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Relaxor-like ferroelectric behaviour favoured by short-range B-site ordering in 10% Ba^{2+} substituted $MgFe_2O_4$

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ABSTRACT

Using the molten salt method, pristine and Ba^{2+} substituted $MgFe_2O_4$ are prepared. The relaxor-like behaviour observed in the dielectric dispersion indicates the existence of B-site short-range ordering with the local $P4_122/P4_322$ symmetry which is confirmed by the Raman spectroscopy. The paper further analyses the origin of polarization using Maxwell–Wagner fit and Nyquist plot. This work suggests a possible way to increase the relaxor-like ferroelectric ordering, larger span of relaxation temperature (ΔT_m) and the effective masking of electronic contribution by the substitution of Ba^{2+} ion.

1. Introduction

The spinel ferrites (AB_2O_4) are room temperature insulating materials which are useful because of their technological applications as a ferromagnetic electrode in magnetic tunnel junctions or as a component in multiferroic heterostructures [1,2]. The studies on their electrical properties pointed out the key factor for its dielectric behaviour as the formation of Fe^{2+} ions and the transfer of electron between Fe^{3+} and Fe^{2+} ions occurring within the octahedral site. So the high permittivity observed even at high frequency has been attributed to the large polarization contributed by the extra electron present in Fe^{2+} ion by disturbing the symmetry of the electron cloud. At low frequencies, the large dielectric permittivity in ferrites is attributed to the Maxwell–Wagner polarization [3]. This can occur when various heterogeneities like depletion layer between sample and electrode, interfacial layer of a grain boundary and/or domain boundary exist in the material [4]. But George et al. [5] have reported a deviation of dielectric dispersion from Maxwell–Wagner effect for the fine powder of inverse $CoFe_2O_4$. However, the studies on this aspect are limited due to the lack of insight towards the existence of some other phenomenon responsible for the dielectric behaviour other than Maxwell–Wagner effect in ferrites [6–9]. Recent work by Schrettle et al. [10] on the magnetite (Fe_3O_4) using dielectric spectroscopy and other methods like PE loop provides the evidence for the existence of relaxor-like polar ordering below the Verwey Transition ($T_v \approx 122$ K). According to them, as the magnetite exhibits cubic inverse spinel structure at room temperature (RT), the Maxwell–Wagner effect dominates the dielectric behaviour of magnetite above T_v, while the relaxor behaviour originating below T_v is because of the transition of cubic to monoclinic and tetrahedral symmetries. Contemporary to this, the polarized Raman studies of $NiFe_2O_4$ single crystal [11] and thin films [12] have provided evidence for the existence of short-range B-site ordering even at room temperature. The occurrence of $P4_122/P4_322$ local symmetry which is non-centrosymmetric is said to be responsible for this B-site short-range ordering which is beyond the probing dimension of X-ray diffraction. The prerequisites for the existence of ferroelectricity are the structural distortion that removes the centre of symmetry and the d^0-ness of the B-site cation [13]. Aforesaid work on the spinel ferrites pound the pavement for studying the ferroelectric nature of $MgFe_2O_4$ (MFO) which has a partially filled Fe^{3+}/Fe^{2+} at A and B sites and Mg^{2+} with d^0-ness at B-site and locally having a non-centrosymmetric $P4_122/P4_322$ symmetry. Though Ba^{2+} has the similar electronic configuration as that of Mg^{2+}, the higher ionic radius Ba^{2+} substitution allows us to explore the role of Mg^{2+} in the dielectric property of MFO. In this light, we intended to study the dielectric behaviour of Ba^{2+} substituted MFO polycrystalline sample for the better understanding of the mechanism of dielectric polarization in spinel ferrite.

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2. Experiment

By employing the molten salt method explained elsewhere [14], pure and 10% Ba^{2+} substituted $MgFeO_4$ (B1M9FO) are prepared by dry mixing the A.R grade $MgSO_4{\cdot}9H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, NaOH and NaCl in a molar ratio of 1:2:8:10 and ground well. After calcining this mixture at 800 °C for 2 h, it is washed thoroughly to remove the unreacted NaOH and NaCl. Then the powder is calcined at 1100 °C for 2 h, to obtain the phase pure $MgFe_2O_4$. The phase formation is confirmed from the XRD using PAnalytical X'pert Pro with CuKα radiation. SEM images of the thermally etched sintered pellets were taken using FE-SEM (Quanta 3D). The Raman spectra are recorded at room temperature with Micro-Raman spectrometer (Reinshaw inVia) with an excitation wavelength of 488 nm. For the electrical measurements, the pellets of thickness 1 mm are sintered at 1200 °C for 2 h on which silver paste and fired at 300 °C for 1 h. N4L PSM1735 (Newton4th Ltd., UK) impedance analyzer is used for the dielectric measurement in the frequency range of 1 kHz to 1 MHz within a temperature region 35–400 °C with a heating rate of 3 °C/min in the heating mode. The dielectric hysteresis measurements are made using precision premier II ferroelectric loop tracer (Radiant Technologies, USA) with a maximum field of 40 kV/cm.

3. Results and discussion

X-ray diffraction studies show the cubic spinel structure with a space group $Fd\bar{3}m$ for the sintered samples. The XRD patterns are shown in Fig. 1 and the lattice parameters are deduced using Celref software. There are neither appreciable secondary peaks detected nor a change in lattice constant on 10%. Ba^{2+} substitution. However higher percentage Ba^{2+} substitution leads the secondary phase formation. The indexed patterns give a cell constant of (a = 8.3835 ?) comparable to the reported JCPDS # 89-3084 for $MgFe_2O_4$. The FE-SEM images shown in Fig. 1 reveal the discrepancy in the microstructure on Ba^{2+} substitution. The grains in MFO are closely packed while that of B1M9FO is unevenly distributed. An average grain size of 600 nm is found for MFO while B1M9FO has a grain size of 275 nm.

The room temperature Raman spectra of the samples have the space group $O^7{}_h$ ($Fd\bar{3}m$) for which the factor group analysis predicts 5 Raman active modes ($A_{1g} + E_g + 3T_g$) [15]. Fig. 2 shows the Raman spectra of MFO and B1M9FO with the modes A_{1g} at 700 and 634 cm^{-1}, E_g at 315 cm^{-1} and $3T_g$ at 540, 470 and 210 cm^{-1}. In general, the A_{1g} mode observed in the region of 620–720 cm^{-1} is assigned to the stretching vibration of Fe^{3+}–O (A_{1g} (Fe) at 634 cm^{-1}) and Mg^{2+}–O (A_{1g} (Mg) at 700 cm^{-1}) [1]. It is known that, in normal spinel structures, only five Raman modes are expected [11,15,16] whereas in inverse spinel structure, additional Raman modes appear. This additional mode observed at 634 cm^{-1} is due to the short range ordering of non-equivalent B-site atoms which has a symmetry lower than $Fd\bar{3}m$. Recently, the polarized Raman spectra measured for $NiFe_2O_4$ single crystal and thin films also provide evidence for the existence of a short-range order of B-site cation which is compatible with the $P4_122/P4_322$ symmetry which results from the lowest energy configuration [11,17]. Hence, the Raman spectra of MFO and B1M9FO samples reveal the existence of non-centrosymmetric $P4_122/P4_322$ local symmetry. The Ba^{2+} ion having a larger ionic radius is expected to increase the structural disorder of the oxygen sublattice. Though new modes are not observed (other than that of MFO) in the B1M9FO in Fig. 2, only a decline in the relative intensity and increase in the line-width of A_{1g} (Fe) at 634 cm^{-1} compared to A_{1g} (Mg) at 700 cm^{-1} is noted. This increase in the line-width indicates that Ba^{2+} ion substitution enhances the short-range ordering.

Temperature and frequency dependant relative permittivity for MFO and B1M9FO are shown in Fig. 3a and b respectively. In Fig. 3a, the dielectric constant for the MFO attains a peak at 235 °C ($T_{m@1kHz}$) for a frequency of 1 kHz. With increase in frequency, the temperature at which the dielectric constant is maximum (T_m), shifts towards a higher temperature. This indicates that the transition around 235 °C exhibits a relaxor behaviour. Similar

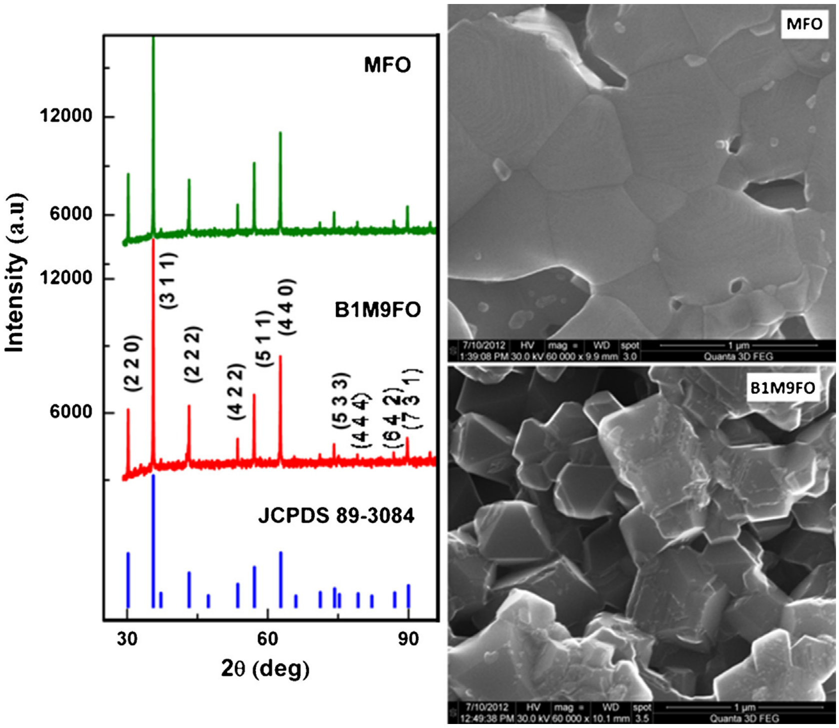

Fig. 1. XRD pattern of pure and 10% Ba^{2+} substituted MFO polycrystalline powder (left). The pattern is matched with the JCPDS data (JCPDS 89-3084). SEM micrograph of sintered MFO and B1M9FO (right).