), and magnetic field sensors are examples of practical uses. BiFeO₃ (BF), which is a multiferroic of the first type—i.e., ferroelectricity and magnetism have different physical sources and develop independently of one another while having a connection—is one of the promising and researched materials in this area. The high Curie (1103 K) and Neel (643 K) temperatures of BF are its principal benefit [3].

The coexistence of antiferromagnetic (Neel temperature (TN) = 643 K) and ferroelectric ordering (Tc = 1103 K) above ambient temperature is the cause of the magnetoelectric coupling [10,17]. As a result, the substance strives for multifunctional features in applications such as sensor [11,17], photo electrocatalysis [12,17], non-volatile data storage [13,17], logic switching photo electrochemical water splitting [14,17], thermoelectric [15,17], and [16,17]. The possible applications on the above are given additional attention by the room-temperature multiferroic characteristics, suitable band gaps, and ultrahigh ferroelectric polarisation of BiFeO₃ [17]. Similar to this, the Seebeck effect is a thermoelectric application that uses a temperature gradient (thermoelectric generator) to create power. The Peltier effect, a thermoelectric cooler, is another device that it powers with energy. More waste heat from renewable sources is available in the atmosphere.

2. Experimental

Lanthanum nitrate, ~~Bismuth Nitrate, Ferrous nitrate, Strontium nitrate, Aluminium nitrate and citric acid~~ were used as reactants for the formation of La doped BiFeO₃ and SrAlO₃. The synthesis route opted for this reaction is solid state route i.e., sol-gel process. Metal nitrates were initially dissolved in distilled water separately using magnetic stirrer. For La doped BFO, solution of Bismuth nitrate, Lanthanum nitrate and Ferrous nitrate were mixed under continuous stirring for 30 min. Then citric acid was added to the solution for gel formation. Ammonia was also used to maintain PH level of the mixture. After vigorous stirring of 4-5 hours, the solution was dried to powder form and then using a mortar pestle, powder was grinded manually to achieve uniformity. The Nano powder was annealed at 650°C for 5 hours. After annealing, it was again grounded using mortar pestle.

Sol-gel process is again repeated to synthesise Strontium Aluminate. After this process, La doped BFO and Strontium Aluminate were mixed in equal proportions and then calcination was performed. Using KBr dye set, a pellet was formed for frequency dependent electrical conductivity studies.

3. Characterization Technique

Using X-Ray Powder Diffraction, including Rietveld (TOPAS) analysis, & total scattering (PDF analysis), and small angle X-ray scattering, the XRD patterns of the synthesised nanoparticles have been documented (SAXS). Analytical in the 2-scanning mode using CuK radiation (1.5406). Using Origin Pro-9.0 64-bit software, XRD data has also been further examined for fitting and baseline correction. Thermogravimetric analysis is also performed for stability analysis of composite system.

Using an LCR metre found in the labs at LPU, Phagwara, measurements of frequency-dependent electrical conductivity have been made.

4. Results and Discussion

4.1 XRD Analysis

The XRD patterns of nanocrystalline with specific formula La doped BiFeO₃, SrAlO₃ and composite of BiLa_{0.1}Fe_{0.9}O₃:SrAlO₃ using the data recorded over 2 θ range 20° - 90° are shown in figure 1,2,3 & 4. It has been noted that SrAlO₃ and La doped BiFeO₃ nanoparticles exhibit perovskite structure from the XRD peaks investigation and compared with literature [6]. Fig. 1 displays the XRD patterns of sintered La doped BiFeO₃, SrAlO₃ and their composite BiLa_{0.1}Fe_{0.9}O₃:SrAlO₃ ceramics. All specimens may be recognised to primarily display the rhombohedral structure (R3c). When 10% La is used to replace Fe in BiFeO₃, no sign of Bi₂₅FeO₃₉ has been seen. The R3c structure of BiLa_{0.1}Fe_{0.9}O₃ is entirely pure. This indicates that 10% has effectively suppressed the impurity phase. Similarly, XRD pattern of SrAlO₃ is found in good agreement with Perovskite structure as shown in figure 2 [7]. XRD pattern of composite ceramic BiLa_{0.1}Fe_{0.9}O₃:SrAlO₃ is shown in figure 3. Particle size of Bismuth Ferrite is 19nm, La doped Bismuth Ferrite is 16nm. Strontium Aluminium Perovskite is 24nm.

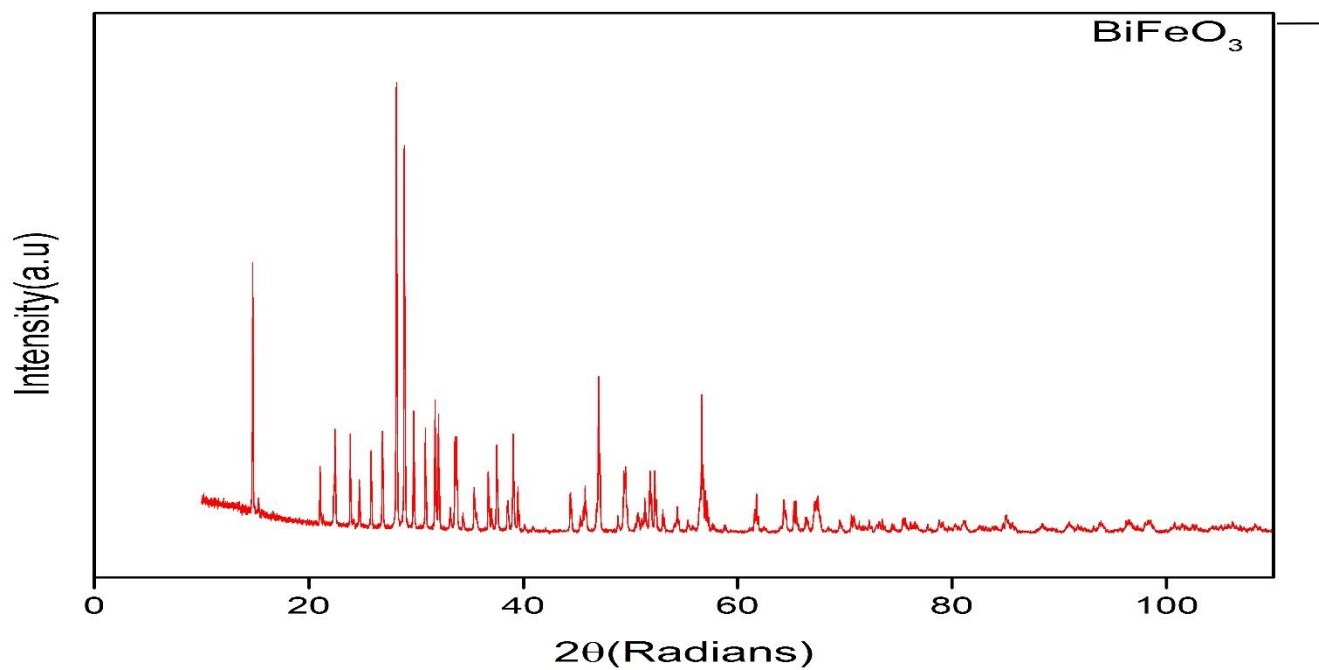


Figure 1. XRD pattern of BiFeO₃

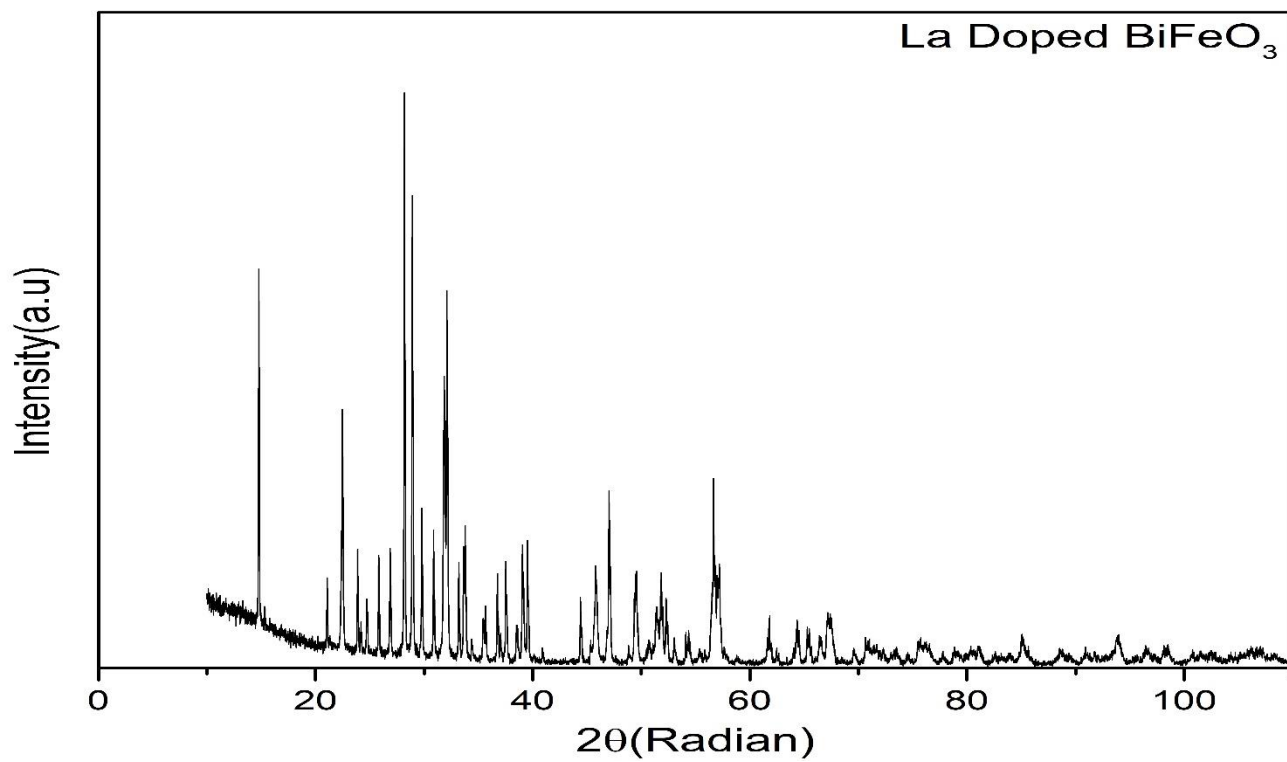


Figure 2. XRD pattern of La doped BFO

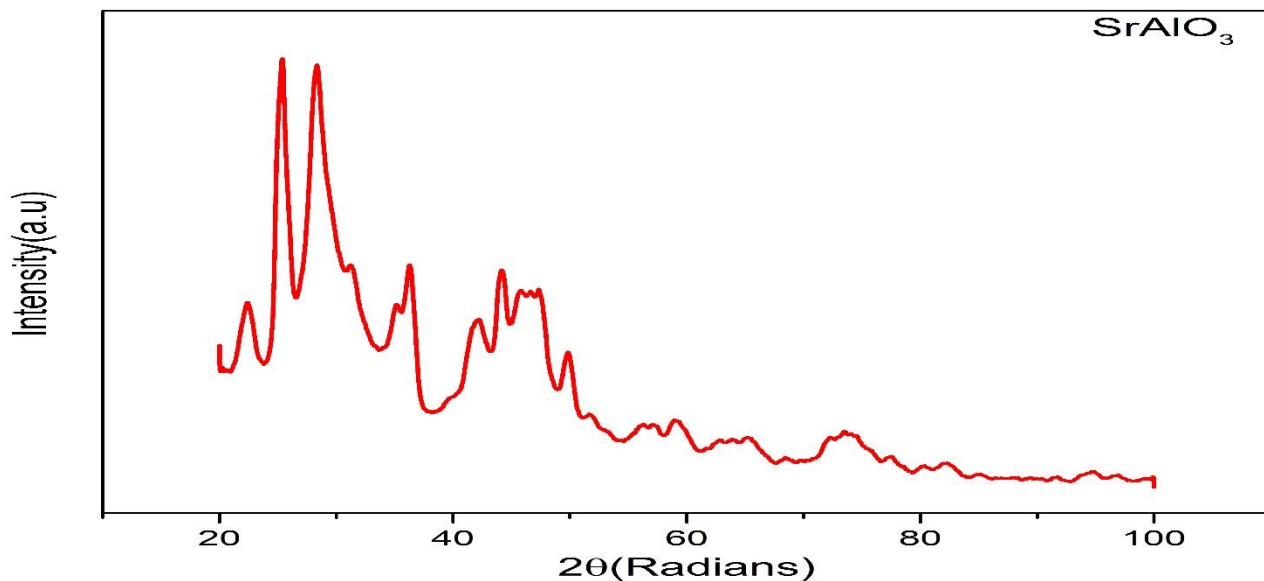


Figure 3. XRD Pattern of SrAlO₃

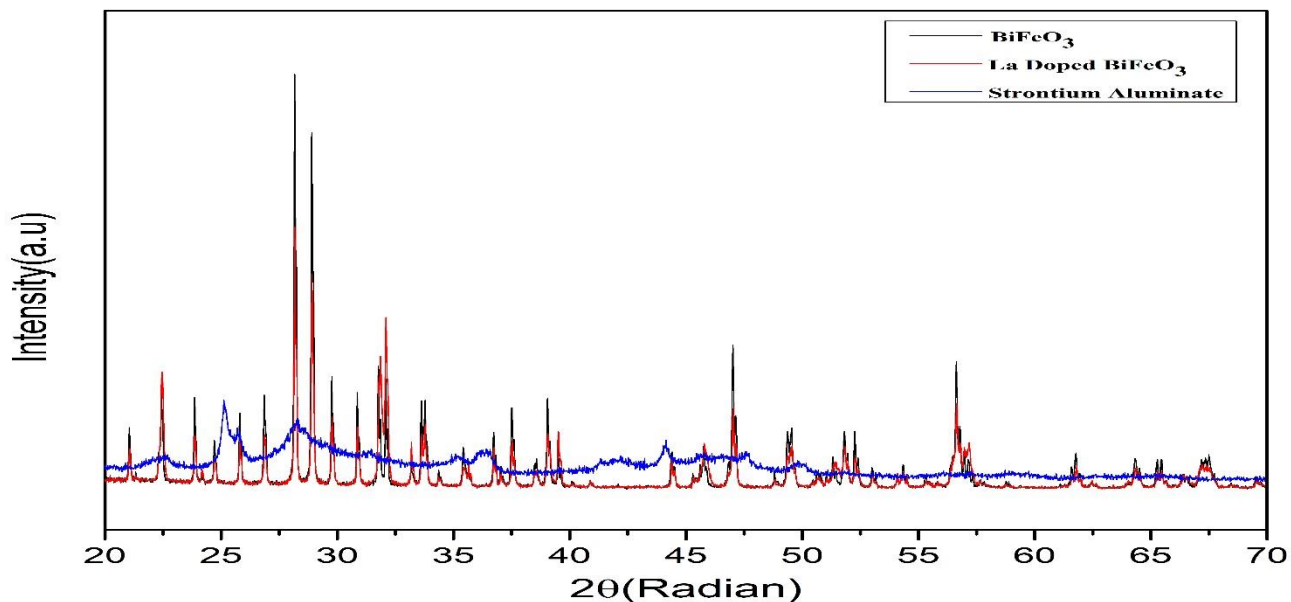


Figure 4. XRD Pattern of composite La doped BiFeO₃:SrAlO₃.

4.2 Frequency dependent measurement of Electrical Conductivity

AC conductivity of composite ceramic La doped BiFeO₃: SrAlO₃ are measured using LCR meter. The measurements were carried out in the frequency range 100Hz-25KHz at room temperature. A programmable automatic LCR meter is used to measure the sample capacitance C_p and the loss tangent $\tan \delta$ directly. All values of the capacitance C_p which taken from the screen of the bridge were parallel with the resistance R . There is an monotonic increase in electrical conductivity with frequency as shown in fig 5. For a good thermoelectric energy application, Electrical conductivity should be high and thermal conductivity must be low as a figure of merit. This composite system reduces the thermal conductivity of Bismuth Ferrite and La doped Bismuth ferrite which makes it suitable thermoelectric applications.

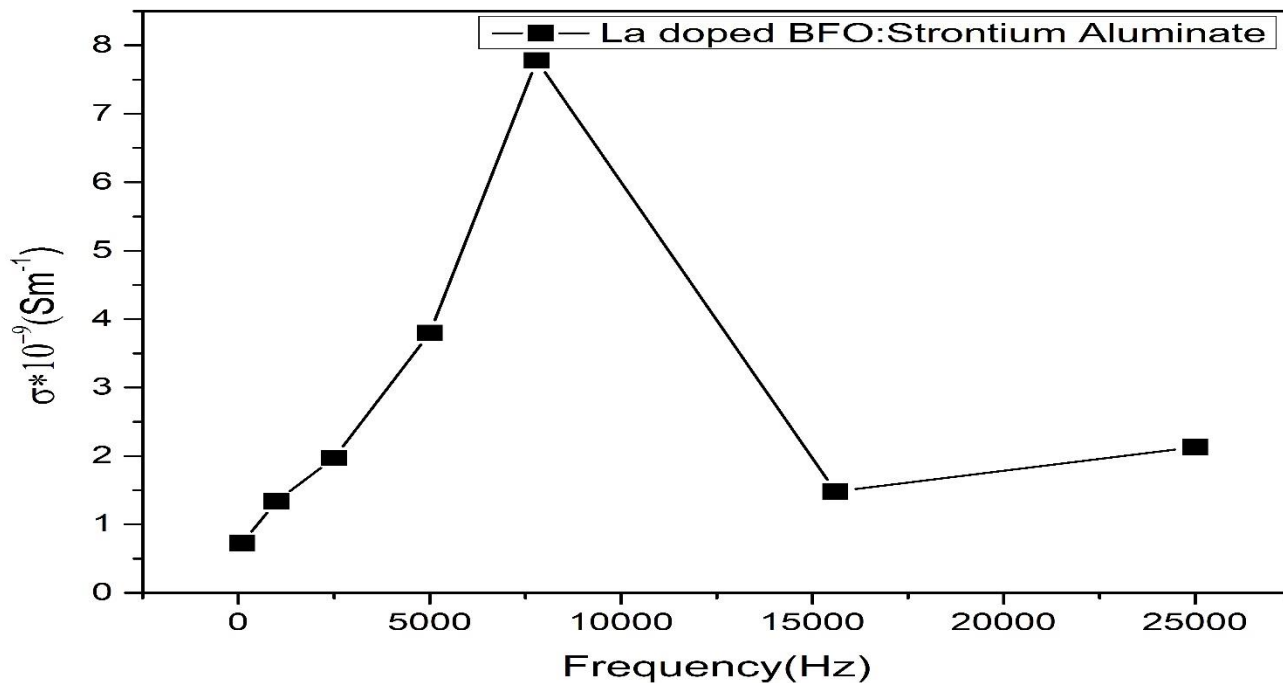


Fig 5. Frequency vs AC conductivity plot of Composite La doped BFO: SrAlO₃

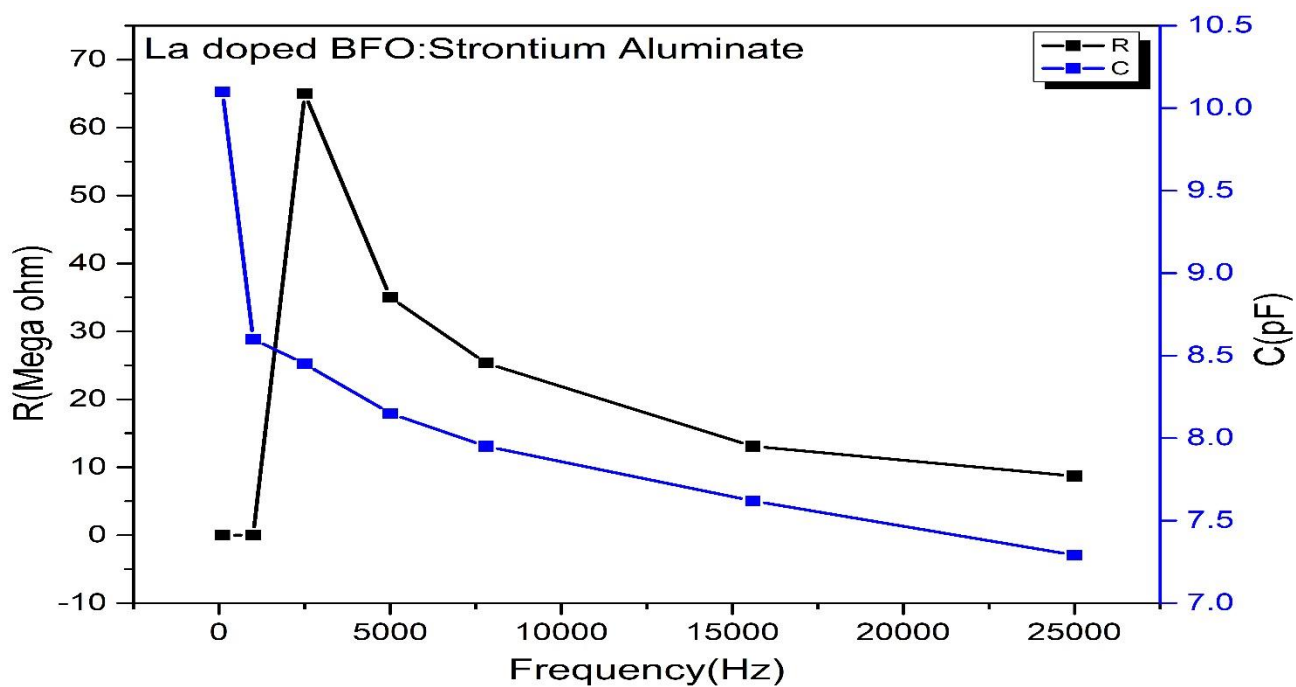


Figure 6. Frequency vs Resistance Plot of La doped BFO: SrAlO₃

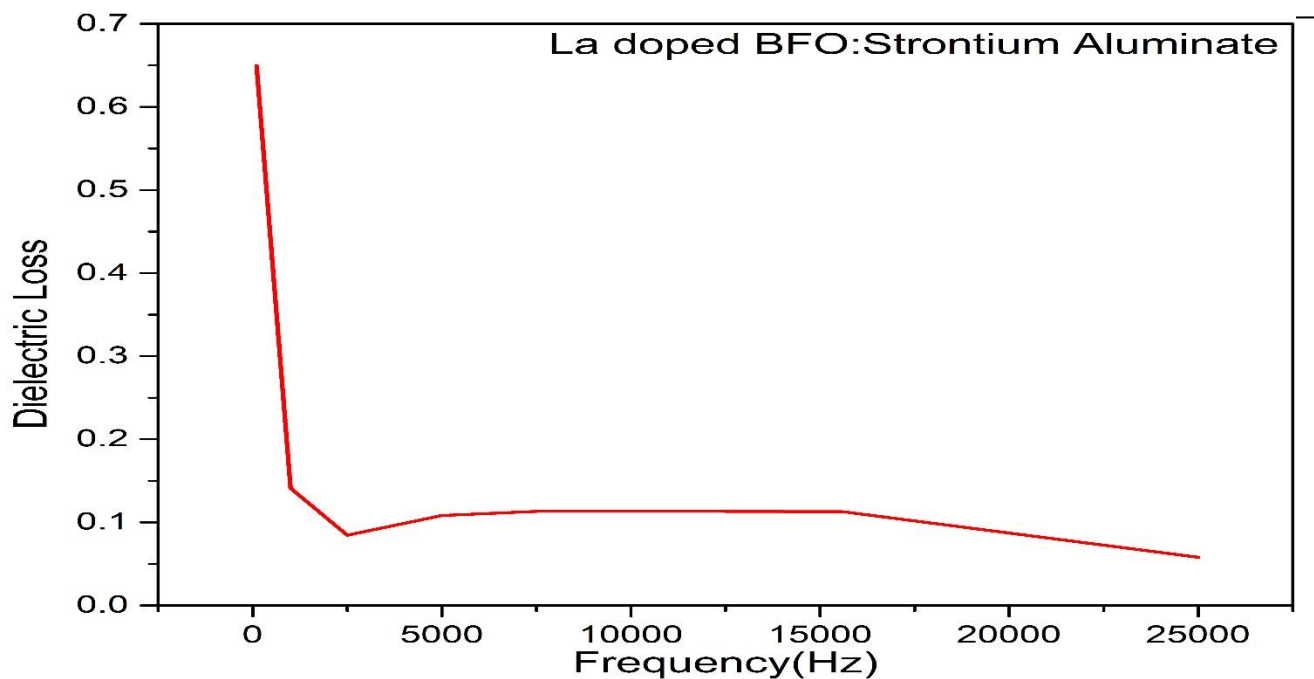


Figure 7. Frequency vs Resistance Plot of La doped BFO:SrAlO₃

5. Conclusion

The sample of La doped BiFeO₃:SrAlO₃ ferroelectric insulator composite ceramics were obtained using sol gel process and further studied for electrical conductivity studies for thermoelectric energy applications. According to X-ray diffraction study, the synthesized materials are mainly Perovskite in structure. It was not detected any foreign phases except those that occur during the production of bismuth ferrite BiFeO₃. A study of the frequency dependence of conductivity made it possible to reveal that the transport of charge carriers obeys the model of correlated overcoming of the barrier between two charged defects caused by oxygen vacancies. Dielectric loss is monotonically decreasing as frequency decreases.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests.

Declarations

Ethical Approval: Not Applicable

Competing Interests: This work includes personal interests.

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Availability of data and materials

All raw materials are taken from research laboratories of Lovely Professional University and further investigations were made at Central Instrumentation Facilities available at Lovely Professional University, Phagwara, Panjab, India.

CONTRIBUTION OF AUTHORS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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References

1. Nuraini, U., & Suasmoro, S. (2017). Crystal structure and phase transformation of BiFeO₃ multiferroics on the temperature variation. In *Journal of Physics: Conference Series* (Vol. 817, No. 1, p. 012059). IOP Publishing. 10.1088/1742-6596/817/1/012059
2. Srivastav, S. K., & S. Gajbhiye, N. (2012). Low temperature synthesis, structural, optical and magnetic properties of bismuth ferrite nanoparticles. *Journal of the American Ceramic Society*, 95(11), 3678-3682. <https://doi.org/10.1111/j.1551-2916.2012.05411.x>
3. Ghosh, S., Dasgupta, S., Sen, A., & Sekhar Maiti, H. (2005). Low-temperature synthesis of nanosized bismuth ferrite by soft chemical route. *Journal of the American Ceramic Society*, 88(5), 1349-1352. <https://doi.org/10.1111/j.1551-2916.2005.00306.x>
4. Gopal Khan, G., Das, R., Mukherjee, N., & Mandal, K. (2012). Effect of metal doping on highly efficient photovoltaics and switchable photovoltage in bismuth ferrite nanotubes. *physica status solidi (RRL)–Rapid Research Letters*, 6(7), 312-314. <https://doi.org/10.1002/pssr.201206211>
5. Han, S. H., & Kim, Y. J. (2004). Synthesis and Luminescent Characteristics of Sr₄Al₁₄O₂₅ Phosphor. *Korean Journal of Materials Research*, 14(8), 529-534. <https://doi.org/10.3740/MRSK.2004.14.8.529>
6. Zheng, X., Xu, Q., Wen, Z., Lang, X., Wu, D., Qiu, T., & Xu, M. X. (2010). The magnetic properties of La doped and codoped BiFeO₃. *Journal of Alloys and Compounds*, 499(1), 108-112. <https://doi.org/10.1016/j.jallcom.2010.03.131>
7. Bakkali, I., & Abla, W. Z. (2021). *Synthèse et caractérisation physico-chimique d'un nouveau matériau de type pérovskite SrAlO₃: application à la photo-dégradation du polluant orange G* (Doctoral dissertation). <http://repository.enp.edu.dz/xmlui/handle/123456789/9967>.
8. Simões, A. Z., Garcia, F. G., & dos Santos Riccardi, C. (2009). Rietveld analysis and electrical properties of lanthanum doped BiFeO₃ ceramics. *Materials Chemistry and Physics*, 116(2-3), 305-309. <https://doi.org/10.1016/j.matchemphys.2009.04.036>
9. Aishwarya, K., & Navamathavan, R. (2023). Effect of grain size and orthorhombic phase of La doped BiFeO₃ on thermoelectric properties. *Journal of Alloys and Compounds*, 947, 169452. <https://doi.org/10.1016/j.jallcom.2023.169452>.

10. El-Shater, R. E., El Shimy, H., Saafan, S. A., Darwish, M. A., Zhou, D., Trukhanov, A. V., ... & Fakhry, F. (2022). Synthesis, characterization, and magnetic properties of Mn nanoferrites. *Journal of Alloys and Compounds*, 928, 166954. <https://doi.org/10.1016/j.jallcom.2022.166954>.
11. Khalaf, M. M., Abd El-Lateef, H. M., Farghal, G., & Ibrahim, E. M. M. (2019). Magnetic Sm-BFO and Ce-BFO nanoflakes as protective coating layers for C-steel in acidic chloride environments. *Measurement*, 132, 99-108. <https://doi.org/10.1016/j.measurement.2018.09.049>.
12. Karpinsky, D. V., Troyanchuk, I. O., Tovar, M., Sikolenko, V., Efimov, V., & Kholkin, A. L. (2013). Evolution of crystal structure and ferroic properties of La-doped BiFeO₃ ceramics near the rhombohedral-orthorhombic phase boundary. *Journal of alloys and compounds*, 555, 101-107. <https://doi.org/10.1016/j.jallcom.2012.12.055>.
13. Tao, R., Shao, C., Li, X., Li, X., Liu, S., Yang, S., ... & Liu, Y. (2018). Bi₂MoO₆/BiFeO₃ heterojunction nanofibers: enhanced photocatalytic activity, charge separation mechanism and magnetic separability. *Journal of colloid and interface science*, 529, 404-414. <https://doi.org/10.1016/j.jcis.2018.06.035>.
14. Kazhugasalamoorthy, S., Jegatheesan, P., Mohandoss, R., Giridharan, N. V., Karthikeyan, B., Joseyphus, R. J., & Dhanuskodi, S. (2010). Investigations on the properties of pure and rare earth modified bismuth ferrite ceramics. *Journal of alloys and compounds*, 493(1-2), 569-572. <https://doi.org/10.1016/j.jallcom.2009.12.157>.
15. Turchenko, V. A., Trukhanov, A. V., Bobrikov, I. A., Trukhanov, S. V., & Balagurov, A. M. (2015). Study of the crystalline and magnetic structures of BaFe_{11.4}Al_{0.6}O₁₉ in a wide temperature range. *Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques*, 9, 17-23. <https://doi.org/10.1134/S1027451015010176>.
16. Zdorovets, M. V., Kozlovskiy, A. L., Shlimas, D. I., & Borgekov, D. B. (2021). Phase transformations in FeCo-Fe₂CoO₄/Co₃O₄-spinel nanostructures as a result of thermal annealing and their practical application. *Journal of Materials Science: Materials in Electronics*, 32(12), 16694-16705. <https://doi.org/10.1007/s10854-021-06226-5>.
17. Aishwarya, K., & Navamathavan, R. (2023). Effect of grain size and orthorhombic phase of La doped BiFeO₃ on thermoelectric properties. *Journal of Alloys and Compounds*, 947, 169452. <https://doi.org/10.1016/j.jallcom.2023.169452>.