



Effect of Ba-Substitution at Sr-Site on the Structural and Dielectric Characteristics of SrMnO₃

M. Amir*, S. Atiq, S. Riaz and S. Naseem

Centre of Excellence in Solid State Physics, University of the Punjab, Quaid-e-Azam Campus, Lahore, Pakistan

*hmamir2009@gmail.com; satiq.cssp@pu.edu.pk; saira_cssp@yahoo.com; shahzad_naseem@yahoo.com

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ABSTRACT

Antiferromagnetic Ba substituted SrMnO₃ has a perovskite structure with a B-site magnetic ion which gives higher magnetic ordering temperatures. Ferroelectric transitions in these perovskites have been observed due to off centering of Mn⁴⁺ ions. In this work, we report synthesis of Sr_{1-x}Ba_xMnO₃ (x= 0.2, 0.4, 0.6 and 0.8) samples using sol-gel auto-ignition method. The prepared samples were sintered at 1000 °C for 4 hours each which ultimately led to the development of the perovskite structure, as determined by X-ray diffraction. The crystallite size was determined by using Scherrer's formula. Frequency dependent dielectric characteristics have been investigated systematically using an impedance analyzer. These studies reveal the decreasing dielectric behavior if the concentration of Ba is increased.

1. Introduction

Magnetism and ferroelectricity have played a vast role in the development of the technological devices in the past years. The idea of combining these two behaviors in a single material have gained much importance after the discovery of the perovskite compounds which show independent ferroelectric and magnetic behavior [1-3]. The materials which show magnetic and ferroelectric behavior simultaneously are known as multiferroics. Multiferroics are classified according to the strength of the coupling between the two behaviors [4]. Thus, they are classified as Type 1 multiferroics or proper ferroelectrics and Type 2 multiferroics or improper ferroelectrics [5].

Recently, many materials have been investigated theoretically [6, 7] and experimentally [8, 9] to conjugate these two exclusive properties because they have totally different origin. Mostly, ferroelectric behavior arises in transition metal oxides which have empty *d* shells while magnetic behavior arises because of the half-filled *d* or *f* orbitals [2]. Recently, Sakai et al. proved that Sr_{1-x}Ba_xMnO₃ (x=0 - 0.5) can generate both properties [10]. They showed that ferroelectricity can be generated due to the off-centering of the magnetic Mn ions in the perovskite Sr_{1-x}Ba_xMnO₃. The off-centering of Mn ions occurs due to the presence of two ionic states as Mn⁺³ and Mn⁺⁴. Similarly, polarization in CaMnO₃ and BaMnO₃ compounds has been formulated and a strong polarization effect is observed while the magnetic behavior is credited to the B-site magnetic ion.

In this research, we have investigated the effect of the substitution of Ba ions in SrMnO₃ compound at the Sr site on the structural and dielectric properties. With this substitution, the lattice constant increases which cause an increase in the unit cell volume. The preparation of the compound is accomplished by sol-gel self-ignition route which gives nano-sized homogenous grains. The structure was identified by comparing the X-ray Diffraction pattern. While dielectric properties were analyzed by using a 6500B series Impedance analyzer.

2. Experimental

The sol-gel auto ignition method is a distinctive fabrication technique which ensures the oxide formation in the desired material. [11]. In this research work, nanostructures of Sr_{1-x}Ba_xMnO₃ (0.2 ≤ x ≤ 0.8) have been prepared using the sol-gel technique. The powdered samples thus obtained are sintered to eliminate residuals. Four different samples of the Sr_{1-x}Ba_xMnO₃ (x = 0.2, 0.4, 0.6 and 0.8) were prepared and named as A, B and C, and D, respectively.

In order to prepare the Sr_{1-x}Ba_xMnO₃ (0.2 ≤ x ≤ 0.8) powder, we dissolved the appropriate amounts of analytical grade pure salts of barium nitrate [Ba(NO₃)₂·6H₂O], strontium nitrate [Sr(NO₃)₂·6H₂O], and manganese nitrate [Mn(NO₃)₂·6H₂O] in 150 mL distilled water. For the combustion reaction to occur, citric acid was used as a fuel agent in a molar ratio of 1:2 for metal nitrates to citric acid. The nitrates and acids were taken from Sigma Aldrich (USA) having purity ≥ 99%. The mixed solution was then dried at a constant temperature

* Corresponding author

of 200 °C and stirred constantly by using a magnetic stirrer. This heating and stirring led to form a xerogel. At this point, the temperature was raised to 300 °C for the combustion to occur. After 20 min, the exothermic auto-combustion reaction takes place and a powder is formed.

The powdered samples obtained are sintered at 1000 °C to attain pure nano-structure compound. The sintered powder was compressed to form pellets of thickness 1.2 mm and diameter 10mm having smooth surface which was required to analyze the dielectric properties.

3. Results and Discussion

3.1 Structural Analysis

Fig. 1 shows the XRD pattern of sample A, B & D. All of the samples show the hexagonal perovskite structure indexed with the JCPD card # 00-025-1471 while the sample D with concentration 80% of Ba have some extra peaks corresponding to JCPD card # 00-014-0228 which belongs to pure BaMnO₃. This incorporation of BaMnO₃ peaks confirms the substitution of Ba in the material. It could also be seen that angles of the peaks is also shifting towards lower values in the XRD pattern of the second and third sample which depicts the change in lattice parameter with the substitution of the Ba atoms on the Sr site [12]. The lattice parameters were calculated using the hexagonal formula given by:

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (1)$$

which can be combined with Bragg's equation to attain the form. This formula is used to determine the hkl values and lattice parameters.

$$\sin^2\theta = \frac{\lambda^2}{4a^2} \left[\frac{4}{3} (h^2 + hk + k^2) + \frac{l^2}{(c/a)^2} \right] \quad (2)$$

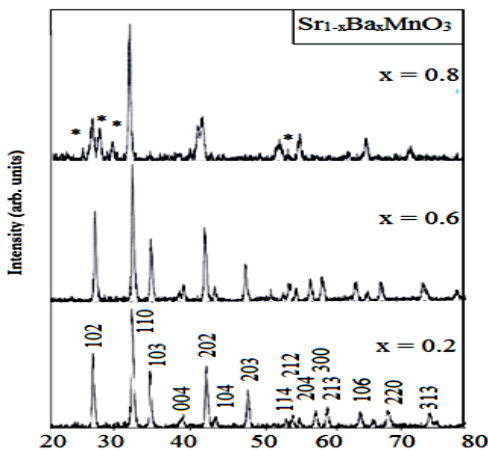


Fig. 1: XRD pattern of Sr_{1-x}Ba_xMnO₃ with x = 0.2, 0.6 and 0.8

The crystallite size is calculated from the Eq. 3:

$$\text{Crystallite size} = \frac{0.9\lambda}{\beta \cos\theta} \quad (3)$$

where λ is wavelength of the CuK α , used in XRD, β is the full width at half maxima of the strongest peak and the θ is the Bragg's angle.

The lattice parameters and crystallite size calculated from the XRD pattern is summarized in Table 1.

Table 1: Lattice Parameters, and Crystallite Size

Sample	Lattice Parameters	Crystallite Size(Å)
A	a (Å) = 5.44 c (Å) = 9.09	212
B	a (Å) = 5.59 c (Å) = 9.18	198
D	a (Å) = 5.62 c (Å) = 9.26	229

3.2 Dielectric Analysis

To study the electric field response of the material dielectric analysis were performed using an impedance analyzer. Using the values of the capacitance, obtained from the impedance analyzer, values of dielectric constant (ϵ') were calculated and plotted against the log of frequency. To calculate the values of dielectric constant $\epsilon' = AC/\epsilon_0 d$ relation is used [13]. The frequency range of our analyzer was 20 Hz to 20 MHz. Variation of dielectric constant versus frequency is shown in Fig. 2.

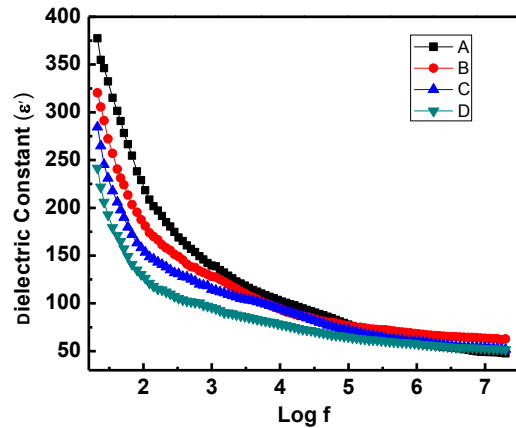


Fig. 2: Plot of dielectric constant versus log of frequency for samples of Sr_{1-x}Ba_xMnO₃ (0.2 ≤ x ≤ 0.8)

From Fig. 2, it is clear that the dielectric values tend to decrease with the increasing frequency. At a certain frequency called as relaxation frequency, the dielectric constant shows a saturation behavior. As can be seen in Fig. 2, the saturation point is reached at very high frequency. The decreasing trend of dielectric constant and high relaxation frequency can be explained with the help of the Maxwell-Wagner effect [14]. According to Maxwell-Wagner theory, the polarization among the charged particles occurs between the grains and pores interfaces, thus named as interfacial polarization. As the frequency is changed the polarity of the grains and pores

interfaces changes. Thus by increasing the frequency, the polarity changes rapidly and at a certain time the frequency becomes so high that the charges don't find time to change their positions and thus relaxation phenomenon occurs.

Fig. 3 shows the variation of the dielectric constant with the concentration of Ba in SrMnO₃ at different frequencies. It can be seen that the highest dielectric constant value is achieved for the sample with concentration of 20% for 1 kHz (black line). After that the value of dielectric constant decreases as the concentration is increased. Similar trend is observed for the rest of the frequencies. This behavior shows that samples are moving towards the semi-conducting phase.

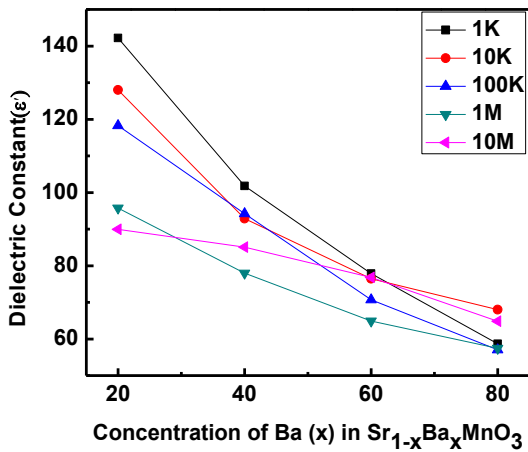


Fig. 3: Plot of dielectric constant vs percentage concentration of Ba (x) in Sr_{1-x}Ba_xMnO₃

Fig. 4 shows the graph of complex part of the dielectric with the frequency which is also termed as Loss

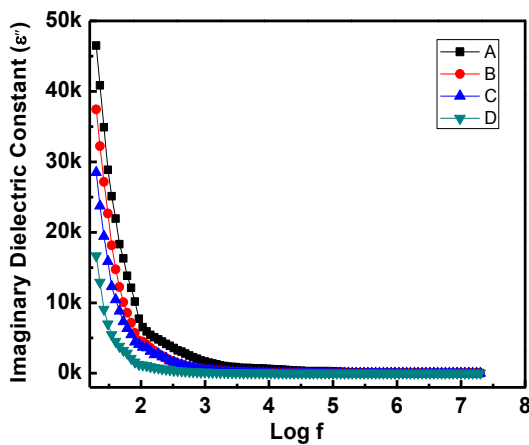


Fig. 4: Plot of Loss Factor versus Log of frequency for samples of Sr_{1-x}Ba_xMnO₃ (0.2 ≤ x ≤ 0.8)

factor. It can be seen that the graphs show the decreasing behavior as the frequency increases and comes to a point of saturation at high frequency. Secondly, the value of

complex dielectric constant decreases as we move towards the samples with higher concentration of Ba. This behavior is easily explained with the Debye relations [15].

$$\epsilon'' = (\epsilon_s - \epsilon_\infty) + \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (4)$$

Tangent loss is also known as the symbol for energy absorption in a dielectric material. When an AC voltage is applied to the dielectric material, it absorbs the electrical energy and then dissipates it as heat. The tangent loss determines the amount of energy dissipated. From Fig. 5 it is clear that at lower frequency more heat is lost as compared to higher frequencies. The reason for this loss of heat at lower frequency is that at low frequency, the material is storing the charge and acting like a pure

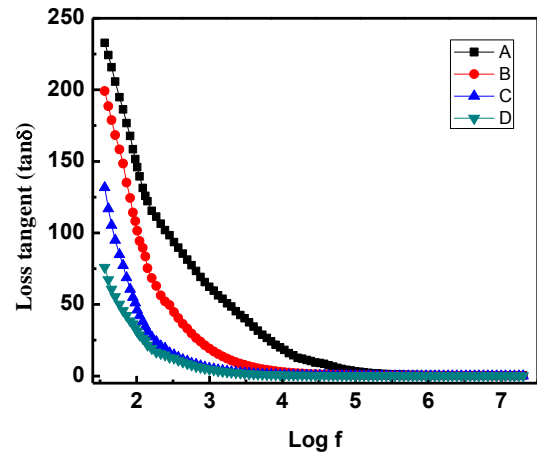


Fig. 5: Plot of Tangent Loss versus log of frequency for samples of Sr_{1-x}Ba_xMnO₃ (0.2 ≤ x ≤ 0.8)

dielectric material but when the charges do not remain in sequence with the frequency, the dielectric parameters decrease so the amount of the heat loss is reduced [16]. This result confirms our argument about a high dielectric constant value at lower frequency.

5. Conclusion

Sr_{1-x}Ba_xMnO₃ (0.2 ≤ x ≤ 0.8) powder were prepared from the Sol-Gel auto-combustion technique and then sintered at 1000 °C to obtain phase pure samples. X-ray diffraction patterns confirm the formation of the hexagonal perovskite structure of Sr_{1-x}Ba_xMnO₃ (0.2 ≤ x ≤ 0.8) samples. Dielectric studies reveal a good dielectric material whose dielectric properties are reduced as the concentration is increased. This result explains the possible presence of the ferroelectric polarization and as well as an increase in magnetic properties is also probable because the electric behavior is decreasing which could be determined by further research on this material.

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