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Ferroelectric transitions in valence compensated $Ba_{1-x}La_xTi_{1-x}Cr_xO_3$ ceramics

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Abstract An attempt has been made to investigate the solid solubility limit between barium titanate, $BaTiO_3$ and lanthanum chromite, $LaCrO_3$. Compositions with $x \leq 0.15$ have shown solid solution formation in the system $Ba_{1-x}La_xTi_{1-x}Cr_xO_3$. Compositions with 0.01 and 0.05 are found to have a tetragonal structure, whereas those with $x = 0.10$ and 0.15 are found to have a cubic structure at room temperature. Dielectric measurements have been carried out at different frequencies in the temperature range 100–550 K. Plots of ε_r versus temperature for composition with $x = 0.01$ show dielectric anomalies at 376 K ($T_{C\text{-}T}$) and 275 ($T_{T\text{-}O}$) where $T_{C\text{-}T}$ and $T_{T\text{-}O}$ denote the temperature for cubic to tetragonal and tetragonal to orthorhombic transition. Dielectric anomaly corresponding to the ferroelectric to paraelectric transition has been found to shift to lower temperatures with increasing concentration of lanthanum and chromium. For compositions with $x \leq 0.05$, T_C has been found to be frequency independent while for $x = 0.10$ and 0.15, T_C has been found to be frequency dependent in a manner similar to relaxor ferroelectrics.

Introduction

Ferroelectric materials are being used in large number of technological applications. $BaTiO_3$ is one of the most important members of this group. Most of the ceramic capacitors at present have compositions based on $BaTiO_3$. This is because its properties can be modified by a wide variety of substitutions, possible at barium or titanium sites independently or simultaneously [1–3]. These substitutions may be isovalent or heterovalent. Dielectric properties of isovalent substituted barium titanate ceramics (either on Ba-sites or on Ti-sites) have been studied extensively [1]. These substitutions influence the $T_{C\text{-}T}$ and $T_{T\text{-}O}$ temperatures of various phase transitions of barium titanate. The effect of these substitutions on the Curie point is well documented [2].

Heterovalent substituted barium titanate ceramics have also been studied extensively in view of their interesting electrical properties. These substitutions can be of two types (i) donor substitution (e.g. La^{3+} on Ba^{2+} site) and (ii) acceptor substitution (e.g. Co^{3+} on Ti^{4+} site). The donor substitutions at A-site or at B-site cause charge imbalance which require formation of effectively negatively charged defects e.g. cation vacancies or electrons. For lanthanum doped $BaTiO_3$ a barium vacancy model ($Ba_{1-x}La_{2x/3}(V''_{Ba})_{1x/3}TiO_3$) was first considered by many authors [4–7]. The presence of barium vacancies near the grain boundaries of semiconducting barium titanate grains was confirmed by electron paramagnetic resonance (EPR) spectra [8, 9]. In later years, another model of titanium vacancies ($Ba_{1-x}La_xTi_{1-x/4}(V''''_{Ti})_{x\backslash 4}O_3$) was proposed by Jonker and Havinga [10], Chan et al [11] and Shaikh and Vest [12] based on their experimental results on

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X-ray diffraction (XRD) and transmission electron microscopy (TEM) of highly donor doped barium titanate ceramics. This model was also supported by Lewis and Catlow [13] who showed theoretically that V_{Ti}'''' was favoured energetically over $2V_{Ba}''$. It has been reported that $BaTiO_3$ doped with small concentration of lanthanum when prepared by sintering in air exhibits semiconducting behaviour. This has been ascribed to slight loss of oxygen during sintering which generates electrons [14].

When there is simultaneous substitution of trivalent ion on Ba-sites as well as Ti-sites (i.e. La^{3+} on Ba^{2+} sites and Fe^{3+} on Ti^{4+} sites) in equivalent amounts, then it is expected that the charge compensation is maintained internally without requiring the creation of defects. Such solid solutions are termed as valence compensated solid solutions. During the last few years, attempts were made to synthesize and study this type of valence compensated solid solutions [15–20]. Some of these $BaTiO_3$ based systems exhibit very interesting dielectric and electrical properties. La^{+3} and Ni^{3+} based system $Ba_{1-x}La_xTi_{1-x}Ni_xO_3$ shows sharp ferroelectric to paraelectric transition for $x = 0.01$ where as La^{+3} the Co^{3+} based system, $Ba_{1-x}La_xTi_{1-x}Co_xO_3$ shows a diffuse phase transition for $x \leq 0.05$ [21, 22]. Because of interesting properties exhibited by these systems, it was considered worthwhile to investigate an analogous valence compensated $Ba_{1-x}La_xTi_{1-x}Cr_xO_3$ perovskite system. Simultaneous substitution of chromium and lanthanum in equal concentration is expected to maintain charge neutrality internally without creating defects. The effect of independent substitutions, viz. lanthanum on the dielectric behaviour of $BaTiO_3$ has already been studied [23]. Curie point has been reported to decrease at the rate of 18°C/atom % addition of La^{3+}. There is no report on the effect of Cr^{3+} substitution on the Ti^{4+} sites on Curie temperature. To the best of our knowledge, no report is available as yet on the dielectric and electrical behaviour of the $Ba_{1-x}La_xTi_{1-x}Cr_xO_3$ system. We have limited our studies up to $x \leq 0.50$ because of our interest in dielectric properties.

Experimental procedure

Compositions with $x = 0.01, 0.05, 0.10, 0.15, 0.20, 0.30$ and 0.50 in the valence compensated system have been synthesized by solid state ceramic route. Appropriate amounts of barium carbonate, lanthanum oxalate, titanium dioxide and chromium oxide, all of purity greater than 99.5%, for all the above mentioned compositions were weighed and mixed in a ball mill for 6 h using acetone as a mixing medium. These powders were dried and calcined in a platinum crucible at 1,250 °C for 12 h. After calcination, the powders were compacted into the form of cylindrical pellets of 12 mm diameter and 1–2 mm thickness using 2% solution of PVA as a binder which were heated slowly up to 500 °C and kept at this temperature for an hour to burn off the binder. These pellets were sintered at 1,300 °C for 12 h followed by cooling at the rate of 6 °C/m up to 600 °C and then the furnace was switched off.

For the purpose of microstructural characterization, the sintered pellets were polished using emery papers of grades 1/0, 2/0, 3/0, 4/0, 5/0 and diamond paste of grades 3, 1 and 1/4 µm on a polishing cloth. All these samples were thermally etched at 1,350 °C for 20 min. Micrographs of the polished samples were recorded using JEOL A 800 SEM. Two pellets in each of the compositions were coated with conducting Ag–Pd paint which was cured by heating at 750 °C for 20 min. Dielectric parameters i.e. capacitance, *C* and dissipation factor, *D* for single phase compositions were measured over the temperature range 100–600 K at 1, 10 and 100 KHz using 4192 A LF impedance analyzer in a locally fabricated sample holder.

Crystal structure, microstructure and density

XRD patterns of these samples were recorded using $CuK_{\alpha 1}$ radiation from which $CuK_{\alpha 2}$ radiation was filtered. Compositions with $x \leq 0.15$ have shown the absence of characteristic lines of constituent oxides in their diffraction patterns, which show that samples with $x \leq 0.15$ were single phase solid solutions. XRD patterns of single phase solid solutions are shown in Fig. 1. Compositions with $0.20 \leq x \leq 0.50$ have shown the characteristic lines of lanthanum oxide and chromium oxide in their diffraction patterns (figures are not given). X-ray diffraction data of the compositions with $x \leq 0.05$ have been indexed on the basis of a tetragonal structure similar to undoped $BaTiO_3$. For $x = 0.10$ and 0.15, the data have been indexed on the basis of a cubic structure. Lattice parameters, determined by least square fitting of the XRD data, are given in Table 1. It is noted that undoped $BaTiO_3$ ($x = 0.00$) is tetragonal. The tetragonality (c/a ratio) decreases with increasing *x*. Compositions within the range $0.10 \leq x \leq 0.15$, are cubic at room temperature. The unit cell volume decreases with increasing *x*. Theoretical densities have been calculated from the molecular weight and volume of the unit cell. Bulk densities have been calculated from the mass and geometrical dimensions for each

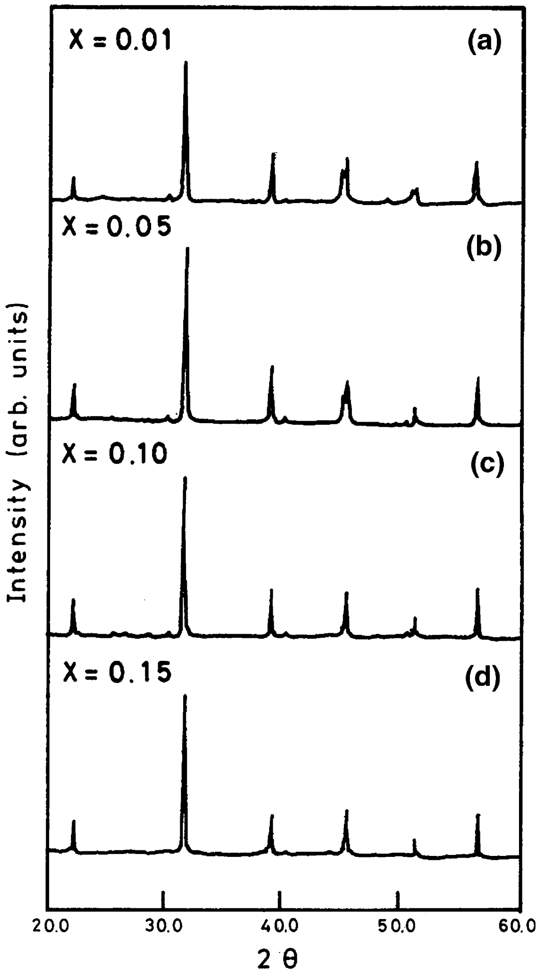


Fig. 1 XRD patterns of the compositions (**a**) 0.01, (**b**) 0.05, (**c**) 0.10, (**d**) 0.15 in the system $Ba_{1-x}La_xTi_{1-x}Cr_xO_3$

composition. Percentage porosities for these compositions, calculated from the theoretical and bulk densities, are given in Table 1. Scanning electron micrographs of the polished and chemically etched surfaces, taken using scanning electron microscope (SEM), are given in Fig. 2. The grain size, calculated by the line intercept method, for the sample with $x = 0.01$ is ~1 μm while for all other samples, it is less than 1 μm. Composition with $x = 0.15$ has an average grain size of sub-micron order. Small grain size for higher compositions may be ascribed to the segregation of dopant ions at the grain boundaries which inhibit the grain growth in these samples [24, 25].

Dielectric behaviour

Plots of relative dielectric constant ε_r, dissipation factor D and imaginary part of relative dielectric constant ε'' versus temperature at 1, 10, 100 KHz for composition with $x = 0.01$, shown in Fig. 3, show the presence of dielectric anomalies at 376 and 275 K. It has shown tetragonal symmetry as well as hysteresis loop, between P and E at room temperature. This indicates that this material is ferroelectric below 376 K. For $BaTiO_3$ ($x = 0.00$), it is noted from the ε_r versus T plot that dielectric anomalies occur at 394, 277 and 196 K (not shown). These temperatures are very close to the temperatures reported for the transition from cubic to tetragonal (C-T), tetragonal to orthorhombic (T-O) and orthorhombic to rhombohedral (O-T) respectively in undoped $BaTiO_3$ [1]. Therefore, peak around 376 K observed in the sample with $x = 0.01$ seems to be due to phase transition from ferroelectric to paraelectric state and peak around 275 K is due to tetragonal to orthorhombic transition. In comparison to $BaTiO_3$, which has T_C ~393 K, 1% substitution reduces the C-T transition temperature, T_C by ~17 K. The temperature of this anomaly does not change with frequency. Anomalies are observed in D versus T plots at the same temperature as in ε_r versus T plots.

Plots of ε_r versus T and D versus T plots for compositions with $x = 0.01$, 0.05, 0.10 and 0.15 are shown in Fig. 4a, b respectively. The dielectric constant is almost frequency independent at low temperatures. The frequency dependence increases with increasing temperature. Composition with $x = 0.05$, exhibits a broad anomaly around 312 K whose position is independent of frequency. A corresponding rather sharp anomaly is observed in D versus T plots also (Fig. 4b). This anomaly is due to ferroelectric to paraelectric

Table 1 Structure, lattice parameters, unit cell volume, PE–FE transition temperature, T_C percentage porosity and average grain size for various compositions (x) in the system $Ba_{1-x}La_xTi_{1-x}Cr_xO_3$

Comp.(x)	Lattice parameters			Structure	T_C,K	% Porosity	Av. grain size (μm)
	a (Å)	b (Å)	c/a				
0.01	3.998 ± 0.001	4.032 ± 0.001	1.008	Tetragonal	376	13	~1
0.05	4.001 ± 0.001	4.016 ± 0.002	1.004	Tetragonal	312	15	~1
0.10	3.996 ± 0.005	–	–	Cubic	180	22	<1
0.15	3.958 ± 0.004	–	–	Cubic	136	25	<1

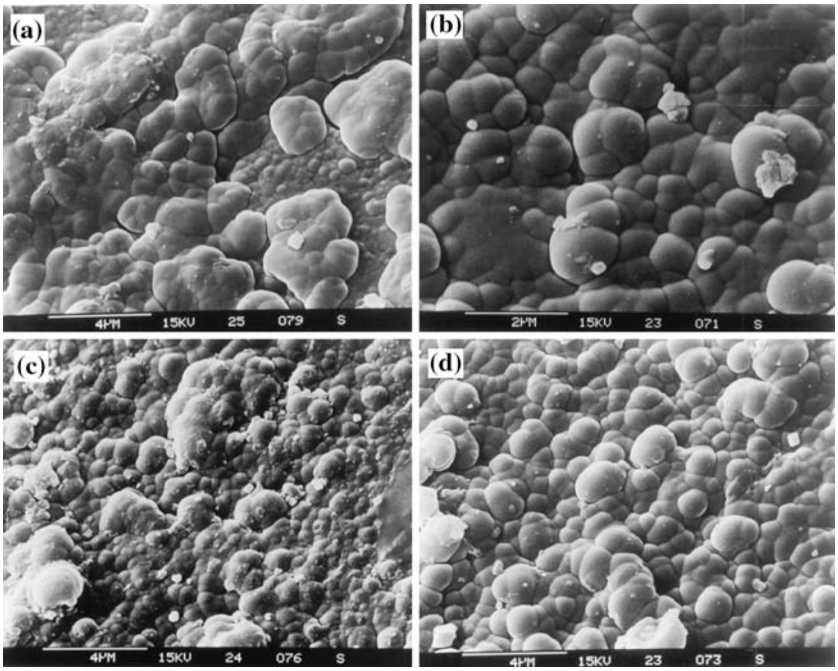


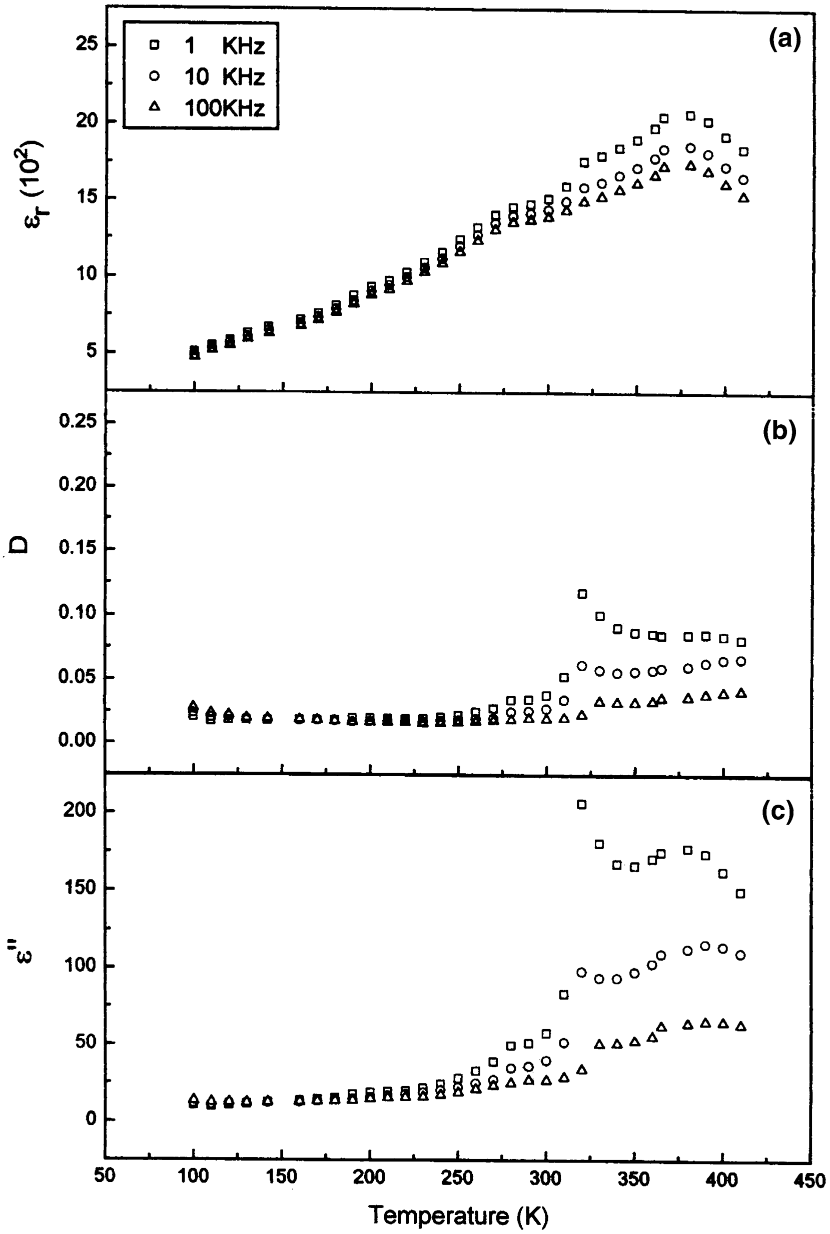
Fig. 2 Scanning electron micrographs of chemically etched surfaces of samples with x (**a**) 0.01, (**b**) 0.05, (**c**) 0.10 and (**d**) 0.15 in the system $Ba_{1-x}La_xTi_{1-x}Cr_xO_3$

transition in this sample. This is in conformity with its crystal structure, which is tetragonal at 300 K. Another broad anomaly (in the form of a shoulder) around 200 K is also noticed in ε_r versus T plots of this composition. This may be due to tetragonal to orthorhombic phase transition. For $x = 0.10$, ε_r versus T plots exhibit a broad anomaly around 180 K (Fig. 4a). The position of this anomaly strongly depends on the frequency of measurement. The peak position moves to higher temperatures with increasing frequency. The corresponding anomaly in D versus T plot seems to occur at higher temperatures. This behaviour is different from that of the compositions with $x = 0.01$ and 0.05 where the dielectric anomalies in ε_r and D versus T plots, are frequency independent. This composition ($x = 0.10$) exhibits frequency dependence ε_r. Composition with $x = 0.15$, exhibits similar behaviour and a broad anomaly occur at 136 K. Thus, it is clear from the above results that transition temperatures for various transitions in this system shift to lower temperatures with increasing concentration x. Compositions with $x = 0.10$ and 0.15 show relaxor ferroelectric like characteristics.

Discussion

Paraelectric to ferroelectric (PE–FE) transition in $BaTiO_3$ is known to occur at 393 K, where the structure changes from cubic to tetragonal. Other transitions from tetragonal to orthorhombic and from orthorhombic to rhombohedral have been reported to occur at 278 and at 183 K respectively [1]. One possibility of shift of T_C on isovalent substitutions is that there will be some distortion due to different ionic radii of the dopants. But the possibility of shift of the Curie temperature, on the basis of the ionic radii, has been ruled out because it does not follow the order of shifting T_C for substitution of Ca, Sr and Pb in $BaTiO_3$ [26]. The other possibility is covalent bond energy of cations with oxygen anions. The order of the bond energy of alkaline earth elements with oxygen in alkaline earth titanates is Ca–O > Sr–O > Ba–O and hence oxygen in the face centre position is less tightly bound with barium as compared to strontium which gives more feed back to shift titanium ions from its centro-symmetric position to off-centre position. This is the reason that $BaTiO_3$ possesses polarization more than $SrTiO_3$ and hence higher Curie temperature than $SrTiO_3$. Similarly, strength of Pb–O and Ba–O bonding in $PbTiO_3$ and $BaTiO_3$ respectively have been reported to influence their Curie temperature respectively [27]. Since Pb–O bonding in $PbTiO_3$ is weaker than Ba–O bonding in $BaTiO_3$, therefore oxygen ion on fcc position is less tightly bound with surrounding Pb^{2+} ions in $PbTiO_3$ as compared to barium ion in $BaTiO_3$. The rigidity of the oxygen in this cage would decide the shift of Ti^{4+} ions, which would be more in $PbTiO_3$ as compared to $BaTiO_3$. The larger shift in Ti^{4+} ion causes larger polarization and hence the larger Curie temperature. This explains why $PbTiO_3$ has higher T_C than $BaTiO_3$. On the other hand $PbTiO_3$, whose co-valent

Fig. 3 Plots of (*a*) dielectric constant, ε_r versus *T*, (**b**) dissipation factor *D* versus *T* at 1, 10, 100 KHz and (**c**) imaginary part of dielectric constant ε'' versus *T* for composition $Ba_{0.99}La_{0.01}Ti_{0.99}Cr_{0.01}O_3$



bond energy of Ti–O bond is smaller, has a higher Curie point than $PbZrO_3$, whose Zr–O bond energy is larger [28].

If we consider the effect of lanthanum substitution on T_C of $PbTiO_3$ and $BaTiO_3$, we have to compare the bond strength of La–O with bond strength of Pb–O and Ba–O bonds. Substitution of La in $PbTiO_3$ reduces its T_C significantly [29]. This is due to the large difference in bond strength of Pb and La with oxygen, being higher in case of La. Though lanthanum and barium lie close to each other in the periodic table, yet their bond strength with oxygen will be different, being more for La–O as compared to Ba–O due to higher valency of La^{3+} ions. This will increase the rigidity of oxygen lying in the face-centred positions in a cage formed by four corner Ba^{2+}/La^{3+} ions. This increase in rigidity will oppose the shift of Ti^{4+} from its body centre position i.e. it will decrease shift of Ti^{4+} from centre of symmetry and hence will reduce its Curie temperature. This is supported by results of Mazadyasni and Brown [24] who observed significant decrease of T_C on small addition of lanthanum to $BaTiO_3$. Morrison et al. [30] explained the lowering of T_C in lanthanum doped $BaTiO_3$ on the basis of concentration of A (Ba) and B (Ti) sites defects with increasing dopant's concentration. According to the

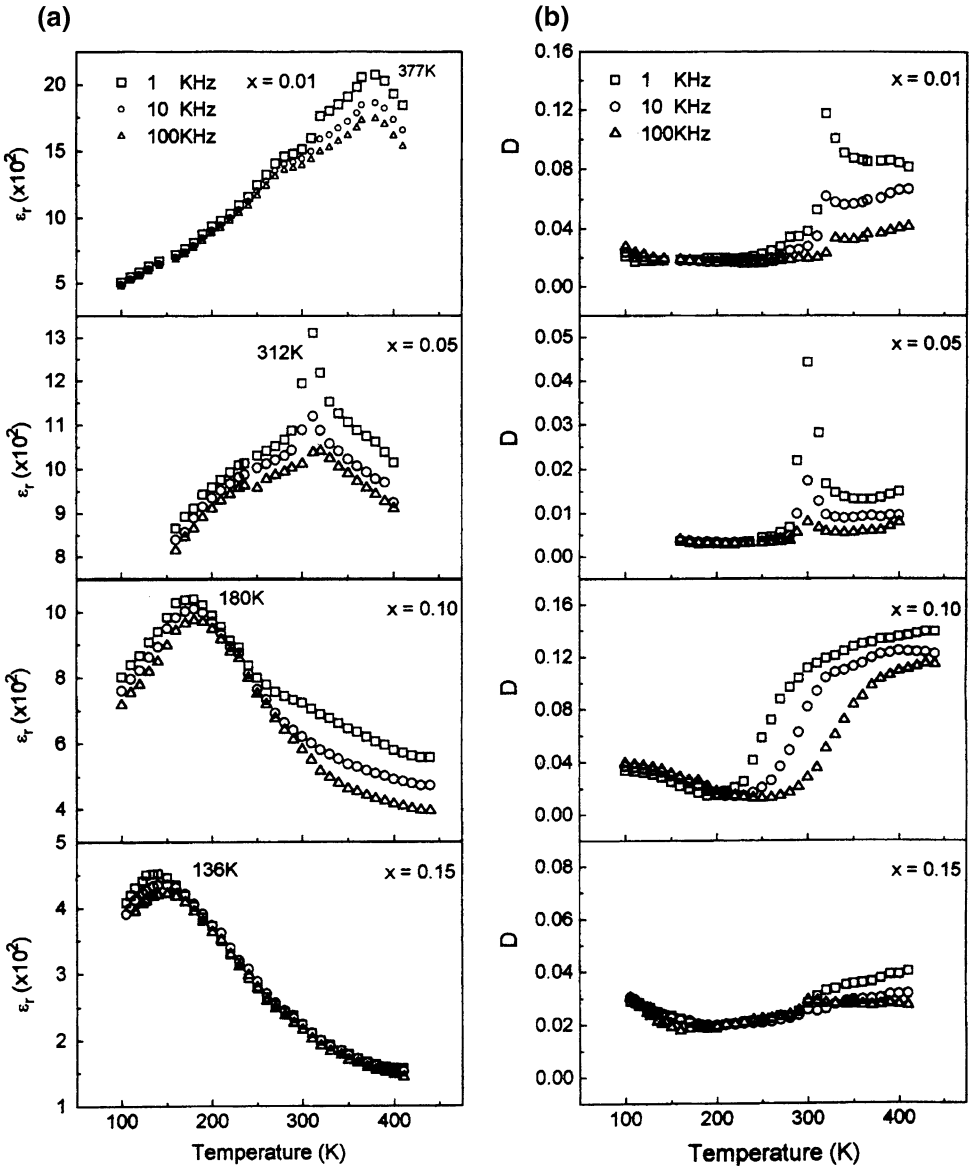


Fig. 4 Plots of (**a**) dielectric constant, ε_r versus T (**b**) dissipation factor, D versus T at 1, 10, 100 KHz for various compositions x in the system $Ba_{1-x}La_xTi_{1-x}Cr_xO_3$

authors [30], the lowering of T_C with La substitution is first due to its smaller size as compared to Ba which makes tetragonal phase unstable and secondly due to creation of titanium vacancies which disrupt the Ti–O–Ti linkages, responsible for ferroelectricity. Both these factors lead to lowering of T_C with increasing x in the system $Ba_{1-x}La_xTi_{1-x/4}(V_{Ti})_{x/4}''''O_3$.

Presence of Cr on Ti site will lead to disrupting of Ti–O–Ti links responsible for ferroelectricity. This will also lead to lowering of T_C with increasing x. This is the reason that two ferroelectric transition anomalies are observed in ε_r versus T plots for x = 0.01 and 0.05, while compositions with x = 0.10 and 0.15 show only one anomaly in the temperature range of measurements. Further, creation of vacancies on Ti-sites will lead to reduction in the electric dipole moment and hence decrease in the peak value of dielectric constant with increasing x. The other low temperature transitions may occur at lower temperatures, which are beyond our range of measurements.

Compositions with x = 0.10 and 0.15 exhibit a behaviour similar to relaxor ferroelectrics. The diffuseness of the anomaly increases with increasing x. Relaxor ferroelectrics exhibit a diffuse peak in their ε_r versus T plots whose position shifts to higher temperature with increasing frequency [2]. D versus T plots also exhibit a diffuse anomaly at temperatures slightly different from that in ε_r versus T plots [20]. Both D and ε_r versus T plots exhibit a strong frequency dependence in the vicinity of the peak temperature. The relaxor like behaviour in these compositions can be explained as follow: The relaxor ferroelectric materials have ferroelectric regions embedded in non-ferroelectric matrix [2]. In the present system, both lanthanum and chromium ions are doped in equal concentration simultaneously. However, due to limitations of solid state ceramic route, there will be some inhomogeneous mixing of these ions. This will lead to different charge compensation for the dopants La and Cr in different regions within the grains. Charge compensation of La^{3+} on Ba^{2+} site by Cr^{3+} on Ti^{4} site will be different in different regions. The breaking of Ti–O–Ti links will also be different in different regions and it will cause inhomogeneity on the octahedral site lattice [31]. With increasing Cr concentration on Ti site, the active Ti–O–Ti links start breaking as mentioned earlier. This will result in the formation of non-ferroelectric regions separating the ferroelectric regions or regions with different magnitude of ferroelectricity and different Curie temperature T_C. The increase in the heterogeneities arising due to increased heterovalent substitutions on equivalent sites i.e. Cr^{3+} on Ti^{4+} sites and La^{3+} on Ba^{2+} sites leads to increased diffuseness of ε_r versus T anomaly. The observation of single anomaly in $x = 0.10$ and 0.15 may also be due to pinching effect of the substituent ions similar to that observed in the case of lanthanum doped barium titanate at a La concentration of 8 atom % i.e. lowering of $T_{C\text{–}T}$ much faster as compared to $T_{T\text{-}O}$ and $T_{O\text{-}R}$ with increasing dopants concentration [30]. Electron microprobe analysis studies of these compositions will be quite useful to study the heterogeneities in these materials.

It has been found in the present investigations that decrease in Curie temperature for 1% simultaneous addition of La^{3+} and Cr^{3+} is ~17 °C. This is close to the value observed for 1% addition of La^{3+} only [1]. This may be due to variety of defects produced in these materials which may have compensating effect.

Conclusions

Solid solution forms up to $x = 0.15$ in the system $Ba_{1-x}La_xTi_{1-x}Cr_xO_3$. Compositions with $x \le 0.05$ have a tetragonal structure while compositions with $x = 0.10$ and 0.15 have a cubic structure. The average grain size in these materials is ≤1 μm. This may be due to the low temperature used for their sintering and/or segregation of dopants at the grain boundaries which inhibit the grain growth. Compositions with $x \le 0.05$ exhibit anomalies in their ε_r versus T plots above 300 K, which shows that these compositions are ferroelectric at room temperature. Ferroelectric to paraelectric transition as well as other transitions observed in barium titanate at low temperatures shift to lower temperature with increasing x. The cross over from ferroelectric for $x = 0.0$ to relaxor ferroelectric have been observed with increasing x. Compositions with $x = 0.10$ and 0.15 exhibit behaviour similar to relaxor ferroelectrics.

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