Investigation on microstructure and dielectric behaviour of $(Ba_{0.999-x}Gd_{0.001}Cr_x)TiO_3$ ceramics

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Abstract. Ceramics of $BaTiO_3$ co-doped with Gd and Cr at Ba-site was synthesized via solid-state reaction route. Surface morphology shows the increase in grain size with the increase of Cr-content below 3 mol%. The high value of ε in the synthesized samples is associated with space charge polarization and inhomogeneous dielectric structure. Gd is diffused well into the most of Ba sites and vacancies leaving very few defects or voids for the generation of absorption current which results in dielectric loss. Below 3 mol% of Cr-concentration, dissipation factor was improved. Increase in a.c. conductivity with rise of temperature is due to increase in thermally activated electron drift mobility of charges according to the hopping conduction mechanism. Moreover, samples show the positive temperature coefficient of conductivity, which is most desirable for developing highly sensitive thermal detectors and sensors. Also, higher frequency indicates motion of charges in the ceramic samples.

Keywords. Ceramics; chemical synthesis; microstructure; dielectric properties; positive temperature coefficient of conductivity.

1. Introduction

ABO_3-based perovskite compounds are the most versatile materials which find a variety of technological applications. Among them, $BaTiO_3$ ceramics is widely preferred in the fabrication of various electrical and electronic devices. This is because of its tunable properties that can be modified by a unique cationic substitution technique (Hennings and Schnell 1982; Goodman 1986; Lin and Wu 1990).

It is possible to perform doping at Ba- and Ti-sites independently or simultaneously. These substitutions can be done by homovalent or heterovalent substituents. Dopants can therefore act as a donor or acceptor ions, depending upon its valency and other ion relevant chemical parameters. It is noteworthy that dopants play a remarkable role in balancing a chemical reaction, stability in the compound composition and bringing significant changes in structure, microstructure, a.c. and/or d.c. conductivity, dielectric parameters, etc.

Fasasi *et al* (2009), Wang *et al* (1998), Radhapiyari *et al* (2003) and Gulwade *et al* (2005) have reported various $BaTiO_3$-based modified compounds. These substitutions were carried out to understand the various ceramic characteristics of the prepared modified perovskites. Dopants at A-site such as rare-earths are effective in displacing or shifting the transition temperature but have a little effect on dielectric properties. However, the substitution at B-site shows remarkable influence on structural, dielectric and electrical properties of $BaTiO_3$-based ceramics. Many researchers have investigated the structural, electrical and dielectric properties of $BaTiO_3$-based ceramics by substituting A and B site dopants in order to understand the structure, phase transition temperature, dielectric maximum and diffuse phase transition type behaviour. Although many isovalent ions at A-site influence in changing T_c, whereas the dielectric parameters will have minimum effect due to doped elements. Similarly, aliovalent ions at A site, particularly, rare-earths will have dramatic effect on various polymorphic phase transition temperatures. To our knowledge, there is scanty literature available on simultaneous substitution by rare-earth and $3d$-ions at A-site of $BaTiO_3$-ceramics. In continuation of our earlier studies (Madolappa *et al* 2011), on synthesis, structure, temperature dependent dielectric behaviour, d.c. resistivity and thermoelectric property of $(Ba_{0.999-x}Gd_{0.001}Cr_x)TiO_3$ $(0.01 \le x \le 0.05)$ (SM11, SM12, SM13, SM14 and SM15), here, we report microstructure and frequency-dependent dielectric behaviour of SM11–SM15 ceramic compounds.

2. Experimental

Ceramic samples as designated in table 1 (SM11, SM12, SM13, SM14 and SM15) were prepared by conventional solid-state reaction method from weighed proportions of barium carbonate, $BaCO_3$ (M/s. S D Fine-Chem Ltd., Mumbai,

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India, purity 99·99%), gadolinium oxide (Gd_2O_3), chromium oxide (Cr_2O_3) and titanium oxide (TiO_2) (all Himedia, India, purity 99·99%). Appropriate quantities of these oxide materials were ground for 4 h and calcined under flow of heat at 900 °C for 8 h. They were further ground for 2 h and subjected to pre-sintering at 950 °C. The product obtained from pre-sintering was ground again for 2 h and pressed into

circular disc-shaped pellets (diameter, ≈10 mm and thickness, ~2–3 mm) using 5 mol% polyvinyl alcohol as a binding agent. Pellets were sintered at 1050 °C for 8 h. For good electrical contacts, a silver paste is applied on both sides of pellet. The morphology of the sintered pellets was investigated by scanning electron microscope (SEM) using JSM/8048/SM, JEOL, Japan. Electrical behaviour was studied using Wayne Kerr 4300 LCR meter with variation of frequency range from 10 kHz to 1 MHz.

Table 1. Average grain size of SM11–SM15 ceramic samples.

Code	Sample composition	Average grain size (μm)	Density (ρ) gm/cc
SM11	$(Ba_{0.989}Gd_{0.001}Cr_{0.01})TiO_3$	0·1168	3·833
SM12	$(Ba_{0.979}Gd_{0.001}Cr_{0.02})TiO_3$	0·7252	3·862
SM13	$(Ba_{0.969}Gd_{0.001}Cr_{0.03})TiO_3$	0·2636	3·945
SM14	$(Ba_{0.959}Gd_{0.001}Cr_{0.04})TiO_3$	0·1739	3·978
SM15	$(Ba_{0.949}Gd_{0.001}Cr_{0.05})TiO_3$	0·1539	3·982

3. Results and discussion

Powder X-ray diffraction (XRD) studies of the calcined samples show single phase with peaks being single in nature for SM11–SM15. All the samples crystallize in cubic crystal structure. Structural details of the samples are discussed elsewhere (Madolappa *et al* 2011). Theoretical density was calculated and given in table 1.
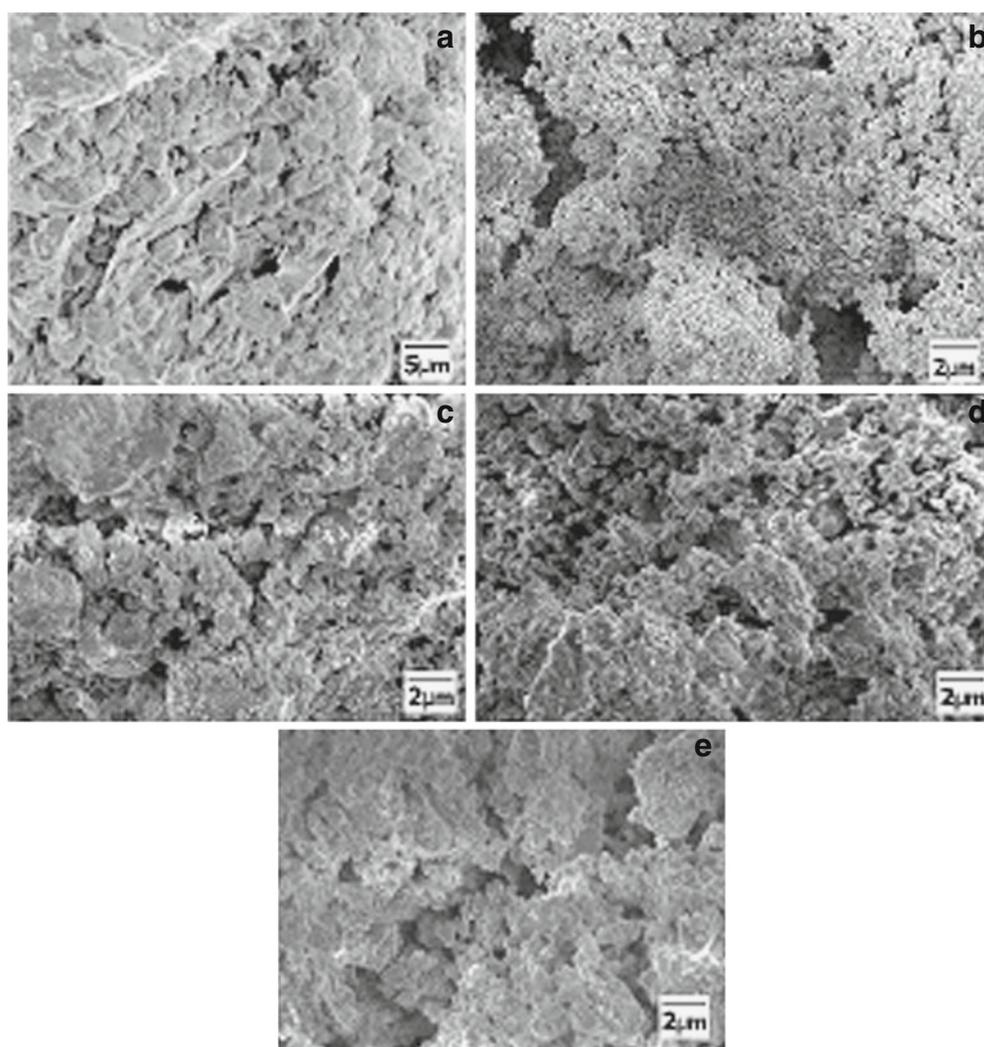

Figure 1. SEM micrographs of $(Ba_{0.999-x}Gd_{0.001}Cr_x)TiO_3$ ceramics with Cr contents: (**a**) $x = 0.01$, (**b**) $x = 0.02$, (**c**) $x = 0.03$, (**d**) $x = 0.04$ and (**e**) $x = 0.05$.

Figure 1 depicts typical scanning electron micrographs of the polished surfaces of SM11–SM15 samples. Except SM13, all other samples display relatively dense structure. Densification occurred due to grain growth and coarsening. The increase in grain size leads to the decrease in grain boundary volume, which resulted in higher density. As seen from figure 1, Cr_2O_3 helps in grain growth below 3 mol%, whereas it inhibits grain growth above 3 mol% doping level. This is because of low solubility of Cr-ions in the sublattice of SM samples. Average grain size was calculated by linear intercept method and is given in table 1. It is observed from figure 1 that average grain size is 0·725 μm for 2 mol% Cr-doped sample, whereas for other samples it is <0·3 μm.

Figure 2 shows frequency-dependent dielectric constant (ε_r) of samples SM11–SM15. There is no evidence of dielectric dispersion at the selected temperature over the frequency range from 10 kHz to 1 MHz for all the samples. Near

1 MHz, there is little variation in the value of ε_r which pertains to space charge polarization. Except SM15, all the SM samples showed ε_r value ∼7000 at 350 °C. The value of ε_r in synthesized samples is not usually intrinsic but rather associated with space charge polarization and inhomogeneous dielectric structure. These inhomogeneities are due to impurities, grain structure and pores. Also, ε_r remains unchanged as the frequency increases. The variation of ε_r with composition could be attributed to the polarized space charge. In these SM samples, it is supposed that there are Gd and Cr ions rich clusters which give rise to an extra polarized space charge. It is basically due to the difference in the radius of substituted ions.

The value of ε_r at higher temperature can be explained by the temperature-dependent characteristic of domain wall motion and/or increase in the drift mobility of electron (Abdelmonlin 2010). At low temperature, domain movement is intricate so that the extrinsic role of domain walls
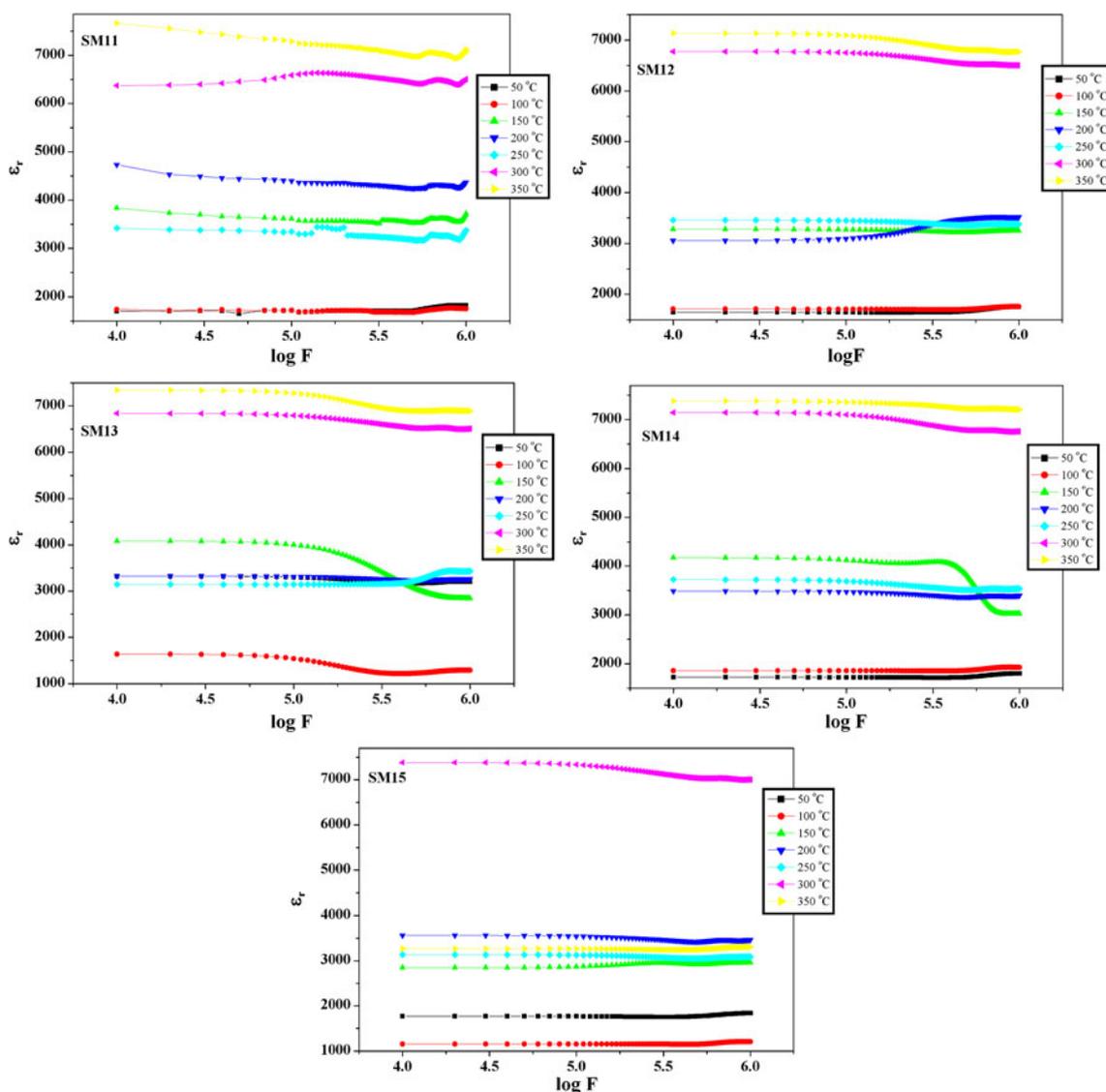

Figure 2. Plot of dielectric constant (ε_r) against log frequency at different temperatures for samples SM11–SM15.

to the dielectric response is small. Above room temperature, it is because of increase in disordered thermal oscillations and random orientation of dipoles in the prepared ceramic compounds.

Figure 3 illustrates frequency-dependent dissipation factor (D) of SM samples. All the SM samples show almost same behaviour, where D increases with increasing temperature and no maxima were observed in the selected temperature. Furthermore, D was observed to increase with frequency and remains same even if the concentration of Cr changes in sample composition. Later, D decreases from 10 kHz up to 580 kHz and again increases sharply above 580 kHz. However, minimum loss of $1 \cdot 1 \times 10^{-3}$ was observed at 550 kHz at 200 °C and maximum loss of 7×10^{-2} was observed at 1 MHz for 250 °C for all the SM samples. This is due

to the smaller ionic radius of Gd which is diffused well into the most of Ba-sites and leaving vacancies for very few defects or voids for the generation of absorption current, which results in dielectric loss. In the low frequency range, D is determined by the influence of ionic conductivity.

The plot of a.c. conductivity ($\sigma_{a.c.}$) vs log f for concentration $0 \cdot 01 \leq x \leq 0 \cdot 05$ is shown in figure 4. Increase in $\sigma_{a.c.}$ with rise of temperature is due to the increase in thermally-activated electron drift mobility of charges according to the hopping conduction mechanism. Moreover, samples show the positive temperature coefficient of conductivity, which is most desirable for developing highly sensitive thermal detectors, sensors, etc. It was also observed that $\sigma_{a.c.}$ increases as a function of frequency. Below 100 kHz, $\sigma_{a.c.}$ is minimum, which is due to the
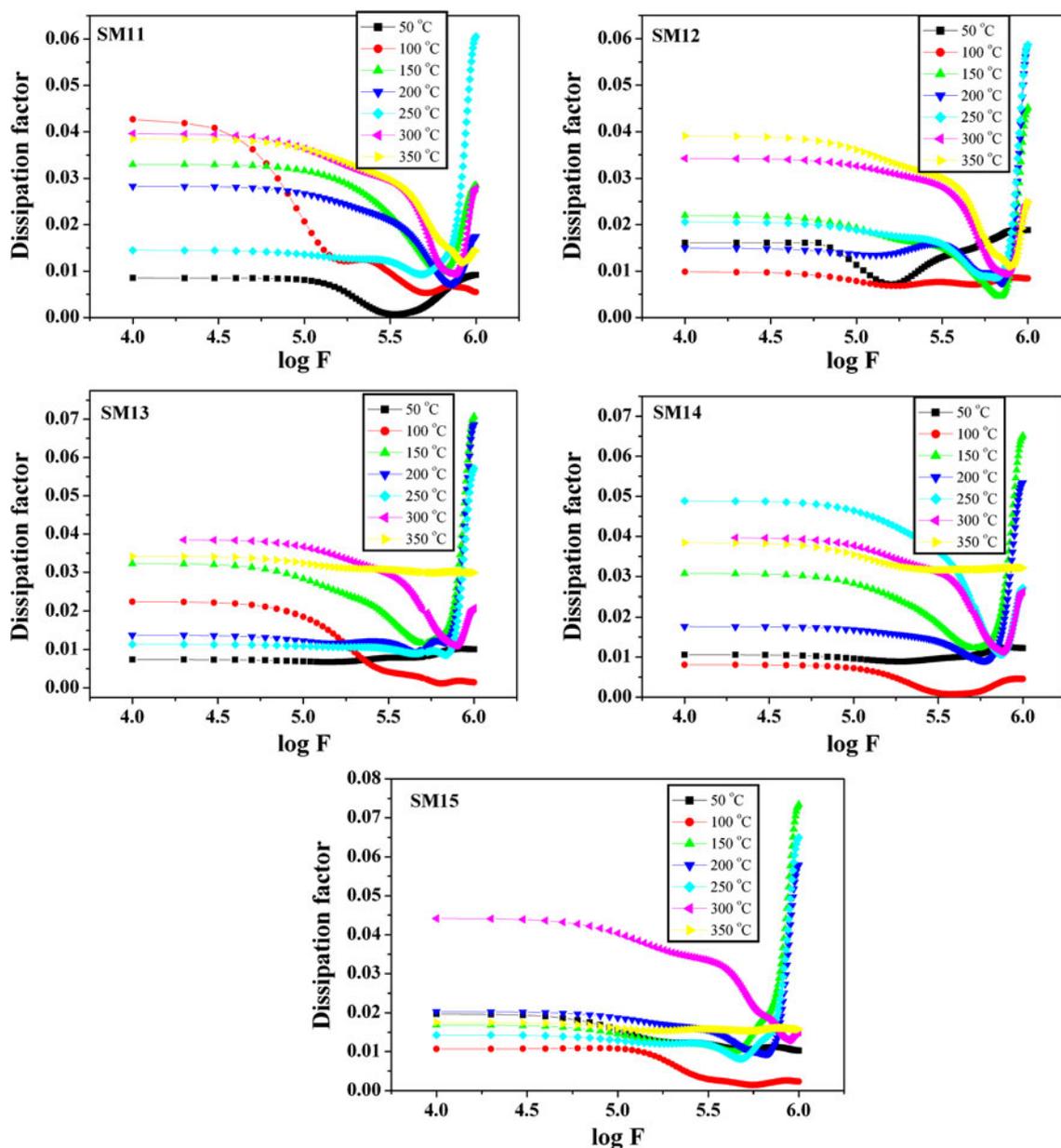

Figure 3. Plot of dissipation factor vs log frequency at different temperatures for samples SM11–SM15.
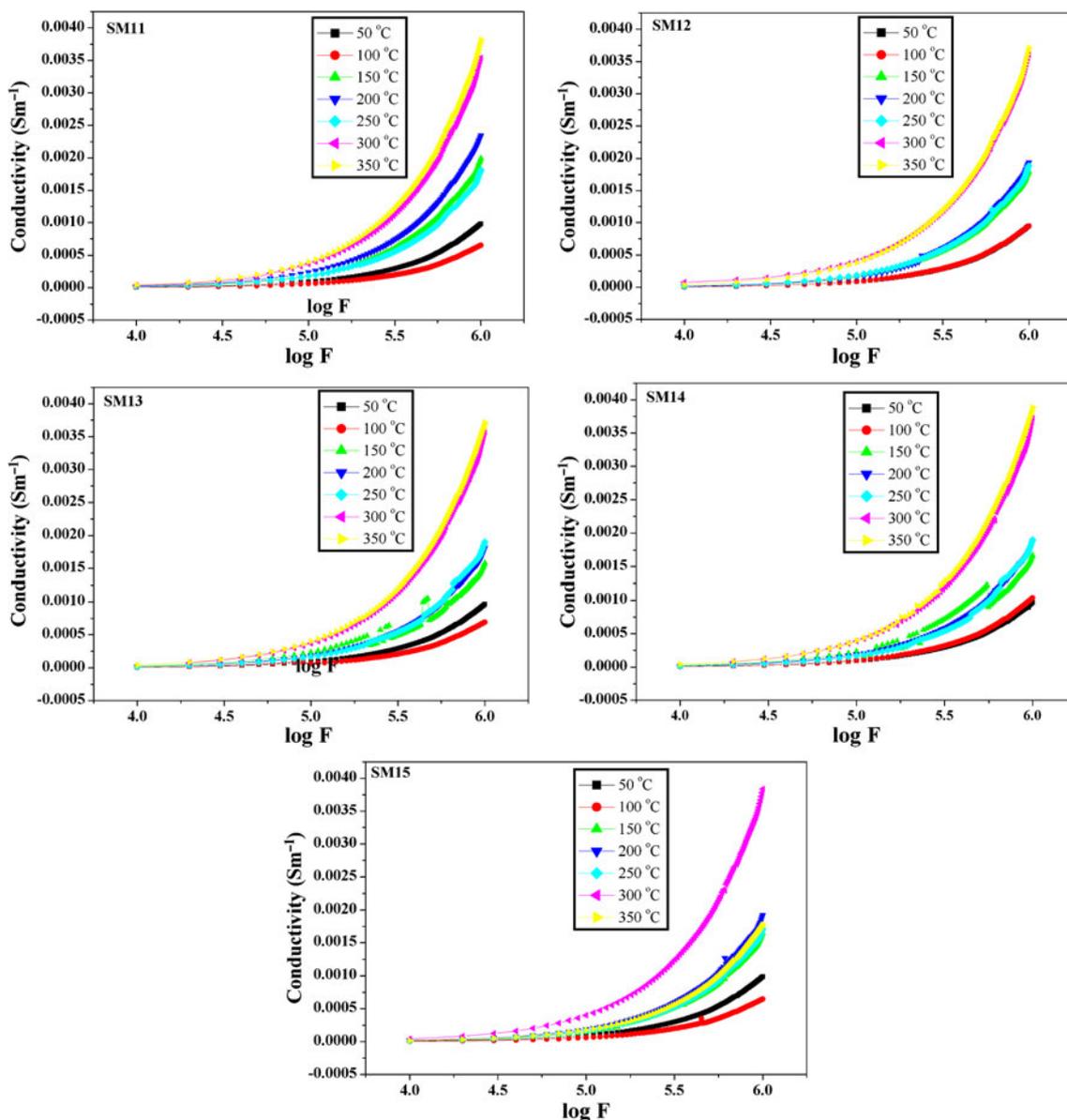
Figure 4. A.C. conductivity as a function of frequency at different temperatures for samples SM11–SM15.

movement of charge carriers on percolated paths whereas above 100 kHz, transport of charge occurred by hopping of cluster of ions. This is a characteristic feature of disordered materials where the hopping mechanism dominates. Here, $\sigma_{a.c.}$ increases because of contribution from the charge carriers. Maximum $\sigma_{a.c.}$ at higher frequencies indicates the charge motion in SM–ceramic samples. Overall behaviour of $\sigma_{a.c.}$ of different concentrations exhibited the universal response similar to disordered materials like ionic-conducting ceramics and also doped-crystalline solids.

4. Conclusions

Gd- and Cr co-doped $(Ba_{0.999-x}Gd_{0.001}Cr_x)TiO_3$ $(0.01 \leq x \leq 0.05)$ ceramic compounds were synthesized by ceramic route and characterized by undertaking frequency-dependent dielectric measurements. Microstructural study shows Cr_2O_3 helps in grain growth below 3 mol%, whereas it inhibits grain growth above 3 mol% doping level. The dielectric constant is explained on the basis of space polarization and dielectric loss is attributed by the ionic radii of dopants. A.C. conductivity at higher frequency indicates the motion of charges in ceramic samples. These samples show positive temperature coefficient of conductivity, which is most desirable for developing highly sensitive thermal detectors and sensors.

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