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Research Article

Steady nature of dielectric behaviour in $Sm_{1.5}Sr_{0.5}NiO_4$ – CCTO composites

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Abstract

The composite materials of 0.5 $Sm_{1.5}Sr_{0.5}NiO_4$, 0.5 CCTO and 0.75 $Sm_{1.5}Sr_{0.5}NiO_4$, 0.25 CCTO mixtures were prepared through the conventional solid state reaction in an attempt to obtain good dielectric properties for practical applications. The structural properties were determined by powder X-ray diffraction and single phases were obtained for $Sm_{1.5}Sr_{0.5}NiO_4$ and $CaCu_3Ti_4O_{12}$ compounds. The dielectric studies analysed over a range of frequencies (100 KHz–10 MHz) and temperatures (30 to 200 °C) revealed a desired dielectric constant values with a low steady nature of dielectric loss factor. Through impedance spectroscopy, the attained dielectric behaviour was due to the highly insulating grain boundaries at lower frequencies and semiconducting grains at higher frequencies.

Keywords

composite, dielectric constant, impedance spectroscopy, powder XRD

1. Introduction

Colossal dielectric constant materials have been in the peak of its research due to various applications such as capacitors and memory devices [1–13]. $CaCu_3Ti_4O_{12}$ **(CCTO)** is one such perovskite material that exhibits high dielectric constant values (10^5). It is nearly independent to rise in temperature and frequency ranges which made it a potential candidate for a wide variety of experiments [14–16]. The main reason for such high values of dielectric constant was due to the barrier layers formed between the grain and the grain boundaries which is explained by the IBLC model. But one of the biggest letdown of CCTO was its high dielectric loss variation with rise in temperature and frequency [17, 18]. This led to the search of other types of materials with low loss factor.

$Sm_{1.5}Sr_{0.5}NiO_4$ is a K_2NiF_4 type of material [8–11] that, through doping mechanism, has high dielectric constant values (10^4) with considerable low dielectric loss (0.1 magnitude) with good temperature stability [19, 20]. Such high values of dielectric constant were attained through hopping mechanism between the highly resistive grain boundaries and grains [21].

Recently many works were done in customizing the dielectric properties of these types of materials by mixing them together to form a composite material [22–28]. The much studied CCTO has been mixed with many ceramic and polymer based materials [25–27]. All these research experiments focus on developing a material with high dielectric constant values while lowering the loss factor. In this paper we made a composite material out of $Sm_{1.5}Sr_{0.5}NiO_4$ and CCTO ceramics in the ratio of 0.5 : 0.5 and 0.75 : 0.25 respectively to reduce the dielectric loss while maintaining a stable dielectric constant so as a whole the composite material can be device worthy. Since this work has not been done before it is interesting to investigate the dielectric properties by the addition of CCTO in $Sm_{1.5}Sr_{0.5}NiO_4$.

2. Experimental methods

Ceramic samples of $Sm_{1.5}Sr_{0.5}NiO_4$ and $CaCu_3Ti_4O_{12}$ (CCTO) were prepared by solid state reaction method separately from stoichiometric amounts of pure Sm_2O_3 (99.9%), $SrCO_3$ (99%), Cr_2O_3 (99.9%) and NiO (99%), $CaCO_3$ (99.9%), CuO (99.9%), TiO_2 (99.6%) respectively, all in powder form. The two mixtures were thoroughly mixed separately in an agate mortar. Next the $Sm_{1.5}Sr_{0.5}NiO_4$ and CCTO mixtures were calcined at 1200 and 1000 °C respectively for 12 h to yield the desired material.

Composites of $Sm_{1.5}Sr_{0.5}NiO_4$ and CCTO were prepared by mixing the pre weighed powders of $Sm_{1.5}Sr_{0.5}NiO_4$ and CCTO in an agate mortar. The first composite mixture had 25% of CCTO mixed with 75% of $Sm_{1.5}Sr_{0.5}NiO_4$ while the second mixture had equal measures of both $Sm_{1.5}Sr_{0.5}NiO_4$ and CCTO. Hereby the two composite mixtures will be labelled as SmCTO25 and SmCTO50 respectively throughout this manuscript. The mixed samples were pressed into pellets of 13 mm diameter under a pressure of 2 tonnes. These pellets were sintered for 10 h in air at 1080 °C for the densification of the pellets. The sintering temperature was chosen so as to obtain the desired dielectric properties of the composite without exceeding the melting point of the mixtures.

The powder XRD data was collected using CuK_α radiation (λ = 1.5418 Å) on a Bruker D8 Advance X-ray diffractometer. Diffraction data was recorded for 2θ values ranging from 10° to 120°, with a step size of 0.02°. The electrical and the dielectric properties were studied using a Hioki 3535 LCR HiTester on the silver coated pellets in the frequency range 100 KHz to 10 MHz and temperature range 30 to 200 °C.

3. Results and discussion

The powder XRD patterns of $Sm_{1.5}Sr_{0.5}NiO_4$ and CCTO as shown in Fig. 1 confirmed that both the samples produced are of a single phase. In Fig. 1*a*, *b*, the diffraction patterns the samples can be easily identified according to the JCPDS files of 88-0119 and 75-2188. From this data the identified crystal structures are tetragonal (*I*4/*mmm*) for $Sm_{1.5}Sr_{0.5}NiO_4$ and cubic ($Im\,\bar{3}$) for CCTO respectively.

Similarly the powder XRD patterns of $Sm_{1.5}Sr_{0.5}NiO_4$–CCTO composites are shown in Fig. 2. In this the positions and the intensities of the standard diffraction peaks of $Sm_{1.5}Sr_{0.5}NiO_4$ and CCTO are also labelled separately for each XRD pattern. From Fig. 2*a* it can be seen that the intensities of CCTO peaks are smaller due to the lower mixture percentage but increases as the percentage of CCTO mixture increases which is observed in Fig. 2*b*.

The SEM images of SmCTO25 and SmCTO50 composites are shown in Fig. 3 respectively. The smaller addition of CCTO in (*a*) SmCTO25 composite has resulted in the slightly smaller grains (224 nm) with thicker grain boundaries than compared to the equal mixture of $Sm_{1.5}Sr_{0.5}NiO_4$ and CCTO with a grain size of 350 nm in Fig. 3*b*.

Fig. 4 shows the variation of dielectric constant ε_r and dielectric loss tan δ of $Sm_{1.5}Sr_{0.5}NiO_4$–CCTO composites with frequency.

From this it can be seen that the dielectric constant of SmCTO25 (Fig. 4*a*) remains stable from 100 kHz to 5 MHz frequency range for the temperature range 30 to 200 °C whereas a slight decrease is observed in that of SmCTO50 (Fig. 4*c*) composite. The main highlight observed from Fig. 4*b*, *d*) is the frequency independent nature of dielectric loss

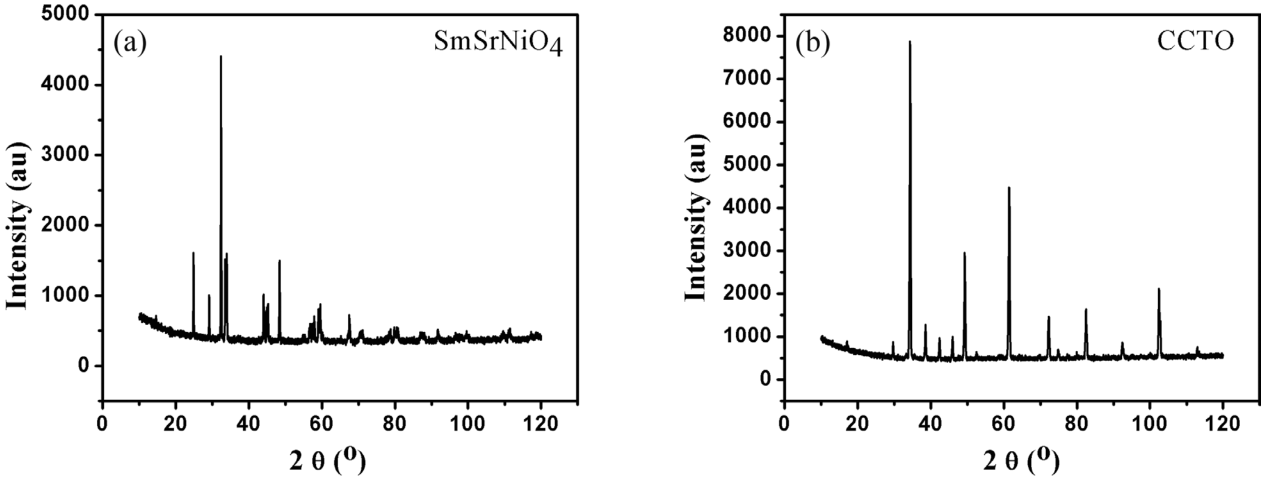

Figure 1. The XRD patterns of (*a*) $Sm_{1.5}Sr_{0.5}NiO_4$ and (*b*) CCTO samples.

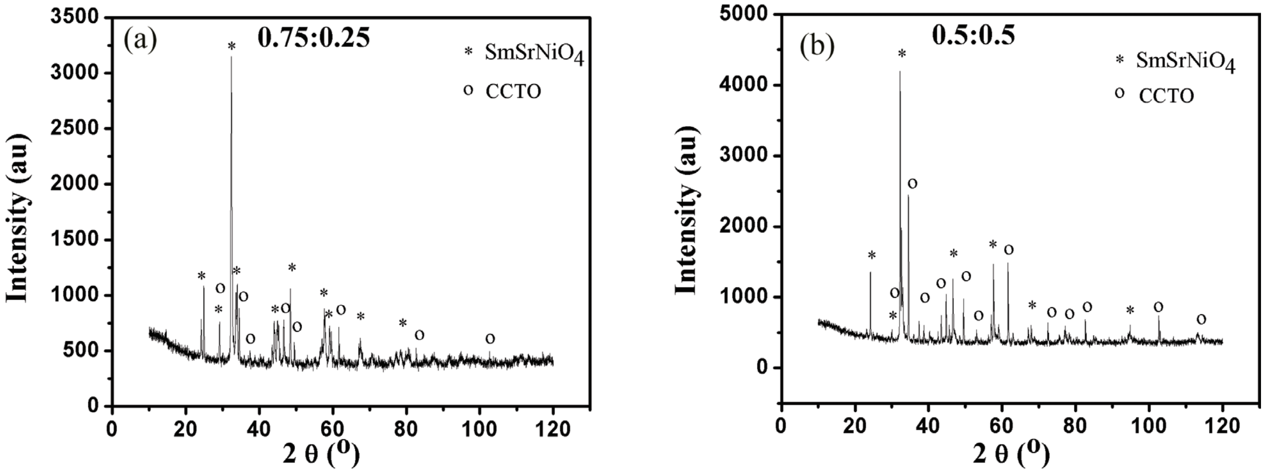

Figure 2. XRD patterns of (*a*) SmCTO25 and (*b*) SmCTO50 composites.

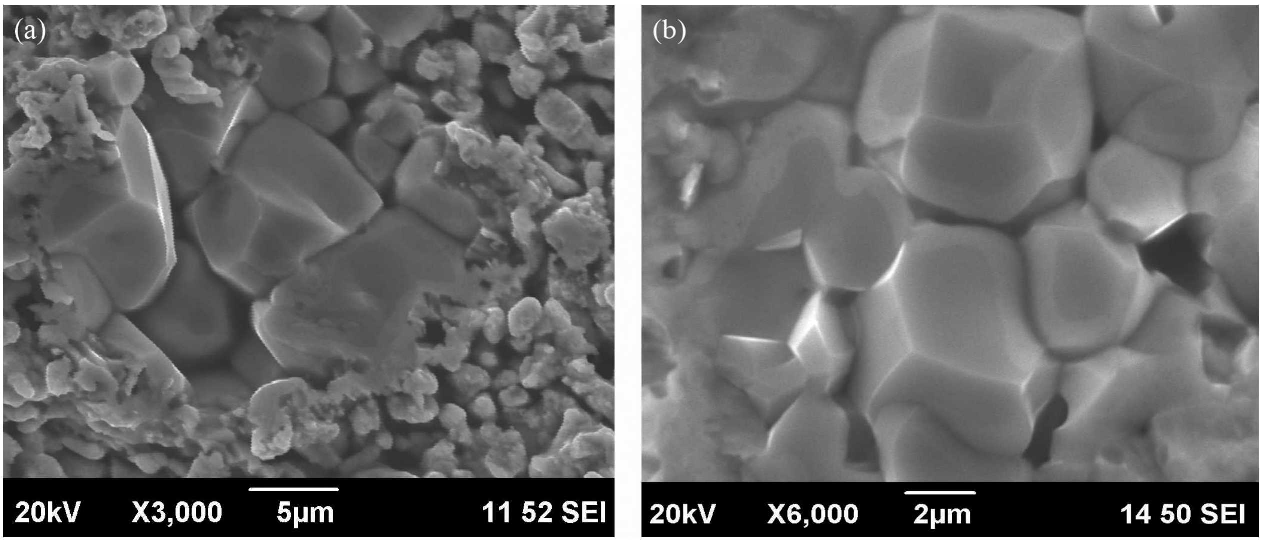

Figure 3. Cross-section SEM image of (*a*) SmCTO25 and (*b*) SmCTO50 composites.

(100 kHz to 2 MHz) with very low values of 0.1magnitudes. Although at the expense of dielectric constant values, this steady nature of low dielectric loss values being independent of frequencies has not been observed.

Similarly the variation of the dielectric properties of the SmCTO25 and SmCTO50 composites with temperature are shown in Fig. 5.

From the Fig. 5*a*, *c*, it is observed that the dielectric constant values increase with rise in temperature for both the composite materials. Here too the main result as seen from Fig. 5*b*, *d*) lies in the lowering of dielectric loss values (tan δ of 0.1 magnitude) with a good temperature stability ranging from 30 to 200 °C. Hence these types of composites can be used as materials for high frequency applications.

The complex impedance plot of the composites (Fig. 6) provides information on the contribution of grains and grain boundaries to the dielectric properties. The semi-circular arcs with non-zero intercepts that are observed from the figure are indicative of the composites being electrically heterogeneous [29–32]. Hence the parallel combination of two RC circuits connected in series can be attributed to the impedance spectrum where the capacitance C_g and resistance R_g corresponds to the grain effects and C_{gb} and R_{gb} corresponds to the grain boundaries of high resistance.

Hence the total impedance from the equivalent circuit can be written as

$$Z^* = \frac{R_g}{1+\left(i\omega R_g C_g\right)} + \frac{R_{gb}}{1+\left(i\omega R_{gb} C_{gb}\right)} \quad (1)$$

The data are fitted by the equivalent circuit consisting of two parallel *RC* connected in series with one *RC* element in which $R_{gb}C_{gb}$ corresponds to the grain boundaries and R_gC_g represents the grains. The fitted parameters at room temperature are shown in Table 1.

It is observed from the table that the resistance values of the grain boundaries are much higher than those of grain resistances. Thus from Fig. 5, the lower frequency arcs with

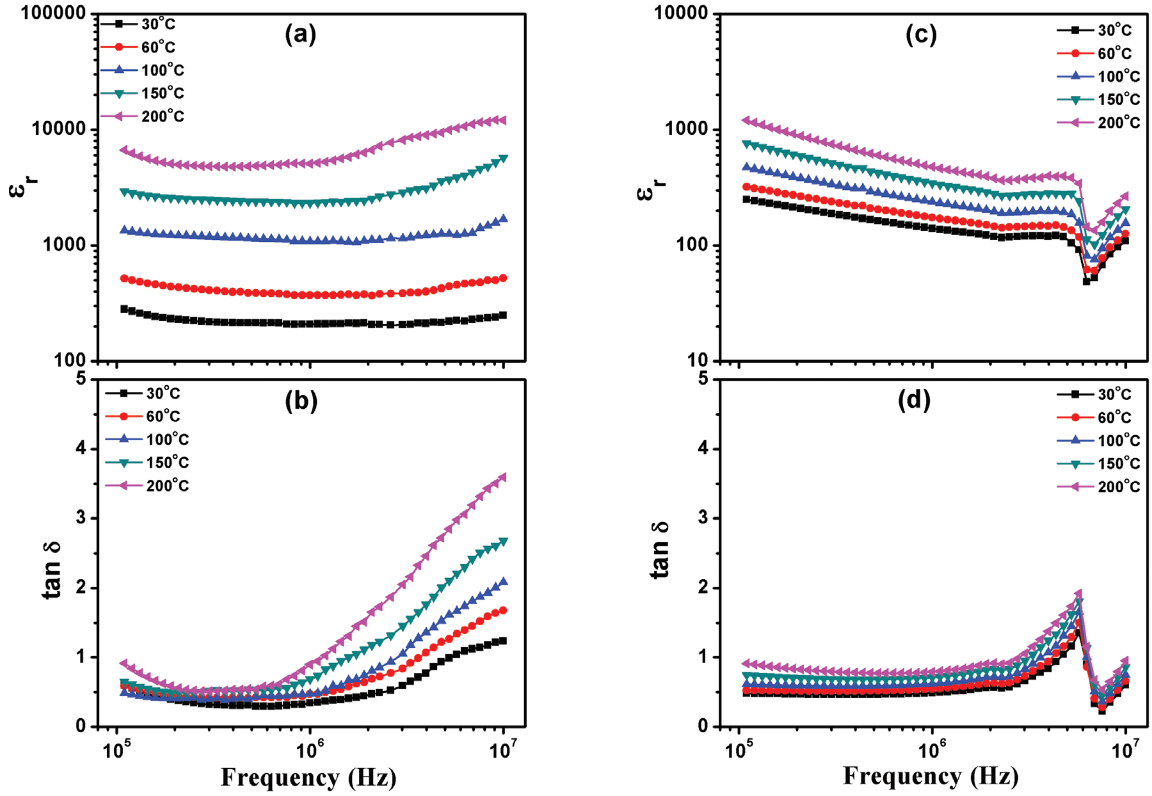

Figure 4. Frequency dependence of dielectric constant ε_r and dielectric loss tan δ for (*a*) and (*b*) SmCTO25 and (*c*) and (*d*) SmCTO50.

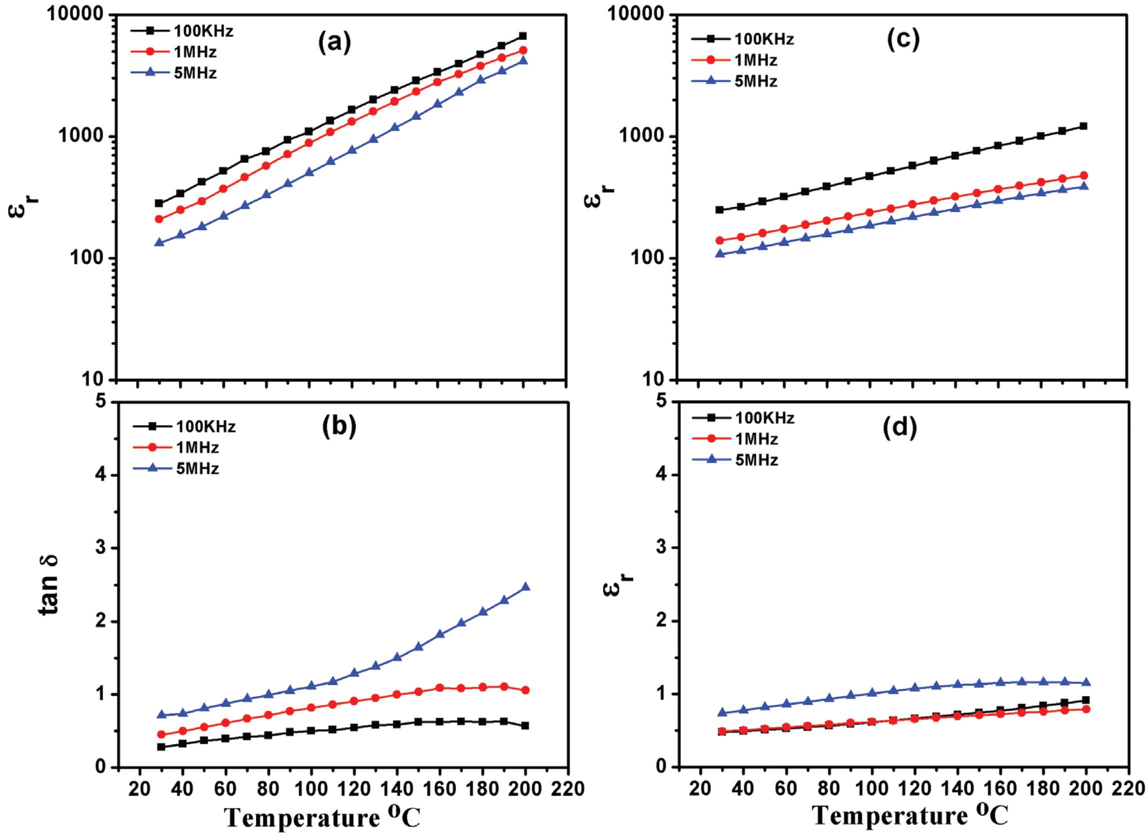

Figure 5. Temperature variation of dielectric constant ε_r and dielectric loss tan δ for (*a*) and (*b*) SmCTO25 and (*c*) and (*d*) SmCTO50.

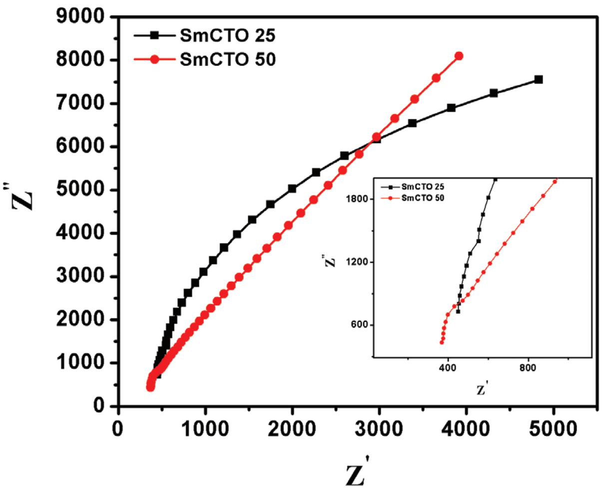

Figure 6. Complex impedance spectrum of $Sm_{1.5}Sr_{0.5}NiO_4$–CCTO composites. The inset shows the high frequency range of the spectrum.

Table 1. $Sm_{1.5}Sr_{0.5}NiO_4$–CCTO composites parameters from impedance spectrum.

Composite Sample	R_g (Ω)	C_g (F)	R_{gb} (Ω)	C_{gb} (F)
SmCTO 25	1250	$1.53 * 10^{-10}$	20015	$3.6 * 10^{-10}$
SmCTO 50	416	$1.40 * 10^{-10}$	17354	$2.15 * 10^{-10}$

high resistance grain boundary regions describe the dielectric response of the composites with a stable dielectric constant values. The inset from Fig. 5 shows that the close intercepts of the high frequency arcs does not affect the resistance values of the grains which might be the reason for the similar nature of dielectric loss for the composite mixtures.

4. Conclusion

The effect of $Sm_{1.5}Sr_{0.5}NiO_4$–$CaCu_3Ti_4O_{12}$ (CCTO) composite on dielectric properties was studied by combining $Sm_{1.5}Sr_{0.5}NiO_4$and CCTO mixtures taken by the ratio of 0.5 $Sm_{1.5}Sr_{0.5}NiO_4$: 0.5 CCTO (SmCTO50) and 0.75 $Sm_{1.5}Sr_{0.5}NiO_4$: 0.25 CCTO (SmCTO25) were yielded through solid state reaction method. Initially the individual compounds were prepared separately and by powder XRD analysis, a single phase crystal structure was obtained with *I*4/*mmm* for $Sm_{1.5}Sr_{0.5}NiO_4$ and *Im* $\bar{3}$ for CCTO space groups respectively. Slightly higher dielectric values were observed for SmCTO25 than SmCTO50 due to the highly insulating grain boundaries. The main observation from this experiment was the steady behaviour of dielectric loss for both the samples for a particular range of frequency and temperature. Thus these composites make it attractive for industrial purposes with high frequency applications.

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