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The structural, electrical and magnetoelectric properties of soft-chemically-synthesized SmFeO₃ ceramics

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Abstract

The structural, electrical and magnetoelectric properties of SmFeO₃ ceramic samples, synthesized using a soft-chemical method, were studied. A structural analysis of the material was carried out by the Rietveld refinement of room temperature x-ray diffraction data. The temperature dependence of the dielectric peaks was analyzed by fitting them with two Gaussian peaks corresponding to two phase transitions-one being electric, and the other being magnetic in nature. The depression angle of the semicircles in a Nyquist plot representing the grain and grain boundary contributions in the sample was estimated. The grain boundary effect, appearing at temperatures above 75 °C, is explained using the Maxwell–Wagner mechanism. The impedance study reveals a semi-conducting grain with an insulating grain boundary, leading to the formation of surface and internal barrier layer capacitors and resulting in a very high dielectric constant. The effect of dc conductivity on the loss tangent at low frequencies and high temperature has been analyzed. The frequency dependence of ac conductivity in the two different regions can be explained on the basis of correlated barrier hopping and quantum mechanical tunneling models. The material is found to exhibit canted antiferromagnetism and improper ferroelectric characteristics. The value of the magnetoelectric voltage-coupling coefficient (α) of a SmFeO₃ ceramic is found to be $2.2 \text{ mV cm}^{-1} \text{ Oe}^{-1}$.

Keywords: XRD, dielectric, impedance, conduction mechanism

(Some figures may appear in colour only in the online journal)

1. Introduction

Multiferroics with more than one ferroic ordering have been regarded as one of the most challenging and exciting materials over the last decade because of their use in the development of electronic devices, spintronics, information storage and communication. For potential applications of multiferroics, it is important to establish a general mechanism that gives rise to coupling between electrical and magnetic ordering [1–3] in the compound. In some multiferroics like BiFeO₃ [4] and RMnO₃ (R = rare-earth ions) [5], coupling between the two order parameters (spin and charge) is weak. Recently, strong coupling between these order parameters in

some multiferroics, like TbMnO₃ [6], and RMn₂O₅ [7], has been reported. It has also been reported that various types of spin ordering or interactions (symmetric exchange, anti-symmetric exchange and spin-ligand interactions) have potentially broken the inversion symmetry and produced spontaneous polarization [8, 9]. Rare-earth ortho-ferrites (RFeO₃) generally crystallize in the centro-symmetry space group Pbnm in their bulk form and show interesting dielectric, optical and magnetic properties [10–14]. Recently, a weak electric polarization of improper origin (induced by magnetic order) has been reported in GdFeO₃ [15], DyFeO₃ [16] and SmFeO₃ [11]. The origin of magnetically induced ferroelectricity in SmFeO₃ can be explained on the basis of a theoretical model called the spin current induction model. According to the model, a small improper polarization appears when a centro-symmetric crystal with a non-collinear spin structure undergoes a para-to-antiferromagnetic transition [17]. In the SmFeO₃ temperature dependence of magnetization, i.e. the para-to-antiferromagnetic (AFM) transition at 670K, spin reorientation at 480 K and spontaneous magnetization reversal at cryogenic temperatures have been reported [18, 19]. Some researchers have reported colossal (very high) dielectric constants in RFeO₃ ceramics [20–22], mainly due to electrical heterogeneity with a semiconducting grain and more resistive grain boundary. Prasad et al [23] have also reported the colossal dielectric behavior of SmFeO3 and explained their findings on the basis of internal barrier layer capacitor (IBLC) mechanisms. Though many of the properties of SmFeO₃ ceramics have been studied, a comprehensive effort is necessary to understand the structural, dielectric, electric conduction and magnetoelectric properties of the material. In the present work, we have extensively studied the above properties of SmFeO₃ ceramics fabricated by chemical methods in different experimental conditions. In addition, a detailed analysis of the impedance spectroscopy is presented. The conduction mechanism of the material can be explained on the basis of correlated barrier hopping models and quantum mechanical tunneling models. The magnetoelectric effect was studied and reported here.

2. Experimental details

2.1. Materials

Analytical-grade samarium oxide Sm_2O_3 , (M/S Loba chemie, 99.9%), ferric nitrate nonahydrate Fe (NO₃)₃.9H₂O (M/S Loba chemie, 99.9%), citric acid C₆H₈O₇.H₂O, (M/s Finar reagents, 99.7%), nitric acid HNO₃ and distilled water were used as the raw materials for the synthesis of SmFeO₃.

2.2. Synthesis of SmFeO₃

A polycrystalline sample of SmFeO₃ was synthesized using the following the steps: first, samarium nitrate was prepared by adding concentrated nitric acid to samarium oxide (Sm₂O₃). The iron nitrate and samarium nitrate solutions were then prepared individually by adding stoichiometric amounts of the raw materials to distilled water under continuous stirring. Appropriate quantities of iron- and samarium-based solutions were mixed and homogenized by continuous stirring at 70-80 °C. Citric acid was dissolved in water such that the total molar amount of acid was equal to the sum total of molar amounts of metal nitrates in the solution. Then, the citric acid solution was added to the mixed solution and stirred well. When the solution had become a viscous liquid, it was dried in an oven at 100 °C for 12h. Then the powder was ground and calcined at 850 °C for 4h in an alumina crucible. The calcined powder was cold pressed into small cylindrical pellets under an isostatic pressure of 5×10^6 Nm⁻² with polyvinyl alcohol (PVA) as the binder. The pellets were sintered at 1200 °C for 6h.

2.3. Characterization

The room temperature x-ray diffraction (XRD) pattern of the calcined powder was recorded at a wide range of Bragg angles θ (20° $\ge 2\theta \ge 80^{\circ}$) using an x-ray diffractometer (Rigaku Miniflex, Japan) to check the formation of the desired compound and its crystal structure. The sintered pellet was polished to make its faces smooth and parallel, and subsequently electroded with high-purity silver paste for electrical measurements. The dielectric and impedance data were obtained using a computer-controlled impedance analyzer (phase sensitive meter) in a wide range of frequencies (100 Hz-5 MHz) at different temperatures (25-300 °C). The electric field dependence of the polarization measurement of the sample was carried out by a high-precession P-E loop tracer (version 4.9.0 of Radiant Technologies, Inc.). A room temperature *M*-*H* loop of the sample was carried out using SQUID. The magnetoelectric coefficient measurement was performed in longitudinal mode by an ME set up (Marine India) connected to a lock-in amplifier on the electrically and magnetically poled samples. In this experiment, the dc magnetic field up to 7 kOe was produced by an electromagnet whereas the ac magnetic field was produced by a Helmholtz coil with 200 turns and a radius of 2.5 cm. The ME voltage which developed across the sample was measured using a lock-in amplifier (SR830).

3. Results and discussion

3.1. Structural analysis

The room temperature XRD pattern of the polycrystalline SmFeO₃ sample calcined at two different temperatures (700 °C and 850 °C) is shown in figures 1(a) and (b). All the XRD peaks of figures 1(a) and (b) were indexed. Using a Sm_Fe_ O3 structure reference model of the 04-009-8408 CIF file, we performed the Rietveld refinement of both the XRD patterns (figures 1(c) and (d)). During refinement, the background, profile, Rietveld scale factors, preferred orientation and the unit cell parameters were refined keeping the structural parameters similar to those of the reference model. The accuracy and reliability of the refinement were mainly decided by the pattern R factor (R_{exp}) and the weighted pattern R factor (R_{wp}) . The Bragg R factor (R_b) and the goodness-of-fit (GOF) are defined by the ratio of R_{wp}/R_{exp} etc. In figures 1(c) and (d), the blue line represents the experimental data, the black solid line represents the computed data and the bottom line within the box represents the difference between the observed and calculated intensity. The refined values of R_{exp} , R_{wp} , R_b and GOF are given in figures 1(c) and (d). The refined values of the parameters are better in figure 1(d) compared to (c). The 'goodness-of-fit' parameter of the sample for figures 1(c) and (d) was found to be 1.01 and 1.00 compared to that of the reference model. As the SmFeO₃ sample calcined at 850 °C fits better with the structural reference model, we have used this sample for further characterization of the material. The refined parameters in both cases indicate that SmFeO₃ crystallizes in an orthorhombic crystal system. The lattice parameters of the samples calcined at 700 °C and 850 °C were found to be



Figure 1. XRD pattern of the SmFeO₃ sample calcined at (a) 700 °C and (b) 850 °C. The Rietveld refinement of the SmFeO₃ sample calcined at (c) 700 °C and (d) 850 °C.

a = 5.58 Å, b = 7.71 Å and c = 5.39 Å as well as a = 5.56 Å, b = 7.85 Å and c = 5.55 Å respectively, which are consistent with the reported ones [20]. With an increase in the calcination temperature from 700 °C to 850 °C, the coherently diffracted domain size, which is generally also referred to as the crystallite size, increases from 51 nm to 65 nm.

3.2. Dielectric characteristics

The temperature dependence of the relative dielectric constant (ε_r) and loss tangent (tan δ) at various frequencies is shown in figures 2(a) and (b) respectively. Initially, up to 50 °C, the dielectric constant seems to be independent of both the frequency and the temperature. Thereafter, the dielectric constant increases with increasing temperature, exhibits two anomalies at 180 °C and 220 °C, and then decreases.

At low frequencies (~100 Hz), with an increase in temperature the dielectric constant increases exhibiting anomalies at 175 °C and 218 °C, and then decreases. At relatively higher frequencies (500 Hz–500 kHz), both peaks (anomalies) merge into one peak which occurs around 215 °C. The noticeable dielectric anomaly shifts towards higher temperatures with increasing frequency [24].

While analyzing the peaks we found that the single peak at higher frequencies is a result of the superposition of two Gaussian-like peaks centered at 180 °C and 220 °C. In order to extract the peak position accurately, two Gaussian peaks are superimposed in the form $\varepsilon_r = \sum_{i=1}^2 A_i \exp \left[-(T - B_i/C_i)^2\right]$, where A_i , B_i and C_i are the amplitude, centroid and width of the peaks respectively. These were used to fit the experimental data of the dielectric constant versus the temperature curve. It was found from the fitting that these peaks correspond to two



Figure 2. (a) Variation of the dielectric constant with the temperature at a different frequency of SmFeO₃. (b) Variation of tan δ with the temperature at a different frequency of SmFeO₃.

different mechanisms. The first peak appears between 175 °C and 189 °C for frequencies 100 Hz–500 kHz, and is the major contributor to the dielectric constant in the low-frequency range up to 20 kHz. The second peak, appearing between 227 °C and 218 °C for frequencies 100 Hz–500 kHz, is the major contributor for frequencies above 20 kHz. The relative strength of the first peak as compared to the second peak continuously decreases with an increase in frequency. On increasing the frequency, the peak shifts slightly to a higher temperature and the maxima of the dielectric constant decreases from 55 000 units at 100 Hz to 500 units at 1.0 MHz. The peak is depressed further and more broadly for frequencies higher than 1 MHz. These characteristics indicate that the polarization mechanism associated with the first peak is of the Maxwell–Wagner type wherein the largest inertia of the migrating ion results in a

sharp drop of peak dielectric constant, and an increase in temperature for the peak position. The second peak around 220 °C is most likely to be associated with the polarization induced by magnetic spin reorientation. This reasoning has its basis on the reported [13] spin reorientation of SmFeO₃ at 480 K (207 °C). The dielectric anomaly triggered by magnetic ordering can be explained on the basis of the Landau–Devonshire theory. With an increase in frequency, the temperature corresponding to this peak decreases. Hence, the dielectric constant suffers two phase changes which are electric and magnetic in nature at the temperatures corresponding to the two Gaussian peak positions for each frequency. The amplitude, centroid and width of both the peaks in the SmFeO₃ sample are listed in table 1.

The temperature dependence of the tangent loss pattern in figure 2(b) reveals a peak which shifts towards a higher

Frequency (kHz)	Amplitude of the peak		Centroid (°C)		Peak width (°C)	
	$\overline{A_1}$	A_2	B_1	<i>B</i> ₂	$\overline{C_1}$	C_2
0.1	55 000	33 000	175.0	227.0	45.0	21.0
1	18700	12100	180.0	219.5	42.5	25.5
10	15000	11100	180.5	216.0	48.0	32.0
100	2354	4924	186.6	215.7	39.0	55.0
500	786	1021	188.6	217.9	79.0	40.0



Figure 3. (a) Variation of the dielectric constant with the frequency at a different temperature of SmFeO₃. (b) (i) Variation of tan δ with the frequency at different temperatures of SmFeO₃ and (b) (ii) the theoretical fitting of the experimental data of tan δ at 200 °C.

temperature with increasing frequency. In the high-temperature region, $\tan \delta$ increases more quickly with an increase in temperature; this is mainly due to increased conductivity at higher temperatures [25].

The frequency dependence of the dielectric constant (ε_r) and the loss tangent (tan δ) at different temperatures is shown in figures 3(a) and (b). The frequency-dependent plot of the dielectric constant of the SmFeO₃ ceramic sample exhibits behavior similar to that observed in high-dielectric-constant materials [26, 27]. The studied material shows a high dielectric constant (with a step-like decrease on increasing frequency, which is accompanied by a loss peak in the frequency dependent plot. The loss peaks shift towards higher frequencies as the temperature increases suggesting the presence of a thermally activated Debye-like dipolar relaxation in the material.

Figure 3(a) displays two permittivity mechanisms with different slopes: a shallow slope at low frequency and a steep slope at high frequency. The low-frequency and high- permittivity slope is due to the GB (grain boundary) effect, whereas the slope of the high- frequency and low-permittivity region is due to the intrinsic bulk effect. The low-frequency dielectric constant of SmFeO₃ assumes very high values (1000–60000) as the temperature increases from 25 °C to 200 °C. This giant

dielectric behavior is due to the Maxwell–Wagner mechanism of space charge polarization. In such cases, the grain is found to have a relatively low resistance and activation energy while the grain boundary has a relatively large resistance and higher activation energy. A conducting grain with an insulating grain boundary produces a surface and internal barrier layer capacitor, which explains the giant/high dielectric constant in the samples [28–31]. This aspect is quantitatively explained while discussing the impedance results in the next section.

Two different relaxation mechanisms are evident from the frequency dependence of the tan δ plot (figure 3(b)(i)). The solid line with a symbol represents the entire tan δ response, whereas the dashed line in the plot represents the intrinsic bulk effect (which is detected in the high-frequency region). As can be seen in figure 3(b)(i), for temperature T (≥ 150 °C) tan δ initially decreases, and then shows a Debye-like relaxation. The initial decrease in tan δ is attributed to the loss associated with conductivity. The two mechanisms contributing to the loss tangent correspond to (i) Debye-type dipolar relaxation and (ii) dc conductivity, which is dominant at lower frequencies and higher temperatures. Considering both these mechanisms, the loss tangent is generally expressed as [32]:

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} + \frac{\sigma_{\rm dc}}{\omega \varepsilon'}.$$
 (1)

Furthermore, as discussed in section 3.4, in the ceramic sample the relaxation times are distributed, which is evident in the depressed semicircle in the Nyquist plot with the central line making an angle θ with the real axis. Taking this aspect of distributed relaxation time in the sample, the complex permittivity can be expressed as [33, 34]:

$$\varepsilon^* = \varepsilon_{\infty} + \frac{\varepsilon_{\rm s} - \varepsilon_{\infty}}{1 + ({\rm i}\,\omega\tau)^{1-\alpha}}$$

where ε_s is the static relative permittivity, ε_{∞} is the high-frequency value of relative permittivity, and τ is the relaxation time obtained from the peak in the $\varepsilon'' \sim \omega$ curve. α is a parameter which represents the distribution of relaxation time and is obtained from the Nyquist plot. For an ideal Debye-type relaxation, $\alpha = 0$. Using the above relation ε' and ε'' appear as

$$\varepsilon' = \varepsilon_{\infty} + \frac{(\varepsilon_{s} - \varepsilon_{\infty}) \left[1 + (\omega\tau)^{1-\alpha} \cos(1-\alpha) \frac{\pi}{2} \right]}{1 + (\omega\tau)^{2(1-\alpha)} + 2(\omega\tau)^{1-\alpha} \cos(1-\alpha) \frac{\pi}{2}}$$
(2)

$$\varepsilon'' = \frac{(\varepsilon_{\rm s} - \varepsilon_{\infty}) \left[(\omega \tau)^{1-\alpha} \sin(1-\alpha) \frac{\pi}{2} \right]}{1 + (\omega \tau)^{2(1-\alpha)} + 2(\omega \tau)^{1-\alpha} \cos(1-\alpha) \frac{\pi}{2}}.$$
 (3)

To comprehend the contribution of both the mechanisms to tan δ , figure 3(b)(ii) has been plotted. The contribution to tan δ corresponding to the Debye relaxation, computed on the basis of the first term of equation (1), is shown as a red line. The contribution of conductivity computed on the basis of the second term of equation (1), is shown as a green line. The sum of these contributions is shown as a blue line, which is in reasonably good agreement with the experimental one (black solid line). All these graphs show the frequency variation of tan δ at a temperature of 200 °C. For computation of the terms,

we have used the data obtained from impedance studies, and the parameter α is taken as $\alpha = \theta/\pi$. As can be seen from the figure, the term associated with conductivity remains dominant at lower frequencies while the Debye-like relaxation is effective at relatively higher frequencies. At a lower temperature, the thermal energy of ions is insufficient for transportation to the grain boundary, and as such the conductivity term will make less of a contribution to tan δ .

The inset figure in the tan δ plot in figure 3(b)(i) shows the variation of relaxation time (τ) with temperature for the SmFeO₃ sample. The electric dipole in ferrites originates from the hopping of the charge carriers. When the charge carriers are thermally activated, the hopping rate increases; the relaxation time hence decreases with temperature. The temperature dependence of the relaxation time can be explained by the following equation [35],

$$\tau = \tau_{\rm o} \exp\!\left(\frac{-E_{\rm a}}{k_{\rm B}T}\right) \tag{4}$$

where E_a is the activation energy of the relaxation process, k_B is the Boltzmann constant and τ_o is the maximum relaxation time. The linear fitting of the theoretical data suggests that only one type of relaxation process corresponds to the bulk effect and the activation energy of the relaxation process is found to be 0.57 eV.

3.3. Impedance spectroscopy

Generally, the impedance properties of the sample arise due to the intragrain, intergrain and electrode processes. The motion of charges can occur in a variety of ways, namely charge displacement (long-range or short-range), dipole re-orientation and space charge formation etc. The frequency dependence of the complex impedance $Z^*(\omega)$ of the present sample can be explained on the basis of the following equation:

$$Z^* = Z' + jZ'' \tag{5}$$

where $Z'(\omega)$ and $Z''(\omega)$ are the real and imaginary part of the complex impedance. The real (Z') and imaginary part (Z'') of the complex impedance ($Z^* = Z' + jZ''$) can be defined by the following equation [36, 37]:

$$Z' = \frac{R}{1 + (\omega \tau)^2}$$
 and $Z'' = -\frac{\omega R \tau}{1 + (\omega \tau)^2}$ (6)

where $\tau = \text{RC}$ is the relaxation time, *R* is the measured resistance, *C* is the measured capacitance and ω is the angular frequency of the electric field. The frequency dependence spectrum of the real part of the impedance is shown in figure 4(a). The spectrum suggests that the value of *Z'* decreases with an increase in temperature in the low-frequency region. This behavior suggests that the material possesses a negative temperature co-efficient of resistance (NTCR) [38].

Figure 4(b) shows the frequency dependence of the spectrum of the imaginary part of the impedance at different temperatures. This spectrum suggests the behavior of the most resistive part in the sample. Closure inspection of the spectrum indicates that there are two relaxation mechanisms with



Figure 4. (a) Variation of Z' with the frequency at different temperatures of SmFeO₃. (b) Variation of Z'' with the frequency at different temperatures of SmFeO₃.

different relaxation times. The peak in the higher frequency region explains the effect of grains [39], and as observed in the dielectric loss spectrum, the peak shifts towards a higher frequency with an increase in temperature. Since the loss tangent and the imaginary part of the impedance are correlated to each other, the low-frequency part (indicated by the arrowed line) has its origin in the grain boundary effect.

3.3.1. Nyquist plot. The complex impedance plots of Z' versus Z'' (Nyquist plot) at different temperatures are shown in figure 5. The complex impedance plots are characterized by the successive semicircular arcs of grain, grain boundary and electrode contributions, and each arc is represented by an equivalent circuit element made of resistance, capacitance etc. The nature of the arc indicates the type of relaxation mechanism for the system. Each perfect semicircular arc with a center on the Z' axis indicates the presence of a mono relaxation time and grain homogeneity. But in real systems, depressed

semicircles are obtained which indicate the distribution of relaxation time due to inhomogenity in the grain size and electromagnetic diffusion [40]. The depression angle is the angle between the real axis and the line joining the center of the circle with its high-frequency intersection on the real axis [41]. It was observed that the room temperature impedance plot (at 25 °C and 50 °C) was composed of one depressed semicircular arc. This indicates the grain contribution and can be represented by a parallel RQC circuit. The constant phase element in the circuit suggests deviation from the ideal Debye-type response. However, as the temperature increases, the grain boundary contributions become stronger than the grain contribution. We postulate that the second semicircle originates from the induced polarization occurring at grain boundaries. The grain and grain boundary contribution can be represented by two parallel RQC circuits connected in series. From the fitted curve, the value of grain resistance (R_g) , grain boundary resistance (R_{gb}) , grain capacitance (C_g) and grain boundary capacitance (C_{gb}) have been evaluated and listed in table 2.

As reported in table 2, the capacitance due to the grain effect at room temperature is around 5.9 pF, while the capacitance associated with the grain and grain boundary effect at 125 °C corresponds to 0.31 nF and 2.67 nF respectively. Similarly, the resistance due to the grain and grain boundary effects at 125 °C is 24.26 k Ω and 282.37 k Ω respectively. The large value of GB resistance can be directly inferred from a simple inspection of the Nyquist plot where the semicircle corresponding to the GB effect is quite large in comparison to that of the bulk effect. The activation energy as calculated from the conductivity versus temperature for the bulk and the grain boundary effect is 0.44 eV and 0.64 eV respectively. The value of the resistance and activation energy clearly indicates a relatively conducting grain surrounded by an insulating grain boundary. This situation leads to the formation of surface and internal barrier layer capacitors (IBLCs), and results in very large dielectric constants.

3.4. AC conductivity study

Using the well-known relation $\sigma_{ac} = \omega \varepsilon_0 \varepsilon \tan \delta$, the ac conductivity of the material was calculated where all the symbols have their usual meaning. The variation of ac conductivity with the inverse of absolute temperature at a selected frequency between 100 Hz and 500 kHz is presented in figure 6. The conductivity variation with temperature can be explained on the basis of the Arrhenius relation [42],

$$\sigma = \sigma_{\rm o} \exp\!\left(\frac{-E_{\rm a}}{k_{\rm B}T}\right) \tag{7}$$

where σ_0 is the pre-exponential factor and k_B is the Boltzmann constant. The above equation can be written as $\ln \sigma = -E_a/k_BT + \ln \sigma_0$. So, the activation energy is calculated from the slope by the linear fitting of $\ln \sigma$ versus the 1000/*T* plot in different temperature regions. From the figure it is observed that the slope in the graphs changes at around 195 °C for 100 Hz but at 225 °C for 500 kHz. The two slopes suggest the existence of two different conduction mechanisms at high



Figure 5. Nyquist plot (Z' versus Z'') of SmFeO₃ at different temperatures.

Table 2. Grain resistance (R_g), grain boundary resistance (R_{gb}), grain capacitance (C_g), grain boundary capacitance (C_{gb}) and depression angles at selected temperatures.

Temperature (°C) $R_{\rm g} ({\rm k}\Omega)$	$C_{\rm g}$ (F)	$ heta_{ m g}$	$R_{\rm gb}~({ m k}\Omega)$	$C_{\rm gb}({ m F})$	$ heta_{ m gb}$
25	1930.30	$5.94 * 10^{-12}$	24.68°	_	_	
125	24.26	$3.16 * 10^{-10}$	16.08°	282.3696	$2.67 * 10^{-9}$	18.01°
225	1.76	$3.955 * 10^{-10}$	13.57°	5.67	$2.65 * 10^{-8}$	27.19°





Figure 6. Variation of ac conductivity with the temperature at a different frequency range.

and intermediate temperatures. As can be seen in figure 6, the value of activation energy (calculated from the slope) was found to decrease from 1.024 eV at 100 Hz to 0.7 eV at 500kHz in the high-temperature region, while it increases from 0.334 eV at 100 Hz to 0.564 eV at 500kHz in the relatively low- temperature region.

The frequency dependence of $\sigma_{\rm ac}(\omega)$ at various temperatures is shown in figure 7. It is clear from the graph that the frequency dependence of $\sigma_{\rm ac}(\omega)$ can be explained by the equation,

$$\sigma_{\rm ac} = A\omega^s \tag{8}$$

where A is a constant depending on temperature, ω is the angular frequency and s is the frequency exponent which is generally less than equal to unity. In a comparative analysis

Figure 7. Variation of ac conductivity with the frequency at different temperatures of SmFeO₃.

of impedance spectra, conductivity data gives two different results in the low-temperature (\leq 75 °C) and high-temperature (\geq 75 °C) region. The low-temperature region shows a slow transition from a weak frequency variant conductivity (~up to 200 kHz) to a strong frequency variant (~200 kHz–5 MHz) conductivity part. The high-temperature conductivity region can be categorized into three distinct regions: a lowfrequency part followed by a weak-frequency-variant region in the frequency range of 10 kHz–1 MHz and then a fastfrequency-variant region ($\nu >$ 1 MHz). It is pertinent to recall here that the Nyquist plot corresponding to temperatures below 75 °C has only one semicircle corresponding to the grain effect, and that at higher temperatures we have two semicircles corresponding to the grain boundary effect dominant at low



Figure 8. Variation of the frequency exponent with the temperatures of SmFeO₃ ceramics.

frequency and grain effect in the high-frequency region. So, low-frequency high-temperature conductivity is mainly due to the grain boundary effect where the Maxwell-Wagner mechanism prevails. The low- and high-temperature intermediate frequency part can be explained by bulk conductivity. There is a change in the slope between the low-frequency range (up to 10kHz) and intermediate-frequency region (10 kHz-1 MHz) which suggests the existence of different conduction mechanisms. There are several theoretical models (quantum mechanical tunneling [43], small polaron hopping [44], overlapping large polaron tunneling [45] and the correlated barrier hopping model [46]) which explain the conduction mechanism. These theoretical models can be used to explain the temperature dependence of the frequency exponent 's'. The value of 's' can be calculated from equation (8), which can be rewritten as:

$\log \sigma_{\rm ac} = \log A + s \log \omega$

hence the slope of the log σ_{ac} versus log ω graph provides the value of 's'. In our work, the value of s has been calculated at different temperatures (25 °C–225 °C) within the frequency range of 100 Hz–500 kHz to recognize both the bulk and grain boundary conduction mechanism. The temperature dependence of 's' is shown in figure 8. As can be seen in the figure, for all temperatures above 50 °C, the log σ_{ac} versus log ω curves for the frequencies bounded by the two black dotted near parallel lines remain parallel, indicating that the slope of s is nearly independent of temperature. Using figure 7, the calculated value of s for this bounded region is found to be 0.16. The temperature- independent frequency exponent 's' indicates that conduction is based on quantum mechanical tunneling [47, 48].

It was observed that the frequency exponent corresponding to the low-frequency region for temperatures greater than 75 °C decreases with increasing temperature, which follows the correlated barrier hopping model [49]. It is worth pointing out that the high dielectric constant in the samples can be explained on the basis of semiconducting grains surrounded by an insulating grain boundary and the formation of surface and internal barrier layer capacitors (IBLCs). The correlated barrier hopping model was first proposed by Pike [50] and describes the transfer of electrons by thermal activation over the barrier between two sites, each having a columbic potential associated with it. According to this model, ac conductivity can be given by the equation [51]

$$\sigma(\omega) = \frac{1}{24} \pi^3 N^2 \varepsilon \varepsilon_0 \omega R_\omega^6 \tag{9}$$

where R_{ω} is the hopping distance at frequency ω and can be expressed as:

$$R_{\omega} = \frac{e^2}{\pi \varepsilon \varepsilon_0 \left[W_m + kT \ln(\omega \tau_0) \right]} \tag{10}$$

where τ_0 is the relaxation time and W_m is the effective barrier height resulting from the overlapping of Coulomb's well for the neighboring sites separated by the distance *R*. The frequency exponent 's' in the CBH model can be approximated as,

$$s = 1 - \frac{6kT}{W_m + kT\ln(\omega\tau_0)}.$$
(11)

The above equation suggests that as the temperature increases, the *s* value decreases. The above equation can be approximated [52] as $s = 1 - \frac{6k_BT}{w_m}$. The barrier height W_m calculated from the slope of (1 - s) with temperature is found to be 0.16 eV. We would like to point out here that the difference between the activation energy in the grain boundary and grain as analyzed using the Nyquist plot in section 3.3 was estimated at 0.2 eV.

3.5. Multiferroic property

The SmFeO₃ sample exhibits multiferroic properties with more than one ferroic ordering. To comprehend the multiferroic property, we performed P-E, M-H and magnetoelectric measurements on the sample at room temperature. Figure 9(a)shows the room temperature polarization measurement (hysteresis curve) of the SmFeO₃ sample, measured at different frequencies with a constant applied field $(4.39 \text{ kV cm}^{-1})$. As shown in the figure, polarization increases with an increase in the applied field, attains a maximum value and then decreases. The hysteresis loops do not exhibit the saturation effect. Rather, the observed decrease of polarization with an increase in the field (after attaining the maxima) is a sign of time delay between the electric field and polarization. The unsaturated PE loops are similar to those reported in the SrFeO_{3- δ} sample [53]. The values of dielectric constant obtained from dielectric studies using the impedance analyzer and the P-E loop tracer tally within a margin of 5-7%. Figure 9(b) shows the room temperature M-H curve of the SmFeO₃ ceramics carried out between -80 kOe to 80 kOe. The sample exhibits canted antiferromagnetic behavior as reported earlier [54].

Lee *et al* [17] reported that ferroelectricity in a centrosymmetric crystal is induced due to canted antiferromagnetic (AFM) ordering. Interestingly, improper ferroelectricity with



Figure 9. (a) Room temperature *P*-*E* hysteresis loop of the SmFeO₃ sample. (b) Room temperature *M*-*H* hysteresis loop of the SmFeO₃ sample. (c) Variation of the ME voltage coefficients with a dc magnetic field.

a very small polarization due to canted AFM ordering was found in most of the centrosymmetric rare-earth orthoferrites [10, 11]. As SmFeO₃ crystallizes in a centrosymmetric space group, it cannot trace a proper saturated loop like a ferroelectric material. It was also observed from the figure that with an increase in frequency, the remnant polarization, saturation polarization and the coercivity of the sample decrease.

3.5.1. Magnetoelectric study. The magnetoelectric effect refers to electric-field-inspired magnetization and magneticfield-induced electric polarization [55]. As has been mentioned, the canted ferromagnetism in the material induces electric polarization resulting in an interaction between the electric and magnetic dipoles, and is the reason for the ME effect. The criterion for the occurrence of this effect in a material is the existence of magnetic and electric ordering in it. The magnetoelectric effect has been reported in both singlephase as well as composite materials. In single-phase materials, ME coupling arises due to the interaction between the magnetic and ferroelectric sub-lattices. However, in composites, coupling arises due to the interaction of piezoelectric and piezomagnetic phases. As discussed earlier, canted AFM ordering in SmFeO₃ induces improper ferroelectric polarization and the coupling between them results in the observed ME effect. In order to obtain a proper ME output, it was necessary to pole the sample both electrically and magnetically so that dipole ordering could take place and the sub-lattices could effectively interact and yield polarization [56].

Coupling of the ME effect is generally characterized by the ME voltage coefficient α_E which can be defined as [57, 58],

$$\alpha_E = \frac{\mathrm{d}E}{\mathrm{d}H} = \frac{V}{h_\mathrm{o}d} \tag{12}$$

where E is the induced electric field, H is the applied magnetic field, V is the ME voltage developed across the sample, h_0 is the magnitude of the ac magnetic field and d is the thickness of the sample. The ME coefficient has been measured by the dynamic method involving the simultaneous application of an ac as well as a dc magnetic field [59]. The voltage developed across the SmFeO₃ sample was measured using an ME set up with a lock-in amplifier. In our experiment, a 15.37 Oe ac magnetic field and a 1 kHz frequency were applied along with a dc magnetic field of varying magnitude (-5 kOe to 5 kOe). The ac field was produced by a Helmholtz coil (N = 200 turns with the radius, r = 2.5 cm and coil resistance, $R = 23.4 \Omega$), which was driven by an ac current generated by a function generator. The magnitude of the ac magnetic field (h_0) generated at the center of the Helmholtz coil can be calculated from the expression:

$$h_{\rm o} = \frac{\mu_0}{4\pi} \frac{2\pi N I r^2}{\left(r^2 + \frac{r^2}{4}\right)^{\frac{3}{2}}} \times 2 = \frac{\mu_0}{\left(\frac{5}{4}\right)^{\frac{3}{2}}} \frac{N I}{r} = 8.99 \times 10^{-3} * \frac{N V}{r R} \text{ Oe.}$$

Here, a 5V ac amplitude was applied to the Helmholtz coil resulting in a magnetic field of 15.37 Oe.

The variation of the ME voltage coefficient with the applied dc magnetic field of the SmFeO₃ sample is shown in figure 9(c) for a longitudinal field arrangement. As reported earlier [60], the ME voltage which developed across the sample due to the application of a magnetic field can be written as:

$$E = V/d = f(H) = \text{constant} + \alpha H + \beta H^2 + \gamma H^3 + \delta H^4 + \dots$$

$$\Rightarrow \frac{dE}{dH} = \alpha + 2\beta H + 3\gamma H^2 + 4\delta H^3 + \dots$$
(13)

The ac field (*h*) superimposed onto the dc field (*H*) can be written as $h = h_0 \sin \omega t$, and the total magnetic field can be expressed as $H_{\text{total}} = H + h_0 \sin \omega t$. The fourth order polynomial fitting of figure 9(c) gives the value of all the coefficients. At a zero magnetic field, the ME voltage coefficient (α) was found to be 2.2 mV cm⁻¹ Oe⁻¹. The second order coefficient (β), third order coefficient (γ) and the fourth order coefficient (δ) were found to have values of 1.48 * 10⁻⁶, -6.56 * 10⁻¹⁰ and -6.31 * 10⁻¹⁴ in appropriate units.

4. Conclusion

A SmFeO₃ ceramic was fabricated by the soft-chemical method. The refined structural parameters obtained by the Rietveld method suggest that SmFeO₃ crystallizes in an orthorhombic crystal structure. Detailed dielectric analysis of the prepared sample exhibits two dielectric anomalies in the temperature range of 25-300 °C for the material. One of them appears in the low-temperature region (around 180 °C) and the other at 220 °C. The polarization mechanism associated with the first peak is of the Maxwell-Wagner type, while that of the second peak is associated with polarization induced by magnetic /spin reorientation. The NTCR behavior of the sample was confirmed from the impendence analyses. The Nyquist plot shows one depressed semicircle below 75 °C corresponding to the grain effect and two depressed semicircles above 75 °C corresponding to both the grain and grain boundary effect. The angle of depression is estimated which gives a measure of the distribution of relaxation times. The contribution of conductivity at high temperature and low frequency has been estimated in the loss tangent graph. The value of resistance and the activation energy of the grain and grain boundary clearly indicate a relatively conducting grain surrounded by an insulating grain boundary. This situation leads to the formation of surface and internal barrier layer capacitors and results in very large dielectric constants. Grain and grain boundary effects were explained and correlated in the dielectric, impedance and conductivity spectra. The temperature dependence of the frequency exponent in ac conductivity studies reveals that the conduction mechanism corresponding to the grain can be explained on the basis of quantum mechanical tunneling (QMT) while the conduction mechanism corresponding to the grain boundary can be explained on the basis of the CBH model. The compound exhibits improper ferroelectric behavior and a canted antiferromagnetic nature at room temperature. Magnetic ordering induces ferroelectric polarization, and interaction between electric and magnetic ordering results in the ME effect. The ME voltage coefficient (α) was found to be 2.2 mV cm⁻¹ Oe⁻¹ at a zero magnetic field as obtained from the magnetoelectric study. The material with a large dielectric constant, low room temperature loss, exhibiting NTCR behavior and room temperature magnetoelectric coupling has promising technological applications in high-density charge storage devices (memory drives), switching devices, actuators, transducers, magnetic field and stress sensors, and devices in optoelectronics and microwave electronics.

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References

- [1] Guerra J D S, Portugal R J, Silva A C, Guo R and Bhalla A S 2014 Investigation of the conduction processes in PZTbased multiferroics: analysis from Jonscher's formalism *Phys. Status Solidi b* 251 1020
- [2] Wesselinow J M and Georgiev I 2008 Theoretical study of static and dynamic properties of orthorhombic multiferroic substances *Phys. Status Solidi b* 245 1653
- [3] Ma J, Hu J, Li Z and Nan C W 2011 Recent progress in multiferroic magnetoelectric composites: from bulk to thin films Adv. Mater. 23 1062
- [4] Catalan G and Scott J F 2009 Physics and applications of Bismuth ferrite Adv. Mater. 21 2463
- [5] Aliouane N et al 2008 Magnetic order and ferroelectricity in RMnO₃ multiferroic manganites: coupling between R- and Mn-spins J. Phys.: Condens. Matter 20 434215
- [6] Kimura T and Lawes G 2005 Magnetoelectric phase diagrams of orthorhombic RMnO₃ (R = Gd, Tb, and Dy) *Phys. Rev.* B 71 224425
- [7] Blake G R, Chapon L C, Radaelli P G, Park S, Hur N, Cheong S W and Rodríguez-Carvajal J 2005 Spin structure and magnetic frustration in multiferroic RMn₂O₅ (R = Tb, Ho, Dy) *Phys. Rev.* B **71** 214402
- [8] Tokura Y, Seki S and Nagaosa N 2014 Multiferroics of spin origin *Rep. Prog. Phys.* 77 076501
- [9] Tokura Y and Seki S 2010 Multiferroics with spiral spin orders Adv. Mater. 22 1554
- [10] Wanga X, Cao S, Wanga Y, Yuan S, Kang B, Wu A and Zhang J 2013 Crystal growth and characterization of the rare earth orthoferrite PrFeO₃ J. Cryst. Growth 362 216
- [11] Zhao H J, Yang Y, Ren W, Mao A J, Chen X M and Bellaiche L 2014 Creating multiferroics with large tunable electrical polarization from paraelectric rare-earth orthoferrites J. Phys.: Condens. Matter 26 472201
- [12] Niu X, Li H and Liu G 2005 Preparation, characterization and photocatalytic properties of REFeO₃ (RE = Sm, Eu, Gd) *J. Mol. Catal.* A 232 89
- [13] Mira S A, Ikrama M and Asokan K 2014 Structural, optical and dielectric properties of Ni substituted NdFeO₃ Optik 125 6903
- [14] Ye J L, Wang C C, Ni W and Sun X H 2014 Dielectric properties of ErFeO₃ ceramics over a broad temperature range J. Alloys Compds 617 850
- [15] Tokunaga Y, Furukawa N, Sakai H, Taguchi Y, Arima T and Tokura Y 2009 Composite domain walls in a multiferroic perovskite ferrite *Nat. Mater.* 8 558
- [16] Tokunaga Y, Iguchi S, Arima T and Tokura Y 2008 Magneticfield-induced ferroelectric state in DyFeO₃ *Phys. Rev. Lett.* 101 097205
- [17] Lee J H, Jeong Y K, Park J H, Oak M A, Jang H M, Son J Y and Scott J F 2011 Spin-canting-induced improper

ferroelectricity and spontaneous magnetization reversal in SmFeO₃ *Phys. Rev. Lett.* **107** 117201

- [18] Marshall L G, Cheng J G, Zhou J S, Goodenough J B, Yan J Q and Mandrus D G 2012 Magnetic coupling between Sm3 + and the canted spin in an antiferromagnetic SmFeO₃ single crystal *Phys. Rev.* B 86 064417
- [19] Jeong Y K, Lee J H, Ahn S J and Jang H M 2012 Temperatureinduced magnetization reversal and ultra-fast magnetic switch at low field in SmFeO₃ Solid State Commun. 152 1112
- [20] Huang S, Shi L, Tian Z, Yuann S, Wang L, Gong G, Yin C and Zerihun G 2015 High-temperature colossal dielectric response in RFeO₃ (R = La, Pr and Sm) ceramics *Ceram. Int.* **41** 691
- [21] Xia W, Wang C C, Liu P, Ye J L and Ni W 2013 Colossal dielectric behavior in TbFeO₃ ceramics *Curr. Appl. Phys.* 13 1743
- [22] Prasad B V, Rao G N, Chen J W and Babu D S 2012 Colossal dielectric constant in PrFeO₃ semiconductor ceramics *Solid State Sci.* 14 225
- [23] Prasad B V, Rao G N, Chen J W and Babu D S 2011 Abnormal high dielectric constant in SmFeO₃ semiconductor ceramics *Mater. Res. Bull.* 46 1670
- [24] Qing T Y, Meng Y and Mei H Y 2013 Structure and colossal dielectric permittivity of Ca₂TiCrO₆ ceramics J. Phys. D: Appl. Phys. 46 015303
- [25] Volkov N V, Eremin E V, Sablina K A and Sapronova N V 2010 Dielectric properties of a mixedvalence Pb₃Mn₇O₁₅ manganese oxide J. Phys.: Condens. Matter 22 375901
- [26] Schmidt R, Pandey S, Fiorenza P and Sinclair D C 2013 Nonstoichiometry in 'CaCu₃Ti₄O₁₂' (CCTO) ceramics *RSC Adv.* 3 14580
- [27] Wu H J *et al* 2013 *M* Significant enhancements of dielectric and magnetic properties in Bi(Fe_{1-x}Mg_x)O_{3-x/2} induced by oxygen vacancies *J. Phys. D: Appl. Phys.* 46 145001
- [28] Sinclair D C, Adams T B, Morrison F D and West A R 2002 CaCu₃Ti₄O₁₂: one-step internal barrier layer capacitor *Appl. Phys. Lett.* **80** 2153
- [29] Gibalov V I and Pietsch G J 2012 Dynamics of dielectric barrier discharges in different arrangements *Plasma Sources Sci. Technol.* 21 024010
- [30] Jana P K, Sarkar S and Chaudhuri B K 2007 Maxwell–Wagner polarization mechanism in potassium and titanium doped nickel oxide showing giant dielectric permittivity J. Phys. D: Appl. Phys. 40 556
- [31] Yang Z, Zhang Y, You G, Zhang K, Xiong R and Shi J 2012 Dielectric and electrical transport properties of the Fe³⁺doped CaCu₃Ti₄O₁₂ J. Mater. Sci. Technol. 28 1145
- [32] Li J, Jia R, Tang X, Zhao X and Li S 2013 Enhanced electric breakdown field of CaCu₃Ti₄O₁₂ ceramics: tuning of grain boundary by a secondary phase *J. Phys. D: Appl. Phys.* 46 325304
- [33] Maity S K, Dutta A, Kumar S and Sinha T P 2013 Electrical properties of Ba₂YbNbO₆: an impedance spectroscopy study *Phys. Scr.* 88 065702
- [34] Majhi K, Prakash B S and Varma K B R 2007 Extreme values of relative permittivity and dielectric relaxation in Sr₂SbMnO₆ ceramics *J. Phys. D: Appl. Phys.* 40 7128–35
- [35] Sivakumar N, Narayanasamy A, Chinnasamy C N and Jeyadevan B 2007 Influence of thermal annealing on the dielectric properties and electrical relaxation behaviour in nanostructured CoFe₂ O₄ ferrite J. Phys.: Condens. Matter 19 386201
- [36] Rouahi A, Kahouli A, Challali F, Besland M P, Vall'ee C, Yangui B, Salimy S, Goullet A and Sylvestre A 2013

Impedance and electric modulus study of amorphous TiTaO thin films: highlight of the interphase effect *J. Phys. D: Appl. Phys.* **46** 065308

- [37] Idrees M, Nadeem M and Hassan M M 2010 Investigation of conduction and relaxation phenomena in LaFe_{0.9}Ni_{0.1}O₃ by impedance spectroscopy *J. Phys. D: Appl. Phys.* 43 155401
- [38] James A R, Prakash C and Prasad G 2006 Structural properties and impedance spectroscopy of excimer laser ablated Zr substituted BaTiO₃ thin films *J. Phys. D: Appl. Phys.* 39 1635
- [39] Mahajan S, Thakur O P, Bhattacharya D K and Sreenivas K 2009 Ferroelectric relaxor behaviour and impedance spectroscopy of Bi₂O₃-doped barium zirconium titanate ceramics J. Phys. D: Appl. Phys. 42 065413
- [40] Garbarz-Glos B, Bąk W, Antonova M and Pawlik M 2013 Structural, microstructural and impedance spectroscopy study of functional ferroelectric ceramic materials based on barium titanate *Mater. Sci. Eng.* 49 012031
- [41] Chandrasekhar K D, Das A K, Mitra C and Venimadhav A 2012 The extrinsic origin of the magnetodielectric effect in the double perovskite La₂NiMnO₆ J. Phys.: Condens. Matter 24 495901
- [42] Behera C, Das P R and Choudhary R N P 2014 Structural and electrical properties of mechanothermally synthesized NiFe₂O₄ nanoceramics *J. Electron. Mater.* 43 3539
- [43] Pollak M and Geballe T H 1961 Low-frequency conductivity due to hopping processes in silicon *Phys. Rev.* 122 1742
- [44] Gopalan E V, Malini K A, Sagar S, Kumar D S, Yoshida Y, Al-Omari I A and Anantharaman M R 2009 Mechanism of ac conduction in nanostructured manganese zinc mixed ferrites J. Phys. D: Appl. Phys. 42 165005
- [45] Ghosh A, Bhattacharya S, Bhattacharya D P and Ghosh A 2008 Frequency dependent conductivity of cadmium vanadate glassy semiconductor J. Phys.: Condens. Matter 20 035203
- [46] Abdel-wahab F A, Maksoud H M and Kotkata M F 2006
 Electrical conduction and dielectric relaxation in semiconductor SeSm_{0.005} J. Phys. D: Appl. Phys. 39 190
- [47] Rahman M A, Saha S K and Hossain A K M A 2014 Structural and electrical properties of (x) Mn_{0.45}Ni_{0.05}Zn_{0.50} Fe₂O₄ + (1 - x) BaZr_{0.52}Ti_{0.48}O₃ multiferroic materials *Mater. Res. Express* 1 026113
- [48] Hazra S, Ghosh A and Chakravorty D 1996 Classical hopping in sol-gel cobalt silicate glass J. Phys.: Condens. Matter 8 10279
- [49] El-Nahass M M, Zeyada H M, El-Samanoudy M M and El-MenyawyE M 2006 Electrical conduction mechanisms and dielectric properties of thermally evaporated N (p dimethyl amino benzylidene)-p-nitroaniline thin films *J. Phys.: Condens. Matter* 18 5163
- [50] Pike G E 1972 AC conductivity of scandium oxide and a new hopping model for conductivity *Phys. Rev.* B **6** 15
- [51] Elliot S R 1987 AC conduction in amorphous chalcogenide and pnictide semiconductors *Adv. Phys.* **36** 135
- [52] Sinha S, Chatterjee S K, Ghosh J and Meikap A K 2014 Dielectric relaxation and ac conductivity behaviour of polyvinyl alcohol-HgSe quantum dot hybrid films J. Phys. D: Appl. Phys. 47 275301
- [53] Manimuthu P and Venkateswaran C 2012 Evidence of ferroelectricity in SrFeO_{3-δ} J. Phys. D: Appl. Phys. 45 015303
- [54] Bashir A, Ikram M, Kumar R, Lisboa-Filho P N and Thakur P 2010 Structural, electronic structure and magnetic studies of $SmFe_{1-x}Ni_xO_3$ ($x \le 0.5$) *Mater. Sci. Eng.* B **172** 242

- [55] Zhanga Y, Zhou J P, Liu Q, Zhang S and Deng C Y 2014 Dielectric, magnetic and magnetoelectric properties of Ni_{0.5}Zn_{0.5}Fe₂O₄-Pb (Zr_{0.48}Ti_{0.52})O₃ composite ceramics *Ceram. Int.* **40** 5853
- [56] Kumar M M, Srinivas A, Suryanarayana S V, Kumar G S and Bhimasankaram T 1998 An experimental setup for dynamic measurement of magnetoelectric effect *Mater. Sci.* 21 251
- [57] Shi M, Zuo R, Xun Y, Wang L, Gu C, Su H, Zhong J and Yu G 2014 Preparation and multiferroic properties of 2-2 type CoFe₂O₄/Pb(Zr,Ti)O₃ composite films with different structures *Ceram. Int.* **40** 9249
- [58] Dipti, Juneja J K, Singh S, Raina K K and Prakash C 2015 Enhancement in magnetoelectric coupling in PZT based composites *Ceram. Int.* 41 6108
- [59] Pahuja P, Prakash C and Tandon R P 2014 Comparative study of magnetoelectric composite system Ba_{0.95}Sr_{0.05}TiO₃-Ni_{0.8}Co_{0.2}Fe₂O₄ with ferrite prepared by different methods *Ceram. Int.* **40** 5731
- [60] Duonga G V, Groessinger R, Schoenhart M and Bueno-Basques D 2007 The lock-in technique for studying magnetoelectric effect J. Magn. Magn. Mater. 316 390