A Composite of (95%) La$_2$CoMnO$_6$+ (5%) Ba$_{0.5}$Na$_{0.5}$TiO$_3$ : Study of Structural and Dielectric Properties

Dharmendra Mewada#, and Rajesh Kumar Katare

Department of Physics, SAGE University, Indore (M.P.), 452020, India

Abstract. This project work reports synthesis, structural and dielectric nature of composite of the type (95%) La$_2$CoMnO$_6$+ (5%) Ba$_{0.5}$Na$_{0.5}$TiO$_3$. The composite was characterized at room temperature for structural and dielectric properties. The structural characterization X-ray diffraction was carried for structural confirmation. The XRD data study convey the sample is dual phase in nature evident from the corresponding diffraction peaks. Monoclinic phase was acquired by La$_2$CoMnO$_6$ and the space group of the phase is P 1 21/n whereas Ba$_{0.5}$Na$_{0.5}$TiO$_3$ phase has acquired cubic structure with space group Pm-3m. The frequency dependent dielectric constant examined reveals high dielectric constant which decreases with increase in applied ac field values. Dielectric loss calculated shows the behaviour like dielectric constant which initially decreases abruptly with applied field and later attains frequency independent values. However, the ac conductivity was observed higher in the as synthesized.

1. Introduction

Oxides of the type ABB’O$_6$ (where A is rare earth and B and B’ are d-block transition metals) generally known as double perovskite exhibit a wide range of composition dependent ubiquitous features. To get insight of the physics underlying and the origin of these interesting physical properties, new double perovskite materials are explored. Further, they are fascinating the researchers due to their high application potential thereby their properties are subject to improvement. They are frequently explored to emphasize on their chemistry so that their production technology is explored to highlight their feasibility in the device applications. The study of these double perovskite materials is basically attractive due to the advancement in the techniques exploited for synthesis and characterization of these complex compositions and crystal structures. These materials have bright future as they are appealing their applicability in information recording higher-density media, spintronics, sensors of magnetic field, and detectors for infrared radiation, and have many other intriguing applications [1-3].

The ferromagnetic, $T_C \approx 225$ K of double perovskite, La$_2$CoMnO$_6$ possesses an insulating behavior. Cation ordering at B-site ions, defects and valences of cations are the main factors that give rise to their magnetic properties of La$_2$CoMnO$_6$. It is worth to mention it here that all these properties significantly depend on the conditions employed for sample synthesis. More than one magnetic transitions can be exhibited by the La$_2$CoMnO$_6$ system as revealed by the available literature. For La$_2$CoMnO$_6$, a FM transition at 220 K arises from an ordered sublattice where Co$^{2+}$ and Mn$^{4+}$ pairs possess high spin whereas low spin Co$^{3+}$ and high spin Mn$^{3+}$ associated to disordered sublattice of La$_2$CoMnO$_6$ gives rise to FM transition below 150 K. Furthermore, La$_2$CoMnO$_6$ samples treated at low temperature exhibit higher transition, $T_C \approx 220$ K where as high temperature firing of this double perovskite inherits lower transition, $T_C \approx 150$ K [4-8].

BaTiO$_3$ (BT) is considered as a potential candidate among of lead-free materials from technological point of view. It is a good ferroelectric materials and it is extensively exploited in variety...
of applications which include sensors, heaters, underwater transducers, multilayer capacitors. To extend the domain of functionality and applications with enhanced properties, as well as versatility, BTO has been modified from synthesis, doping, size dependence and many other aspects [9,10].

In the recent past, researchers were attracted due to the fact that grain boundary effects highly influence their physical properties of a material. The fact was attempted to be exploited in the enhancement of magnetic and other ferroic properties. However, the best method to exploit the concept was executed by the formation of composites where one phase is insulating, ferroelectric and the other is magnetic. These composites have shown dramatic properties for multifunctional material applications. As a result, they became the hot spot of materials research in the current also. In this piece of work, we throw light on the synthesis of (95%) La$_2$CoMnO$_6$ + (5%) Ba$_{0.5}$Na$_{0.5}$TiO$_3$ composite. Here La$_2$CoMnO$_6$ is ferromagnetic and Ba$_{0.5}$Na$_{0.5}$TiO$_3$ is ferroelectric in nature [11,12]. We characterized them for the structural and electric properties.

2. Preparation
We synthesized composite (95%) La$_2$CoMnO$_6$ + (5%) Ba$_{0.5}$Na$_{0.5}$TiO$_3$ by the method of solid state reaction. The procedure of solid state route consists of the following steps

**Weighing** ⇆ **Mixing** ⇆ **Calcination** ⇆ **Grinding** ⇆ **Palletization** ⇆ **Sinterin**

In the present work, the composite (95%) La$_2$CoMnO$_6$ + (5%) Ba$_{0.5}$Na$_{0.5}$TiO$_3$ was synthesized using La$_2$CoMnO$_6$ and Ba$_{0.5}$Na$_{0.5}$TiO$_3$. These compounds were used to prepare composite materials. Both these compounds were individually synthesized by solid state method. Herein, the quantities of the already synthesized samples as revealed by the molecular formula were weighed and mixed in an agate-mortar for a time duration of 5 hours. The mixture was then calcined for 5 h at 1000 °C. To obtain the final fine powder, the calcined material was ground for 1 h. To transfer the powder into the pellets, the powder is mixed with a binder known as polyvinyl alcohol (PVA). The pellets of disc shape were formed applying pressure of 5 tonnes per inch. The dimensions of the pellet was set to be 10 mm in diameter and width of 1 mm. To get hard and compact form of materials, we sintered the pellets so formed at 1000 °C for 5 h. The pellet was silver polished to form good electrical contacts for dielectric experimentation. The powdered sample is also ready for the characterization.

3. Experimentation
To prepare composite of the type (95%) La$_2$CoMnO$_6$ + (5%) Ba$_{0.5}$Na$_{0.5}$TiO$_3$, we employed solid state route and the composite was investigated for structural and dielectric properties.Bruker D8 Advanced spectrometer was used to emphasize on phase formation.

4. Dielectric Properties
The dielectric measurements were carried out using a laboratory made sample holder. The sintered pellets for dielectric measurement were silver polished to get better electric contacts and fired at 100°C for 1 h. The room temperature dielectric data was recorded for the synthesized sample on the instrument of Model E4980A Precision 101 LCR meter (2 Hz-2 MHz) from Keysight Technologies.

5. Results and Discussions
The composite (95%) La$_2$CoMnO$_6$ + (5%) Ba$_{0.5}$Na$_{0.5}$TiO$_3$ was characterized by XRD technique to confirm the structure acquired and f phase formation of the sample. We recorded the XRD data in the angular range of 20° ≤ θ ≤ 60° with a step size of 0.02°. Using Origin 8 software, the data was plotted after rearranging of the XRD data. The analysis of XRD spectra of composite (95%) La$_2$CoMnO$_6$ + (5%) Ba$_{0.5}$Na$_{0.5}$TiO$_3$ as displayed in Figure 1, reveals the presence of two phases. The phase La$_2$CoMnO$_6$ has acquired monoclinic structure (P 1 21/m) and the phase Ba$_{0.5}$Na$_{0.5}$TiO$_3$ has crystallized in cubic structure (Pm-3m). From the XRD data, it is evident that the characteristic XRD peak is very intense witnessing higher crystallinity exhibited by the sample. Further, the narrow FWHM reveals patterns the large grain size [8-10].
The calculated lattice parameters were \( a = 5.5195 \text{ Å} \), \( b = 5.4879 \text{ Å} \), \( c = 7.7826 \text{ Å} \) for La\(_2\)CoMnO\(_6\) phase with volume and density of 235.7382 \( \text{Å}^3 \) and 7.518 \( \text{g/cm}^3 \), and for Ba\(_{0.5}\)Na\(_{0.5}\)TiO\(_3\) phase, the lattice parameters were \( a = b = c = 4.0098 \text{ Å} \) with volume and density 64.4713 \( \text{Å}^3 \) and 4.500 \( \text{g/cm}^3 \).

The average crystallite size was calculated using Debye-Scherrer formula, \( D = \frac{k\lambda}{\beta\cos\theta} \) was found to be 85.5nm.

The as synthesized (95%) La\(_2\)CoMnO\(_6\) + (5%) Ba\(_{0.5}\)Na\(_{0.5}\)TiO\(_3\) composite material was studied for dielectric nature in the frequency range of 20Hz-1MHz at room temperature. The dielectric constant as a function of frequency is displayed in the Figure 2. The plot reveals higher dielectric constant with a decreasing trend with increase in the frequency [11-14].
The dielectric loss as a function of frequency also shows a decreasing behaviour when the value of applied field is increased as depicted by Figure 3

![Figure 3](image1.png)

**Figure 3.** Dielectric loss of (95%) La$_2$CoMnO$_6$ + (5%) Ba$_{0.5}$Na$_{0.5}$TiO$_3$ composite system.

The ac Conductivity studies reveals no response to the applied frequency to a certain limit as shown in Figure 4 and after that limit, the conductivity increases enormously with further increase in the applied field. This is attributed to the release of trapped charges by the defects after a threshold value of the ac field reaches [14-16].

![Figure 4](image2.png)

**Figure 4.** ac conductivity of (95%) La$_2$CoMnO$_6$ + (5%) Ba$_{0.5}$Na$_{0.5}$TiO$_3$ composite system
We are able to distinguish between electrode polarization effect and grain boundary conduction process from the study of electric modulus. Despite this, we look for relaxation time electrical conductivity and bulk properties. From Figure 5, the Cole-Cole plot, a shape of depressed semicircle curves is obvious with its centers positioned below real axis. This means it does not exhibit ideal Debye behavior. The sample exhibits a spread of relaxation distributed time constants[15,16]. As large dipoles are developed at the interfaces, higher values of applied field are not obeyed thereby orientation of dipolar bands gives rise to a new process. In addition to this, it also indicative of asymmetrical distribution of relaxation times.

Figure 5. Cole-Cole plot of (95%) $\text{La}_2\text{CoMnO}_6 + (5\%) \text{Ba}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ composite

Figure 6. Nyquist plot of (95%) $\text{La}_2\text{CoMnO}_6 + (5\%) \text{Ba}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ composite

Figure 6, known as Nyquist plot displays a nearly fit semicircle. The semicircle obtained is accordingly attributed to charge transport within the crystallites and grain boundary effects. The existence of grain
interior property is inferred display of single semicircular. The intercept of the semicircular arc with the real axis can be exploited to estimate the bulk resistance (Rb) of the material [14-18].

6. Conclusion
We synthesized biphase composite of the type of (95%) La$_{2}$CoMnO$_{6}$ + (5%) Ba$_{0.5}$Na$_{0.5}$TiO$_{3}$ via solid state reaction route successfully. The analysis of XRD data inferred monoclinic phase for La$_{2}$CoMnO$_{6}$ and cubic phase for Ba$_{0.5}$Na$_{0.5}$TiO$_{3}$. High dielectric permittivity was witnessed with comparatively lower dissipation values from the dielectric nature study. The structural stability and good dielectric nature ensures its potential for electric device applications. Non-Debye character is revealed from the modulus and impedance studies

Acknowledgement
UGC DAE CSR, an institute is acknowledged by the authors for extending its facilities. Authors are thankful to Dr. M. Gupta and Dr. R. Rawat for XRD and Dielectric characterizations respectively. We are grateful to Dr. N. Kaurav for providing lab facility. Finally, Govt. Holkar Science College is acknowledged for this opportunity.

References
[1]. Goodenough, J. B.; Wold, A.; Arnott, R. J.; Menyuk, N. Phys. Rev.1961, 124, 373–384.
[2]. Blasse, G. J. Phys. Chem. Solids 1965, 26, 1969–1971.
[3]. Anderson, M. T.; Greenwood, K. B.; Taylor, G. A.; Poeppelmeier, K. R. Prog. Solid State Chem. 1993, 22, 197–233.
[4]. Jonker, G. H. J. Appl. Phys. 1966, 37, 1424.
[5]. Goodenough, J. B. Phys. Rev. 1955, 100, 564–573.
[6]. Kanamori, J. J. Phys. Chem. Solids. 1959, 10, 87–98.
[7]. Dass, R. I.; Goodenough, J. B. Phys. Rev. B 2003, 67, 014401.
[8]. M. Saleem et al., Mater. Res. Express 6, 026304 (2019).
[9]. Dass, R. I.; Yan, J.-Q.; Goodenough, J. B. Phys. Rev. B 2003, 68, 064415.
[10]. T. Takenaka, K. Maruyama, and K. Sakata, Jpn. J. Appl. Phys., Part 1 30, 2236, 1991.
[11]. M. Saleem and A. Mishra, Chinese Journal of Physics 61 166 (2019).
[12]. V. Tandon, M. Saleem, N. Kaurav, and R. C. Dixit, AIP Conference Proceedings 2270, 110009 (2020).
[13]. Y. M. Chiang, G. W. Farrey, and A. N. Soukhojak, Appl. Phys. Lett. 73, 3683, 1998.
[14]. M. Saleem and D. Varshney, J. Alloys Compd. 708, 397 (2017)
[15]. H. Zheng, Y.-L. Dong, X. Wang, W.-J. Weng, G.-R. Han, N. Ma, P.-Y. Du, Angew. Chem. Int. Ed. 48 (2009) 8927–8930.
[16]. M. Saleem, A. Mishra and D. Varshney, J. Supercond. Nov. Magn. 32, 1475 (2019).
[17]. S.Q. Ren, L.Q. Weng, S.-H. Song, F. Li, et al., J. Mater. Sci. 40 (2005) 4375–4378.
[18]. M. Saleem, M. Padole, A. Mishra, Journal Of Advanced Dielectrics, 9, 1950034 (2019)