JOURNAL OF MATERIALS SCIENCE 24 (1989) 3469–3474

Dielectric properties of $SrTiO_3$ single crystals subjected to high electric fields and later irradiated with X-rays or γ-rays

B. K. CHOUDHURY, K. V. RAO, R. N. P. CHOUDHURY
Physics Department, Indian Institute of Technology, Kharagpur 721302, India

The dielectric constant (K), loss ($\tan\delta$), and hence conductivity (σ), of $SrTiO_3$ single crystals have been measured in the frequency region 10^2–10^7 Hz and in the temperature range 30°–350° C. Quenching, subjecting the crystals to high electric fields (a.c. or d.c.) and X-ray or γ-ray irradiation, or a combination of these treatments, is found to bring about interesting changes in these properties. An attempt is made to understand the results.

1. Introduction

A study of the dielectric properties of alkali halide crystals which are subjected to high electric fields (a.c. or d.c.) and later irradiated with X-rays or γ-rays gave interesting information regarding the defect processes that occur in them [1, 2]. Such studies were subsequently extended to some other ionic crystals yielding useful results [3].

$SrTiO_3$ belongs to the perovskite group of materials having a number of industrial applications, such as photochromic and cathodochromic material which is also used in memory devices, optical processors, etc. [4, 5]. Though the presence of even a small concentration of barium, lead and other similar impurities make $SrTiO_3$ a ferroelectric [6], pure $SrTiO_3$ is not ferroelectric down to liquid helium temperature [7]. The dielectric constant has been reported to increase with decreasing temperature (below room temperature) [8]. The electrical transport properties and the influence of oxygen on the electrical conductivity of $SrTiO_3$ have been well studied [9, 10].

It is the aim of this communication to report the data of our measurements on the dielectric constant (K) and loss ($\tan\delta$) of $SrTiO_3$ which have been subjected to high electric fields (a.c. or d.c.) and later irradiated with X-rays or γ-rays. The dielectric measurements have been carried out in the frequency region 10^2–10^7 Hz and in the temperature range 30° to 350° C.

2. Experimental techniques

The high quality $SrTiO_3$ single crystals used in the present work were a gift from Professor A. Smakula, Director of Crystal Physics Laboratory, MIT, Cambride, USA. The samples have been cut from boules and their final dimensions are 1.0 cm × 1.0 cm with thickness varying from 0.07 to 0.1 cm. The samples are quenched from a temperature of 800° C.

For the application of the electric field, the samples carried thin aluminium foils on large area faces to serve as electrodes. Then the crystals were subjected to the field for 1/2 h. The a.c. field was applied with a step-up transformer of 33 kV. The d.c. field was applied by an electronically controlled conventional power supply, the voltage of which can be varied between 0 and 5 kV. The field across the sample was calculated. These electrodes were removed after the field application was complete.

X-ray irradiation of the samples was carried out with Philips tube operating at 35 kV, 10 mA keeping the samples at a distance of 2 cm from the window. The samples were irradiated for 2 h (half the time on either side of the sample.) γ-ray irradiation was carried out with a Co^{60} source of strength 10^3 curie giving a dose of 78 k rad h^{-1}.

The dielectric measurements are taken on a GR716 type capacitance bridge in the frequency region 10^2–10^5 Hz [11] and on a Marconi circuit Magnification Meter type TF329G in the range 10^5–10^7 using a resonance curve principle [12]. The accuracy of measurement of K is 2% and of loss ($\tan\delta$) it is about 5%. Measurements have been taken on at least two samples under the same conditions and the agreement between data has been found to be within the accuracy mentioned.

3. Results

Figures 1a and b present the variation of dielectric constant (K) and loss ($\tan\delta$) at room temperature (30° C) with frequency for $SrTiO_3$ crystals under different conditions. K of $SrTiO_3$, having larger values at lower frequencies, decreases with frequency attaining a constant value beyond 3×10^5 Hz; similar behaviour is exhibited by $\tan\delta$. The values of K and $\tan\delta$ of $SrTiO_3$ at 30° C and at 10^6 Hz are 276 and 3.4×10^{-3}, respectively. Quenching or field treatment (a.c. or d.c.) is found to decrease the low frequency K and $\tan\delta$ values significantly but has no appreciable effect on the high frequency values. (It may be mentioned here that K and $\tan\delta$ of field treated $SrTiO_3$ samples were found to decrease slightly up to about an hour before attaining steady values; the data reported in this paper

0022–2461/89 \$03.00 + .12 © *1989 Chapman and Hall Ltd.*

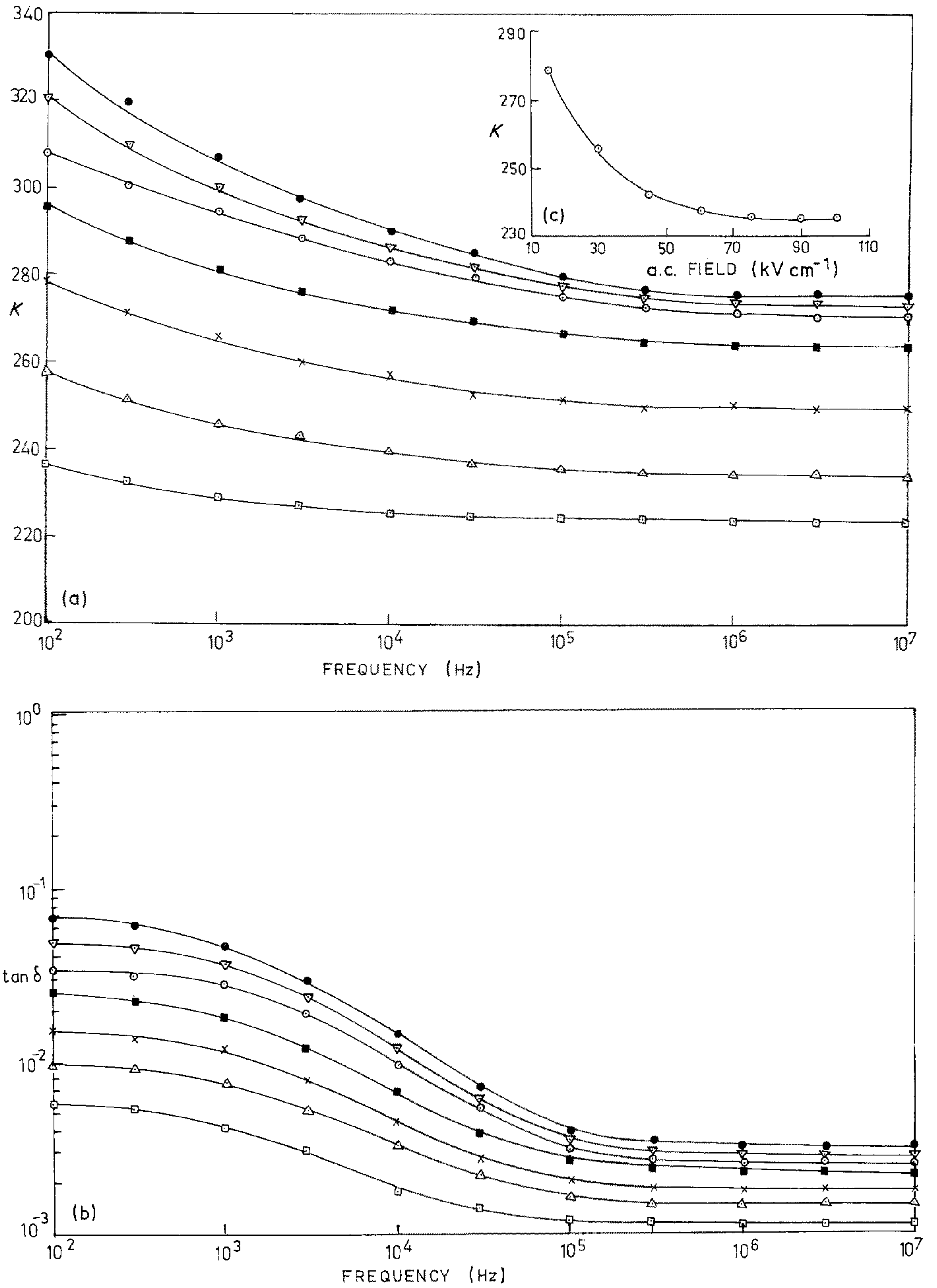

Figure 1 (a) Dielectric constant (K) and (b) loss (tan δ) at 30° C as a function of frequency for $SrTiO_3$ crystals under different conditions. (●) As-cut; (▽) quenched + 60 kV cm^{-1} a.c. + γ-rays (72 h); (⊙) quenched; (■) quenched + 60 kV cm^{-1} a.c. + X-rays (2 h); (x) quenched + 30 kV cm^{-1} d.c. field; (△) quenched + 30 kV cm^{-1} a.c. field; (□) quenched + 60 kV cm^{-1} a.c. field. (c) K at 10^2 Hz against a.c. field for quenched $SrTiO_3$.

are these steady values.) Inset of Fig. 1a shows the decrease of K at 10^2 Hz for $SrTiO_3$ which are quenched and subjected to a.c. fields of different strengths. There is considerable decrease of K with a.c. field up to about 60 kV cm^{-1} beyond which the decrease is not significant. (As the dielectric behaviour of K and tan δ of $SrTiO_3$ subjected to d.c. fields is essentially the same as that exhibited by a.c. field treated samples, the work with d.c. fields has not been pursued further.) X-ray or γ-ray irradiation of quenched and a.c. field treated samples has been found to increase K and tan δ values at low frequencies (in comparison to the data of quenched and a.c. field treated samples).

Variation of K and tan δ at 30° C with frequency of $SrTiO_3$ crystals which are quenched and subjected to 60 kV cm^{-1} a.c. field and subsequently γ-ray irradiated for 72 h are shown in Fig. 2. Another sample of $SrTiO_3$ was prepared from the same boule (so that this has the same values of K and tan δ at room temperature as the other sample initially had (before quenching etc.) for which data are presented in Fig. 2) it was then quenched and subjected to a 60 kV cm^{-1} a.c. field, X-ray irradiated for the dose when the K and tan δ values at 30° C and 10^2 Hz are the same as for the other sample. Both these samples exhibited a decrease of K and tan δ with frequency, the changes in these

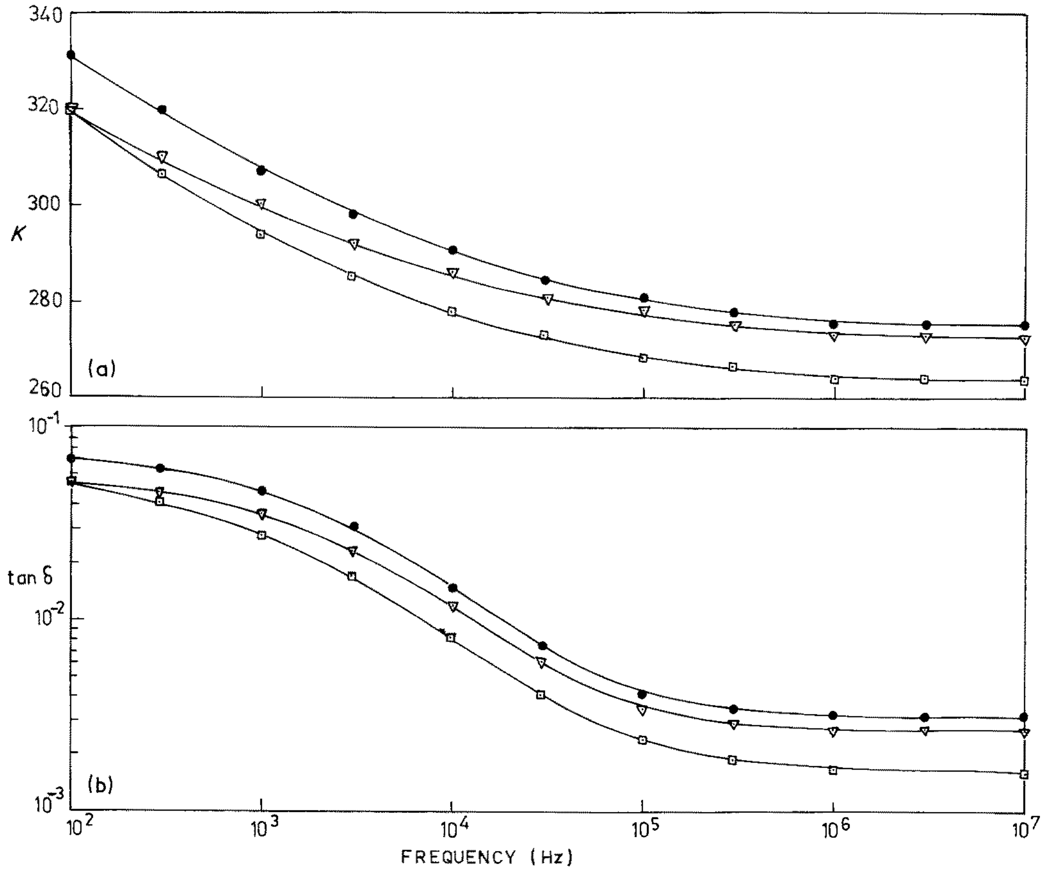

Figure 2 Variation of (a) dielectric constant (K) and (b) loss (tan δ) at 30° C with frequency of $SrTiO_3$ crystals which are quenched and subjected to 60 kV cm^{-1} a.c. field and subsequently γ-ray or X-ray irradiated for the dose at which K and tan δ values at 10^2 Hz are the same. (●) As-cut; (▿) quenched + 60 kV cm^{-1} a.c. field + γ-rays (72 h); (□) quenched + 60 kV cm^{-1} a.c. field + X-rays.

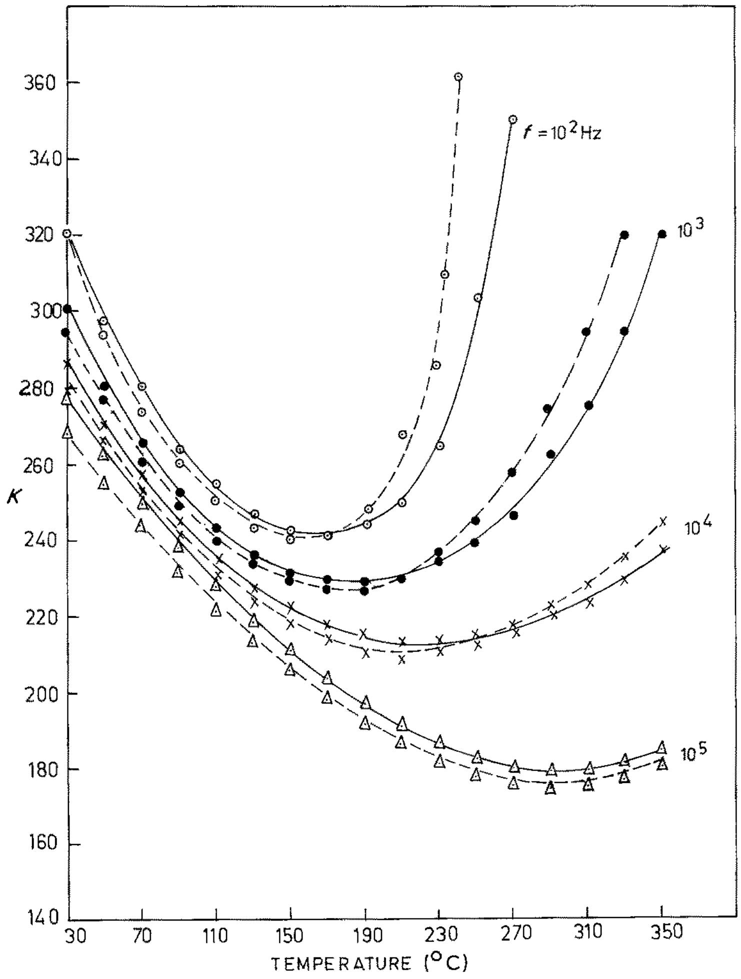

Figure 3 Variation of dielectric constant (K) with temperature at different frequencies (f) for the $SrTiO_3$ crystals. (——) Quenched + 60 kV cm^{-1} a.c. field + γ-rays (72 h); (- - -) quenched + 60 kV cm^{-1} a.c. field + X-rays.

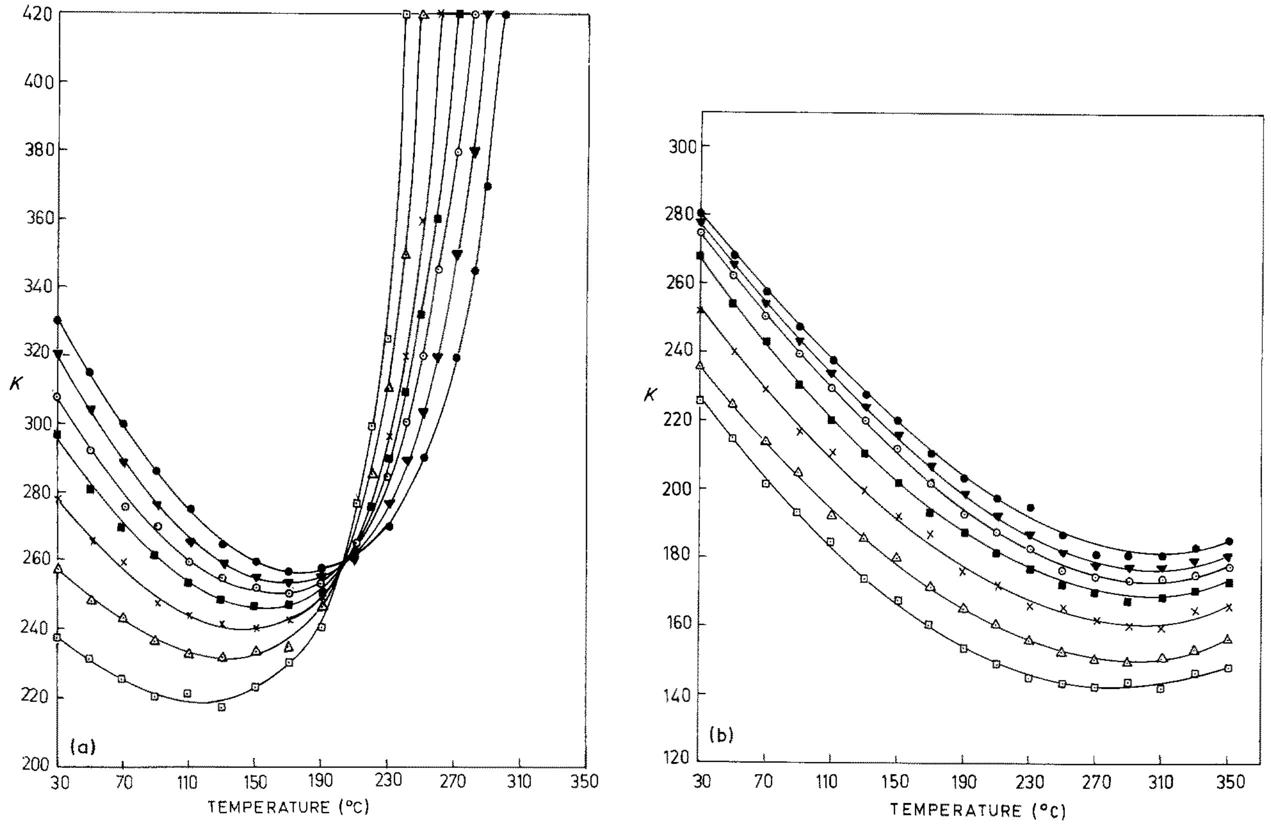

Figure 4 Dielectric constant (K) and as a function of temperature at (a) 10^2 Hz and (b) 10^5 Hz for $SrTiO_3$ crystals under different conditions. (●) As-cut; (▼) quenched + 60 kV cm^{-1} a.c. field + γ-rays (72 h); (■) quenched + 60 kV cm^{-1} a.c. field + X-rays (2 h); (×) quenched + 30 kV cm^{-1} d.c. field; (△) quenched + 30 kV cm^{-1} a.c. field; (□) quenched + 60 kV cm^{-1} a.c. field; (⊙) quenched.

parameters being larger in the sample which has been quenched, a.c. field treated and X-ray irradiated.

The dielectric constant as a function of temperature at different frequencies for the two $SrTiO_3$ crystals under the above mentioned conditions is shown in Fig. 3. K decreases with temperature up to a certain temperature (depending on frequency, e.g. 170° C at 10^2 Hz) beyond which K increases with temperature and is considerably frequency dependent. The inversion temperature T_i (where the temperature coefficient

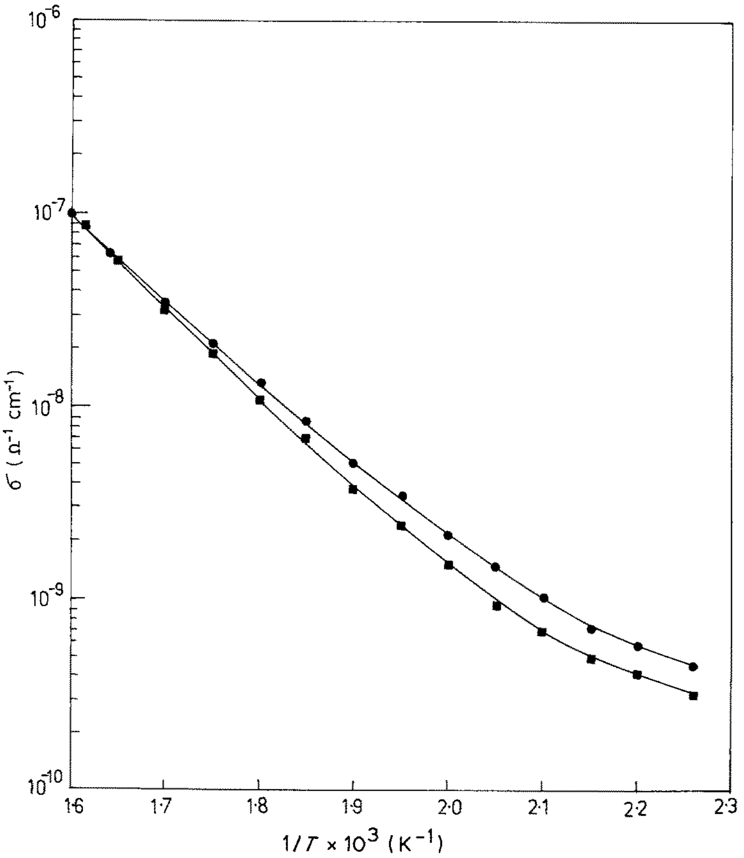

Figure 5 Conductivity (σ) as a function of temperature at 10^3 Hz for $SrTiO_3$ crystals. (●) As-cut; (■) quenched + 60 kV cm^{-1} a.c. field + X-rays (2 h).

TABLE I Summary of the dielectric properties of $SrTiO_3$ single crystals subjected to various treatments

Material treatments at 30° C	K at 30° C		tan δ at 30° C		Inversion temperature T_i (° C)		Activation energy (eV)
	10^2 Hz	10^6 Hz	10^2 Hz	10^6 Hz	10^2 Hz	10^5 Hz	
As-cut single crystal	330	276	7.0×10^{-2}	3.4×10^{-3}	175	300	0.80
Quenched sample (800 to 30° C)	308	272	3.3×10^{-2}	2.6×10^{-3}	163	296	0.86
Quenched + 30 kV cm^{-1} d.c. field (1/2 h)	278	250	1.5×10^{2}	1.8×10^{-3}	146	290	0.95
Quenched + 30 kV cm^{-1} a.c. field (1/2 h)	257	235	9.5×10^{-3}	1.45×10^{-3}	134	285	1.05
Quenched + 60 kV cm^{-1} a.c. field (1/2 h)	236	224	5.6×10^{-3}	1.1×10^{-3}	119	278	1.15
Quenched + 60 kV cm^{-1} a.c. field + X-ray irradiation (2 h)	296	264	2.5×10^{2}	2.3×10^{-3}	155	293	0.90
Quenched + 60 kV cm^{-1} a.c. field + γ-ray irradiation (72 h)	320	274	5.0×10^{-2}	2.9×10^{-3}	170	298	0.84

of dielectric constant changes sign) is found to have a larger value at higher frequency and is also dependent on the condition of the sample.

K as a function of temperature at 10^2 and 10^5 Hz for $SrTiO_3$ crystals under different conditions (Fig. 4) shows that the changes in K with temperature in both the regions where K decreases (or increases) with temperature are comparatively more prominent at the low frequency.

By using, instead of dielectric loss, the dielectric conductivity

$$\sigma = \omega K \tan \delta \, K_0$$

where K_0 is vacuum dielectric constant, σ of the $SrTiO_3$ samples under different conditions at various frequencies and temperatures has been calculated. Log σ against $1/T$ plots have been drawn (Fig. 5) and the activation energy for conduction in the high temperature region (200 to 350° C) calculated.

A summary of the data is presented in Table I.

4. Discussion

The dielectric constant of a material is composed of four contributions: electronic, ionic, dipolar and space charge polarizations. All these may be active at low frequencies. In fact, the behaviour of the variation of dielectric constant with frequency indicates which contributions are present.

The space charge contribution will depend on the purity and perfection of the crystals. Its influence is negligible at very low temperatures and is noticeable in the low frequency region. The dipolar orientational effect can sometimes be seen in some materials even up to 10^{10} Hz. The ionic and electronic polarizations always exist below 10^{13} Hz.

Considering our data, the larger values of K and tan δ of $SrTiO_3$ crystals at lower frequencies may be attributed to charged lattice defects like oxygen vacancies [13]. It is known that quenching of alkali halide crystals and some other solids, or subjecting these solids to high a.c. or d.c. fields, produces in them lattice defects like vacancies [1, 3]. Similar defects may be produced in $SrTiO_3$ crystals under these treatments. These charged defects may be trapped at the defect regions in the $SrTiO_3$ crystals bringing about internal field variations which may clamp the domain type regions thereby decreasing the values of K and tan δ at low frequencies [14]. These defects seem to be produced up to a field strength of about 60 kV cm^{-1} a.c. beyond which there is apparently no further increase in the concentration of such defects.

It is also known that prolonged X-ray or γ-ray irradiation of alkali halide crystals or other solids produces free electrons and lattice defects. Our results showing an increase in K and tan δ at low frequencies in $SrTiO_3$ samples which are quenched, field treated at 60 kV cm^{-1} and later X-ray or γ-ray irradiated (over the values exhibited by the quenched and field treated $SrTiO_3$) seem to indicate that lattice defects are produced (and some may be released) from the domain type regions due to irradiation which increase the space charge polarization (and hence K and tan δ at low frequencies). As X-ray irradiation will be a surface effect involving a thin layer of material on the surface of the $SrTiO_3$ crystals, the changes in K and tan δ at low frequencies will be less pronounced in quenched, field treated and X-ray irradiated crystals compared to those in quenched, field treated and γ-ray irradiated $SrTiO_3$ samples (as γ-ray irradiation will produce defects in the bulk of the crystal), compared to the values of K and tan δ exhibited by quenched and field treated $SrTiO_3$ samples (Fig. 2).

Attempts have been made earlier to explain the decrease in dielectric constant with temperature in $SrTiO_3$ crystals [15]. From the present work, it is found that beyond a certain temperature K starts increasing with temperature and becomes considerably frequency dependent (K having larger values at lower frequencies) indicating that at sufficiently high temperatures, space charge polarization (due to defects) dominates [16]. Thus it is easy to understand the existence of an inversion temperature (T_i) for the dielectric constant of these crystals and its increase to higher frequencies for the same sample containing a certain concentration of defects. But when the concentration of defects in a sample increases due to irradiation, then the space charge polarization becomes comparatively more dominant at low frequencies and T_i is also lowered, as observed in the present measurements. These conclusions are borne out to be true from the data presented in Fig. 4.

The activation energy for conduction in the high temperature region for $SrTiO_3$ crystals (0.8 eV) indicates that oxygen vacancies seem to be responsible for conduction [9, 10]. It is found that this activation energy value is found to increase when $SrTiO_3$ is quenched or quenched and a.c. field treated but again decreases in these field treated samples if they are X-ray or γ-ray irradiated samples. Though further experiments are in progress to throw some light on this interesting behaviour of conductivity, in general it appears that these changes in activation energy seem to be connected with both the concentration and mobility of the charge carriers which are apparently oxygen vacancies in $SrTiO_3$ crystals.

Acknowledgements

The authors are grateful to Professor A. Smakula for kindly sparing these high quality $SrTiO_3$ crystals.

References

1. P. K. CHAKRABORTY, Phd Dissertation, Indian Institute of Technology, Kharagpur, India, 1985.
2. D. ENAKSHI and K. V. RAO, *J. Mater. Sci.* **4** (1985) 1298.
3. A. DE and K. V. RAO, *Phys. Status Solidi* (*a*) **106** (1988) K101.
4. R. L. BERNAY and O. L. CONAN, *Phys. Rev.* **B23** (1981) 37.
5. W. PHILLS and Z. J. KISS, *ibid.* **180** (1969) 924.
6. G. A. SMOLENSKII and A. I. AGRONOVASKAYA, *Doklady Akak. Nauk, SSSR* **97** (1959) 237.
7. K. V. RAO and A. SMAKULA, *J. Appl. Phys.* **36** (1965) 3953.
8. A. LINZ, *Phys. Rev.* **91** (1953) 753.
9. M. CAPIZZI and A. FORVA, *Phys. Rev. Lett.* **25** (1970) 1298.
10. Y. YACOBY and O. NAVEH, *Phys. Rev.* **B7** (1973) 399.
11. W. B. WESTPHAL, Technical Report Laboratory for Insulation Research MIT (USA) No. 182 (1963) p. 10.
12. K. V. RAO, *J. Phys. Chem. Solids* **20** (1961) 193.
13. K. V. RAO and A. SMAKULA, *J. Appl. Phys.* **36** (1965) 2031.
14. K. V. RAO, *Ferroelectrics* **17** (1977) 389.
15. G. GOODMAN, *J. Amer. Ceram. Soc.* **43** (1960) 105.
16. K. V. RAO and A. SMAKULA, *Mater. Res. Bull.* **6** (1971) 1047.

Received 20 June
and accepted 7 December 1988