Dielectric properties of BaTiO$_3$ and La doped BaTiO$_3$ ceramics

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Abstract. The dielectric constant and loss tangent of barium titanate and barium titanate doped with 0·4% (mole) La ceramics have been studied in the frequency range 22 KHz—70 MHz at room temperature and in the temperature range 20°C–170°C at 22 KHz using a Q-meter. It is observed that the dielectric constant at room temperature of the samples increases nearly a hundred fold on doping. The maximum of the dielectric constant broadens and shifts to a lower temperature in the La doped samples. The loss tangent is also relatively high in the doped sample. The dielectric constant and loss tangent of the doped samples decrease faster with frequency than that of the undoped samples.

Barium titanate (BaTiO$_3$) is used most extensively as a dielectric in capacitors. The desired properties are obtained by employing additives and processing techniques. The various methods of preparing BaTiO$_3$ powders, their sintering behaviour and the resulting dielectric properties have been studied by many workers. The dielectric behaviour of ceramic BaTiO$_3$ and its solid solutions, formation of defect structures, and blending materials to achieve the desired properties have been extensively reviewed (Subbarao 1980; Subbarao *et al* 1981). The observations reported here are conducted to gain some insight into the relation between crystalline disorder and dielectric properties.

To perpare the samples starting material was obtained by the thermal decomposition of BaTiO (C$_2$O$_4$)$_2$·4H$_2$O, following Claubaugh *et al* (1956). Doping with La was carried out at the precipitation stage. In order to understand the effect of individual dopants the starting material should have as low impurity level as possible. The powder was pelletised with double distilled water as the slurrying medium. The pellets were heated at a fast rate (from 700 to 1400°C in one hour) and sintered at 1400°C for one hour in air to obtain ceramic with 95% single crystal density and 20–35 μm grain size. The cooling rate was slow (from 1400°C to room temperature in 24 hours). Samples were cylindrical with 0·45 cm radius and 0·20 cm thickness. The dielectric constant and loss tangent (tan δ) of barium titanate ceramic and barium titanate doped with 0·4% (mole) La in the temperature range from 20 to 170°C and frequency range from 22 kHz to 70 MHz have been measured using a Q-meter (model 4342 A, HP USA).

The real part of the dielectric constant (K') of the sample is calculated using the relation

$$K' = 1 + \Delta C/C_0,$$

where ΔC is the difference of C_2 and C_1, the capacitances of the sample holder with and without sample respectively, at maximum Q-deflection and C_0 is the geometrical capacitance of the sample. The loss tangent is given by

$$\tan \delta = K''/K',$$

where K'' is the imaginary part of the dielectric constant, given by

$$K'' = d(C_2 Q_1 - C_1 Q_2)/0{\cdot}08854 A Q_1 Q_2,$$

where Q_2, C_2 and Q_1, C_1 are the maximum Q-values with and without sample respectively. $A(\text{cm}^2)$ is the cross sectional area of the sample and $d(\text{cm})$ the thickness. The measurements were made run to run on the same sample and sample to sample for all samples prepared with similar method. The observations were fluctuating within the experimental error and were averaged.
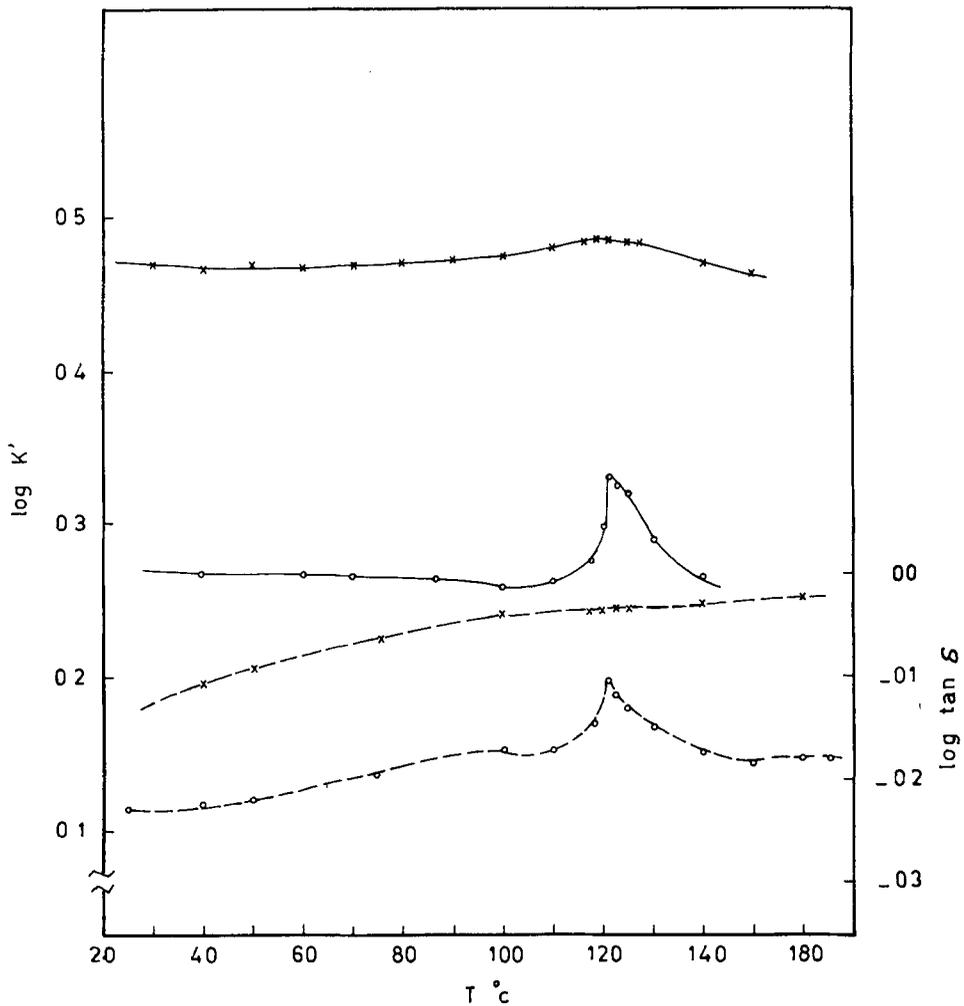
Figure 1. Variation of log of dielectric constant (K') and log of loss tangent $(\tan \delta)$ of BaTiO$_3$ and BaTiO$_3$ + 0·4% (mole) La ceramics with temperature at 22 kHz (curves —○—○— and --○--○-- are for K' and $\tan \delta$ of BaTiO$_3$ ceramics, curves —×—×—×— and --×--×-- are for K' and $\tan \delta$ of BaTiO$_3$ + 0·4% (mole) La ceramics).
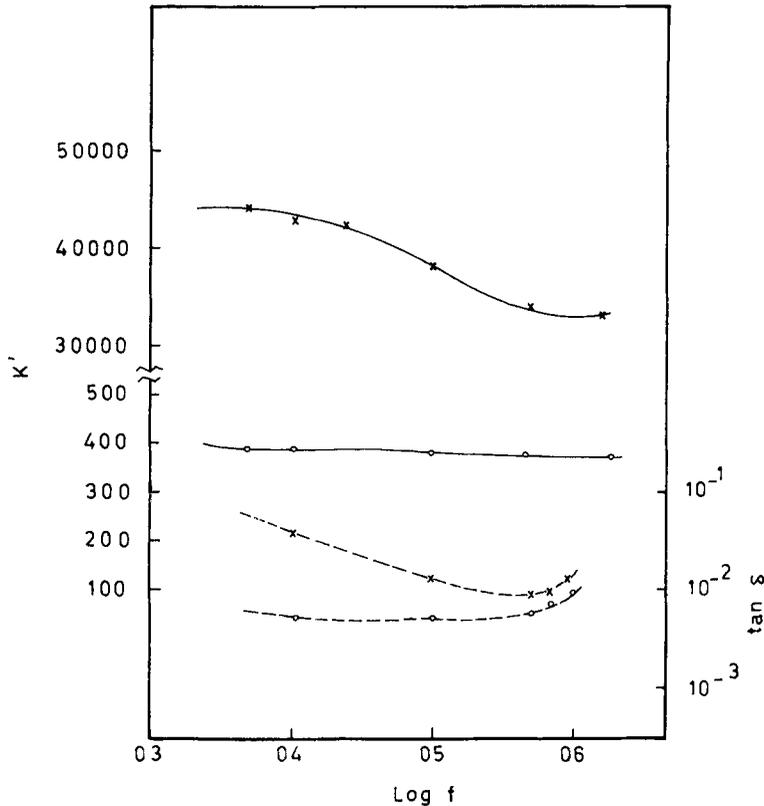
Figure 2. Variation of dielectric constnat (K') and loss tangent (tan δ) of $BaTiO_3$ and $BaTiO_3 + 0.4\%$ (mole) La ceramics with log of frequency (log f) at room temperature, 25°C (legend same as in figure 1).

The variation of K' and tan δ with temperature of $BaTiO_3$ and $BaTiO_3$ doped with 0.4% (mole) La ceramics at 22 kHz is given in figure 1. Undoped $BaTiO_3$ ceramics show a maximum around transition temperature. In the doped samples the maximum broadens and shifts to lower temperature. This indicates decrease in transition temperature by doping which is similar to that noticed for H_2-reduced $BaTiO_3$ (Hardtl and Wernicke 1972). Figure 2 shows variation of dielectric constant (K') and tan δ of $BaTiO_3$ and $BaTiO_3 + 0.4\%$ (mole) La ceramics with frequency at room temperature, i.e. 25°C. It is observed that dielectric constant of doped sample decreases with frequency faster than that of undoped samples which suggests increase in polarization due to impurity in the former. Similarly, the relatively high value of tan δ is also indicative of high concentration of defects in the doped samples.

At the low concentration (0.05 to 0.4%) of La in the composition $Ba^{2+}_{1-x}La^{3+}_x Ti^{3+}_x \cdot Ti^{4+}_{1-x}O_3$, charge neutrality is achieved by converting one Ti^{4+} into Ti^{3+} state for each trivalent rare earth ion incorporated in Ba-sites for the perovskite lattice forming Ba-vacancies (vacancy compensation). The experimental results obtained by us can be explained on the basis of the inhomogeneous distribution of point defects in polycrystalline $BaTiO_3$. More of the Ba-vacancies are produced at the grain boundaries through interactions involving secondary phases like $BaTi_3O_7$ and $Ba_6Ti_{17}O_{40}$. These phases abstract barium or oxygen ions from lattice sites of the

bulk, generating the corresponding vacancies. Since the diffusion of oxygen vacancies is faster, the oxygen uptake from the surrounding atmosphere keeps pace with cooling, whereas Ba-vacancy diffusion is slow resulting in their higher concentration at the grain boundaries than in the bulk, particularly when sample is cooled at finite rates. If the cooling is slow the grains become insulating through the elimination of Ti^{3+} and oxygen vacancy as well as the deeper diffusion of Ba-vacancy. Hence electron trapping is inhomogeneous more at the grain boundaries resulting in the increase of dielectric constant. Higher concentration of cationic vacancies lowers the Curie temperature even in the absence of free carriers. It is therefore possible that the grain boundary layers have more cubic character than the interior of the grain so that the electron trapping can take place even around the room temperature. It has been observed that (Hagemann 1978) bulk and wall effect are controlled by defects in $BaTiO_3$ lattice which can be altered by doping. According to the reports on oxygen vacancies (Hardtl and Wernicke 1972), the Curie temperature shifts by $50°$ per 10^{20} point defects per cm^3. Since phase transition in perovskite ferroelectrics is associated with the softening of zero centred transverse optical mode (Panwar *et al* 1989), it is conceivable that the cation vacancies as well as impurity ions affect the soft mode behaviour and hence the Curie temperature.

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