Antiferroelectric phase transition in (Sr$_{1-x}$Ca$_x$)TiO$_3$ (0.12 < x ≤ 0.40): I. Dielectric studies

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Abstract
Results of a detailed dielectric study of phase transition in Sr$_{1-x}$Ca$_x$TiO$_3$ in the composition range $0.18 \leqslant x \leqslant 0.40$ are reported. It is shown that the temperatures T'_m and T''_m corresponding to the peaks in the real ($\varepsilon'(T)$) and imaginary ($\varepsilon''(T)$) parts of the dielectric constant, respectively, are not only coincident but also frequency independent, suggesting that these anomalies are due to a thermodynamic phase transition and not a dipole glass/relaxor ferroelectric transition. The Curie–Weiss temperature, as determined from the $\varepsilon'(T)$ data above the transition temperature, is found to be negative. Using Landau theory considerations, the negative Curie–Weiss temperature is interpreted in terms of an antiferroelectric phase transition. It is proposed that the smearing of the $\varepsilon'(T)$ data in the composition range $0.016 \leqslant x \leqslant 0.12$ reported by Bednorz and Muller is due to the frustration introduced by the antiferroelectric interactions caused by Ca^{2+} substitution and the ferroelectric interactions of the SrTiO$_3$ matrix.

1. Introduction

SrTiO$_3$ is well known for its quantum paraelectric behaviour [1]. Its dielectric constant increases upon cooling down to about 4 K below which it levels off due to zero-point quantum fluctuations. Substitution of Sr^{2+} by Ca^{2+} [2, 3], Ba^{2+} [4] or Pb^{2+} [5] is known to stabilize the ferroelectric (FE) phase against quantum fluctuations. Ferroelectricity has also been induced in SrTiO$_3$ by the isotope exchange of ^{18}O for ^{16}O [6]. Of these, the Ca^{2+} substitution has received wide attention [7–13].

Bednorz and Muller [3] measured the real part of the dielectric constant (ε') of SCT single crystals in the composition range $0 \leqslant x \leqslant 0.12$. They have shown that the transition temperature (T'_m) corresponding to the peak in the $\varepsilon'(T)$ data rises with Ca^{2+} concentration (x) up to $x \approx 0.016$ as per the relationship $T'_m \sim (x - x_c)^{0.5}$. Such a relationship is expected for quantum ferroelectrics [14]. Bednorz and Muller [3] have suggested that there is a crossover from the quantum to the classical regime around $x = 0.016$. In the classical regime, i.e., $0.016 < x < 0.12$, T'_m is nearly temperature independent. Further, for this composition range, variation of dielectric constant with temperature is increasingly more smeared out as x increases, and $\varepsilon'(T)$ does not obey the Curie–Weiss law but shows an effective exponent

(γ) as per the relationship $\varepsilon' \sim C(T - T_C)^{-\gamma}$. The effective exponent (γ) approaches 1.75 for $x = 0.06$ [3]. Similar effective exponents are known for relaxor ferroelectrics [15]. No satisfactory explanation exists for the smearing of $\varepsilon'(T)$ and the departure from Curie–Weiss behaviour in the SCT system for $0.016 < x < 0.12$.

Earlier, Mitsui and Westphal [2] measured $\varepsilon'(T)$ on ceramic samples of SCT with Ca^{2+} content up to $x = 0.20$. A perusal of the $\varepsilon'(T)$ data given by Mitsui and Westphal [2] reveals that the dielectric anomaly at T'_m is increasingly more suppressed and smeared out with increasing concentration of Ca^{2+}. Further, Mitsui and Westphal [2] have shown that T'_m remains nearly constant ($\sim$35 K) in the composition range $0.04 \leqslant x \leqslant 0.12$ but starts increasing again for $x > 0.12$. No explanation exists for this increase in T'_m for $x > 0.12$.

For a regular ferroelectric transition, the P–E hysteresis loop is of nearly square shape. It disappears just above the transition temperature (T'_m). For a dipole glass or relaxor ferroelectric transition, one observes a slim P–E loop and the remanent polarization gradually tails off to zero at a temperature well above T'_m [16, 17]. Slim hysteresis loops have been reported by Bianchi *et al* [7] on SCT single crystals for $x = 0.007$. Mitsui and Westphal [2] have reported slim hysteresis loops up to $x = 0.10$ on ceramic specimens. Ranjan *et al* [13] have noted that the remanent polarization measured by Mitsui and Westphal [2] gradually tails off to zero far above T'_m in a manner similar to what is known for dipole glasses [17] and relaxor ferroelectrics [16]. The relaxor ferroelectric/dipole glass behaviour in the quantum ferroelectric (QFE) regime, i.e., $0.002 < x < 0.016$, has been explained in terms of phonon-assisted dissipative quantum tunnelling of the Ca^{2+} dipoles between the potential minima in the four-well potential [7]. The smearing of the $\varepsilon'(T)$ in the classical regime has been attributed to a second order phase transition into the ferroelectric domain state. The random fields (RFs) generated by Ca^{2+}–V_o centred dipoles are believed to be responsible for the RF-domain state [3]. Further, the relaxor ferroelectric or dipole-glass-like behaviour in the classical regime ($0.016 < x < 0.12$) has been attributed to ferroelectric cluster and domain wall dynamics [18].

Mitsui and Westphal [2] have reported the absence of a P–E loop for $0.10 < x \leqslant 0.20$. This suggests that the dielectric anomaly for $x > 0.12$ may not be due to a ferroelectric/relaxor ferroelectric/dipole glass transition. The only study carried out in the past by Granicher and Jakits [19] for $x \geqslant 0.20$ was restricted to the measurement of the real part of the dielectric constant ($\varepsilon'(T)$) at a fixed frequency, which is inadequate in deciding the origin of the dielectric anomaly in SCT for $x > 0.12$. In order to understand the origin of the dielectric anomaly in SCT for $x > 0.12$ and beyond $x = 0.20$, one needs not only $\varepsilon'(T)$ data but also $\varepsilon''(T)$ (the imaginary part of the dielectric constant). Granicher and Jakits [19] conjectured that SCT in the concentrated limit may be antiferroelectric but could not obtain unambiguous dielectric and structural evidence for the same. The present work was undertaken to provide unambiguous confirmation for an antiferroelectric phase transition in SCT for $0.12 < x < 0.43$. The results of temperature dependent dielectric and structural studies are presented in parts I and II respectively. A brief report of this work has recently been published [13].

2. Experiment

Samples were prepared by a conventional solid state route. Analytical grade $SrCO_3$, $CaCO_3$ and TiO_2 powders (purity 99.5%) were mixed in stoichiometric proportion in a ball mill (Netsch) for 6 h using ZrO_2 balls as milling agent and acetone as mixing medium. The ball-milled powder was calcined at 1150 °C for 6 h. The as-calcined powders were again ball-milled to break the agglomerates and then pelletized in a cylindrical die of diameter 1.2 cm at a load of 65 kN. After burning off the binder (2% PVA solution) at 550 °C for 12 h, the pellets were sintered at 1300 °C for 6 h. The sintered density of the pellets was nearly 99% of the theoretical

x-ray density. Dielectric measurements were carried out on such dense pellets. Both the faces of sintered circular pellets of ~0.1 cm thickness were gently polished with 0.25 μm diamond paste for about 2 minutes and then washed with acetone to clean off the surface. Isopropyl alcohol was then applied to remove the moisture, if any, left on the pellet surfaces. Fired-on silver paste was subsequently applied on both the faces of the pellet. It was first dried at 100 °C in an oven and then cured by firing at 500 °C for 30 minutes.

For dielectric measurements below room temperature, a locally designed set-up was used. The sample was placed on a flat brass plate that served as one of the electrodes. The other electrode was made up of a spring-loaded brass rod which pressed the pellet from the top. A chromel–alumel thermocouple placed near the pellet was used for measuring the temperature of the pellet. A cylindrical-shaped heating arrangement surrounding the pellet and the electrode assembly was used. This kind of heating arrangement has the advantage of providing good thermal equilibrium conditions around the pellet region as compared to the arrangement in which one heats the sample from the bottom side of the pellet. This heater-cum-electrode assembly was placed inside a glass tube with the bottom end sealed, through a pair of hanging thin metal rods fixed on an insulating plate. This insulating plate, made of pyrophillite, covered the glass tube from above with the help of a rubber O-ring sandwiched between the two. The glass tube was then subsequently dipped in a cryocan filled with liquid nitrogen. The interior of the cell was continuously evacuated with a rotary pump during the measurements so as to avoid moisture deposition inside the cell. Temperature was measured with an accuracy of 0.1 K using a Keithley thermometer (model 740). A Hewlett Packard 4192 impedance analyser was used for the measurement of capacitance and loss tangent (tan δ).

3. Evidence for a thermodynamic phase transition in $Sr_{1-x}Ca_xTiO_3$ for $x > 0.12$

For a thermodynamic ferroelectric or antiferroelectric phase transition, the temperatures T'_m and T''_m corresponding to the peaks in $\varepsilon'(T)$ and $\varepsilon''(T)$ respectively, coincide. For dipole glass or relaxor transition, on the other hand, $T''_m < T'_m$ [16, 17]. Further, T'_m/T''_m are frequency independent for a thermodynamic phase transition whereas for relaxor and dipole glass transitions T'_m and T''_m shift to higher temperatures on increasing the measuring frequency [16, 17]. T'_m is the phase transition temperature for a thermodynamic phase transition whereas it represents the onset of freezing of dipolar clusters for dipole glasses/relaxors. In order to decide whether the dielectric anomaly in SCT for $x > 0.12$ is due to a thermodynamic phase transition or due to a dipole glass/relaxor transition, we present the $\varepsilon'(T)$ and $\varepsilon''(T)$ data as a function of frequency in this section.

The determination of $\varepsilon''(T)$ of SCT samples was quite challenging since the loss tangent (tan δ) is found to be very low (~10^{-3}). On increasing the measuring frequency, it decreases further and becomes of the order of 10^{-4} at 100 kHz. Since the HP4192A impedance analyser (like any other commercial impedance analyser) can measure loss tangent up to 0.0001, it was not possible to get any meaningful results for frequencies higher than 100 kHz. However, the main objective of our measurements may not be affected, since Bianchi *et al* [7] have reported that the glassy features (like T''_m being less than T'_m and shifts in T'_m and T''_m as a function of frequency) in $\varepsilon'(T)$ and $\varepsilon''(T)$ are full blown below 100 kHz for SCT with $x = 0.007$. Measuring tan δ of the order of 10^{-3} to 10^{-4} required extra precautions. Even the slightest inferior quality of the fired-on electrode could easily mask the intrinsic values of tan δ in the vicinity of a phase transition. Further, the stability of the impedance analyser was also quite crucial.

Figures 1(a), (b) and (c) depict the variation of ε' and ε'' with temperature for SCT with $x = 0.30$ (SCT30), $x = 0.25$ (SCT25) and $x = 0.23$ (SCT23), respectively. It is evident from this figure that ε' gradually increases on lowering the temperature below 300 K until
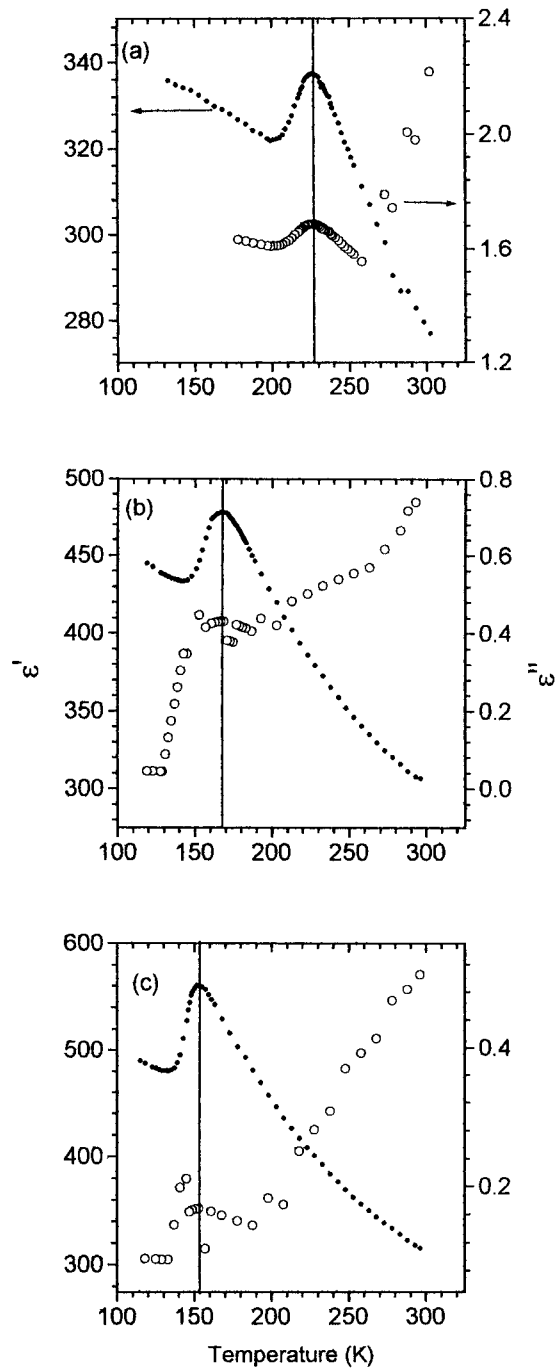
Figure 1. Variation of real ε' and imaginary ε'' parts of dielectric constant (measured at 10 kHz) with temperature for $Sr_{1-x}Ca_xTiO_3$ with (a) $x = 0.30$, (b) $x = 0.25$ and (c) $x = 0.23$.

it shows a peak at 226, 167 and 153 K for SCT30, SCT25 and SCT23 respectively. Unlike $\varepsilon'(T)$, $\varepsilon''(T)$ decreases on lowering the temperature below 300 K as can be seen from these figures. However, around 260 K for SCT30 and 175 K for SCT23 and SCT25, ε'' starts

rising and shows a peak at 226, 167 and 153 K for the three compositions SCT30, SCT25 and SCT23. Some of the data points not falling on the $\varepsilon''(T)$ curves in figures 1(b) and (c) are due to extraneous factors. The remaining data points are, however, sufficient for depicting the correct trend of the $\varepsilon''(T)$ curve for SCT25 and SCT23. For SCT30, the impedance analyser was very stable during the measurements, as a result of which the variation of ε'' around the transition temperature is very smooth. It is evident from these figures that the temperature (T'_m) at which $\varepsilon'(T)$ is maximum coincides with the peak temperature (T''_m) of ε'' (T) as expected for a thermodynamic phase transition. As said earlier, for a dipole glass or relaxor transition, T''_m is considerably lower than T'_m [16, 17].

Figure 2 depicts the variation of $\varepsilon'(T)$ and $\varepsilon''(T)$ at four different frequencies (5, 10, 50 and 100 kHz) for SCT30. The $\tan \delta$ values are found to decrease with increasing frequency and for 100 kHz it is very close to the sensitivity of the instrument (0.0001). Hence no measurements were carried out for frequencies beyond 100 kHz. It is evident from these figures that both T'_m and T''_m are independent of the measuring frequency up to 100 kHz. This further confirms that the anomalies in $\varepsilon'(T)$ and $\varepsilon''(T)$ are due to a thermodynamic phase transition and not a dipole glass or relaxor transition. As said earlier, for a dipole glass or relaxor transition, T'_m and T''_m shift to the higher temperature side on increasing the measuring frequency. For example, T''_m [7] shifts by about 4 K for SCT with $x = 0.007$ on increasing the measuring frequency from 1 kHz to 100 kHz as expected for a dipole glass/relaxor transition.

4. Variation of T'_m with Ca^{2+} concentration

As per the work of Bednorz and Muller [3], T'_m for SCT increases up to about 33 K on increasing the Ca^{2+} content from $x = 0.0018$ to $x = 0.016$. For the composition range $0.016 < x \leqslant 0.12$, T'_m shows very weak dependence on x [2, 3]. Mitsui and Westphal [2] have reported that for $0.12 < x \leqslant 0.20$, T'_m again starts increasing with x. In the previous section, we have seen that the anomaly in $\varepsilon'(T)$ in SCT for $x > 0.20$ is due to a thermodynamic phase transition. In this section, we report the composition dependence of the phase transition temperature (T'_m) in SCT with $0.18 \leqslant x < 0.40$. For $x \geqslant 0.43$, the anomaly in $\varepsilon'(T)$ disappears [20].

We find that the peak temperature (T'_m) increases with increasing Ca^{2+} concentration for the composition range $0.18 \leqslant x < 0.40$. For example, $T'_m = 107$ K for $x = 0.18$ whereas it is 364 K for $x = 0.40$. The variation of T'_m with Ca^{2+} concentration is shown in figure 3. For the sake of completeness, we have also included the data of Bednorz and Muller [3] for $x \leqslant 0.12$ and those of Mitsui and Westphal [2] for $x = 0.16$ and 0.20 in this figure. It is evident from this figure that T'_m values obtained by us and those by Mitsui and Westphal ($x = 0.16, 0.20$) increase with Ca^{2+} content (x) in a linear fashion in the composition range $0.16 \leqslant x \leqslant 0.40$. The slope of the curve (dT'_m/dx) is found to be approximately 11 K per mole per cent of CaTiO$_3$ in SrTiO$_3$. The extrapolation of the best fit line to T'_m versus x data for this composition range intersects the Bednorz and Muller [3] data near $x = 0.12$ as can be seen from figure 3.

It is interesting to note from figure 1 that the dielectric constant below T'_m first decreases and then starts increasing again. This points towards the possibility of a second dielectric anomaly at still lower temperatures. Since our measurements were restricted to temperatures above 100 K, we could not observe this second anomaly for $x < 0.35$. We have, however, been able to confirm the existence of the second dielectric anomaly for $0.35 \leqslant x \leqslant 0.40$ [20]. If one assumes linear dependence of T'_m on x for the second dielectric anomaly also, T'_m for the second transition becomes 0 K for $x \approx 0.20$ as shown in figure 3. This suggests that in the composition range $0.12 < x \leqslant 0.20$, $\varepsilon'(T)$ will exhibit a rising trend below the antiferroelectric phase transition temperature. The absence of the second transition in the $\varepsilon'(T)$ data for $x = 0.20$ given by Mitsui and Westphal [2] in the temperature range 10 to 300 K is in
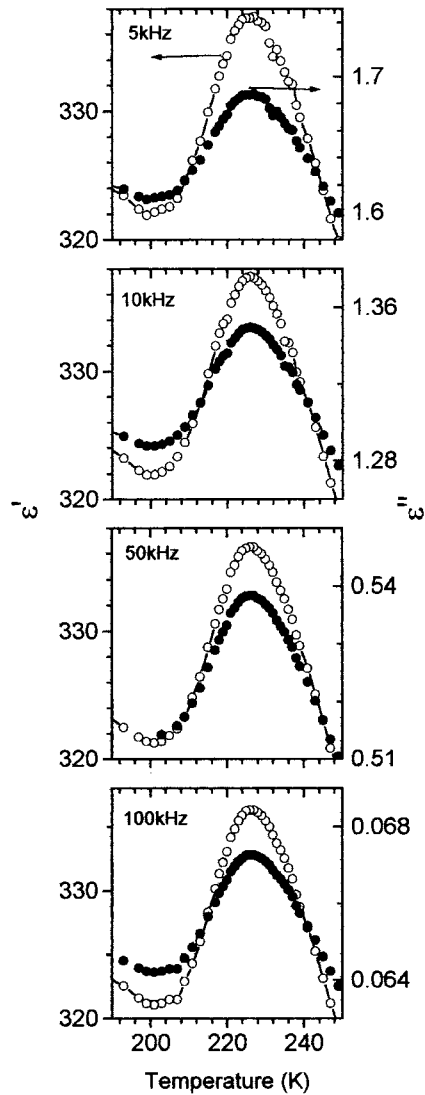
Figure 2. Variation of ε' (open circles) and ε'' (filled circles) with temperature at four different frequencies: 5, 10, 50 and 100 kHz for SCT30.

agreement with our prediction.

The results of Mitsui and Westphal [2] as well as Bednorz and Muller [3] show that the value of dielectric constant (ε'_{max}) at T'_m decreases with increasing Ca^{2+} content for $0.0107 \leqslant x \leqslant 0.20$ even though the slope of the T'_m versus x plot changes twice, i.e. first around $x = 0.016$ [3] and then around $x = 0.12$ [2]. We have found that ε'_{max} continues to decrease with increasing Ca^{2+} content for still higher Ca^{2+} concentrations up to $x = 0.40$.
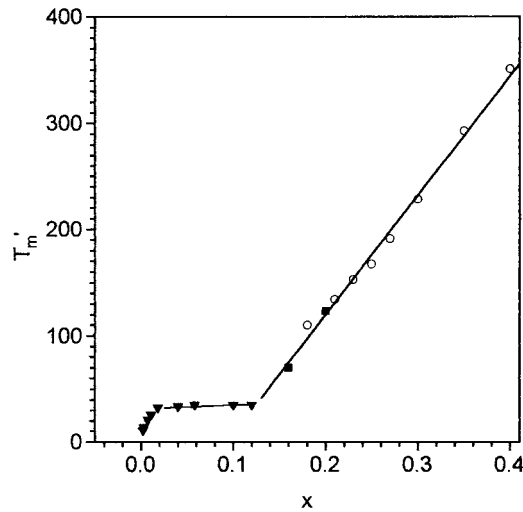
Figure 3. Variation of dielectric anomaly temperature (T'_m) with calcium concentration (x) in SCT. The data points represented by filled inverted triangles and squares are taken from the work of Bednorz and Muller (1984) and Mitsui and Westphal (1961) respectively. The open circles correspond to our work.

5. Curie–Weiss fit

We have already seen that the dielectric anomalies for the composition range $0.18 \leqslant x \leqslant 0.40$ are due to a thermodynamic phase transition which could be of ferroelectric or antiferroelectric origin. For ferroelectric as well as antiferroelectric transitions, $\varepsilon'(T)$ above T'_m is known to follow Curie–Weiss behaviour:

$$1/\varepsilon'(T) = (T - T_C)/C$$

where T_C is the Curie–Weiss temperature and C is the Curie constant. For a second order phase transition, T_C is same as the thermodynamic phase transition temperature (T'_m) obtained by dielectric measurements. For a first order phase transition, T_C is known to be less than T'_m [21]. Bianchi *et al* [7] have shown the validity of the Curie–Weiss law for SCT with $x = 0.007$. The Curie–Weiss temperature (T_C) obtained by these workers nearly coincides with the peak temperature (T'_m) in $\varepsilon'(T)$ as expected for a second order phase transition. However, for higher Ca^{2+} content ($0.04 \leqslant x \leqslant 0.10$), one observes departure from Curie–Weiss behaviour just above T'_m. The range of temperature (ΔT) over which this departure occurs increases with increasing Ca^{2+} content: $\Delta T \approx 5$ K, 5 K, 10 K and 20 K for $x = 0.0075, 0.0179, 0.04$ and 0.10, respectively. The fact that the departure from Curie–Weiss behaviour is observed over a temperature range as large as 20 K for $x = 0.10$ is due to a relaxor ferroelectric transition for which a simple Curie–Weiss law does not hold good [15]. On increasing the Ca^{2+} content beyond $x = 0.12$, we find that there is not only sharpening of the dielectric anomaly but also a marked decrease in the temperature over which departure from Curie–Weiss behaviour is observed. This is illustrated in figure 4 for $x = 0.23, 0.25, 0.30$ and 0.35. This figure depicts the variation of $1/\varepsilon'$ with temperature along with the Curie–Weiss fits to the data above T'_m. It is evident from this figure that the Curie–Weiss behaviour is observed up to about $(T'_m + 10)$ K for all the compositions. The departure from the Curie–Weiss behaviour is thus restricted to about 10 K above T'_m irrespective of the Ca^{2+} content. So, unlike the SCT compositions with $x < 0.12$ where the temperature range (ΔT) over which the departure from Curie–Weiss

behaviour is observed increases with increasing Ca^{2+} content, ΔT for $0.23 \leqslant x \leqslant 0.35$ is not only independent of Ca^{2+} content but also half the corresponding value for $x = 0.10$.
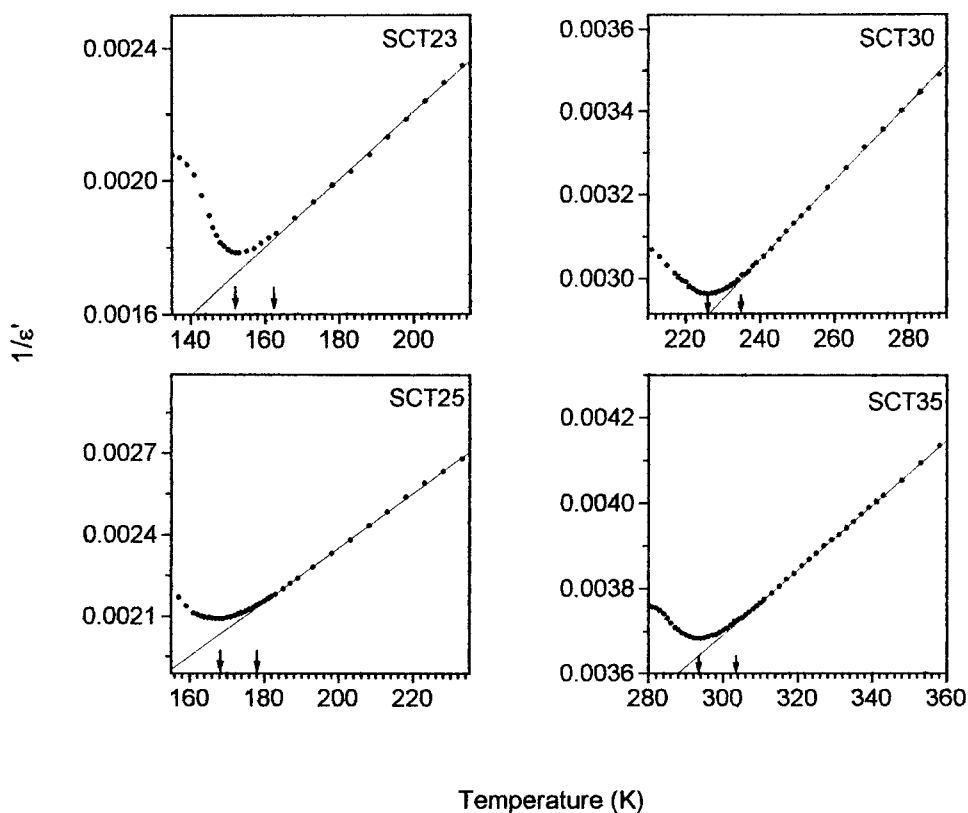

Figure 4. Variation of dielectric stiffness (ε'^{-1}) with temperature for $Sr_{1-x}Ca_xTiO_3$ with $x = 0.23$ (SCT23), 0.25 (SCT25), 0.30 (SCT30) and 0.35 (SCT35). The straight lines are Curie–Weiss fits to the data points.

More significantly, the Curie–Weiss temperature (T_C) for $0.18 \leqslant x \leqslant 0.35$ turns out to be negative. This is illustrated in figure 5 for $x = 0.30$. The variation of T_C with Ca^{2+} content for $0.18 \leqslant x \leqslant 0.40$ is shown in figure 6. It is evident from this figure that T_C is becoming more negative with increasing Ca^{2+} content. The sign of T_C seems to change around $x = 0.12$. The change in the sign of T_C from negative to positive through zero around $x = 0.12$ is an exciting observation since it implies that the Curie–Weiss law will be reduced to a simple Curie law around this composition. The highly smeared $\varepsilon'(T)$ response observed by Bednorz and Muller [3] for $x = 0.12$ may therefore be due to the freezing of superparaelectric clusters [16].

For ferroelectric transitions, Curie–Weiss temperature (T_C) is known to be positive. Even for relaxor ferroelectrics and dipole glasses, T_C is not known to be negative [15–17]. It is therefore unlikely that the dielectric anomaly in SCT for $0.18 \leqslant x \leqslant 0.40$ is a result of a ferroelectric, relaxor ferroelectric or dipole glass transition. Further, for SCT crystals [7] and ceramics [2] with Ca^{2+} content up to $x = 0.10$, P versus E hysteresis loops are observed. These loops are very slim, similar to those reported for relaxor ferroelectrics [16] and dipole glasses [17]. These hysteresis loops for SCT crystals [7] and ceramics [2] are observed at fields as low as 1 and 1.7 kV cm^{-1} respectively. No P versus E hysteresis loop characteristic of either ferroelectric or relaxor ferroelectric phases was observed by us below the dielectric
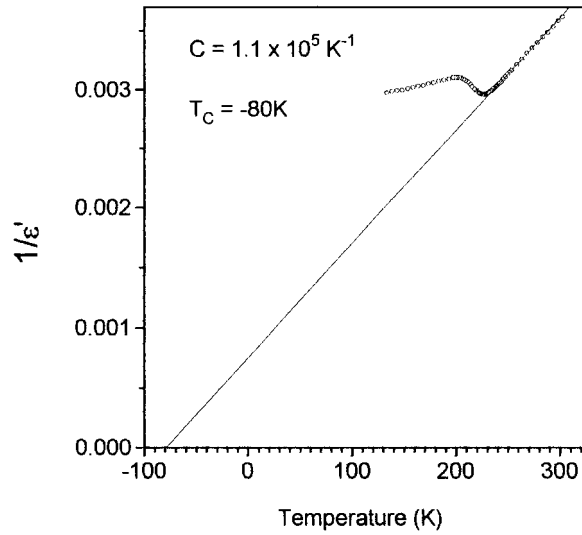
Figure 5. Curie–Weiss fit to $\varepsilon'(T)$ data for SCT30 showing negative value of Curie–Weiss temperature (T_C).
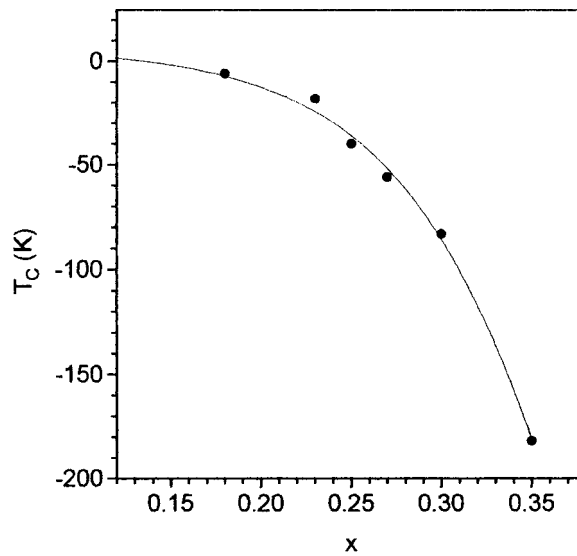

Figure 6. Variation of Curie–Weiss temperature (T_C) with Ca^{2+} concentration in SCT.

anomaly temperature (T_m') for SCT compositions with $0.18 \leqslant x \leqslant 0.40$ even after applying fields as high as 60 kV cm^{-1}.

The observation of negative Curie–Weiss temperature (T_C) in the SCT compositions for $0.18 \leqslant x \leqslant 0.40$ is reminiscent of antiferromagnetic transitions in alloys where negative T_C is well known [22]. In the light of the negative T_C and the absence of P versus E loops, we propose that the dielectric anomalies in SCT for $0.18 \leqslant x \leqslant 0.40$ are due to an antiferroelectric phase transition.

6. Discussion of results

It is evident from the foregoing that the nature of the dielectric anomaly for $0.18 \leqslant x \leqslant 0.40$ differs from that for $x < 0.12$ in several respects. (i) T_C is negative for $0.18 \leqslant x \leqslant 0.40$ whereas it is always positive for $x < 0.12$. (ii) The slope of T'_m versus x changes around $x = 0.12$. (iii) The smearing of $\varepsilon'(T)$ decreases above $x = 0.12$. (iv) The temperature range of departure from Curie–Weiss behaviour suddenly decreases from a value of about 20 K for $x = 0.10$ to 10 K for $0.18 \leqslant x \leqslant 0.35$. (v) No P–E hystersis loop is observed below the dielectric anomaly temperature (T'_m). We can understand the significance of the negative Curie–Weiss temperature, found in the Curie–Weiss fit to the observed $\varepsilon'(T)$ data in the paraelectric phase, in the framework of Kitttel's phenomenological theory of antiferroelectric transition [23].

An antiferroelectric crystal is composed of two collinear sublattices with equal and opposite polarizations. In general, one may have two independent sublattice polarizations P_i and P_j corresponding to the two sublattices. The Landau free energy density can be expanded in powers of P_i and P_j as [24]:

$$G(T, P_i, P_j) = G_0(T) + f(P_i^2 + P_j^2) + g P_i P_j + h(P_i^4 + P_j^4) + j(P_i^6 + P_j^6) + \cdots \qquad (6.1)$$

where g is the coupling strength of the sublattice polarization in the antiferroelectric phase. If $h > 0$, this expression leads to a second order phase transition, whereas for $h < 0$ and $j > 0$ a first order phase transition occurs.

For $g > 0$ and $2f - g$ showing the following type of temperature dependence near the transition temperature,

$$f = (1/2)g + \lambda(T - T_0)$$

a transition from the high temperature paraelectric to the low temperature antiferroelectric phase can occur [24].

In this phenomenological model of antiferroelectricity, the dielectric constant above the transition temperature is given by

$$\varepsilon'(T) = 1/[g + \lambda(T - T_0)].$$

This expression can be recast to the Curie–Weiss form

$$\varepsilon'(T) = C/[T - T_C]$$

by choosing $C = 1/\lambda$ and $T_C = T_0 - g/\lambda$. Obviously, for $g/\lambda > T_0$, T_C will be negative. This is exactly what is observed in SCT in the composition range $0.18 \leqslant x \leqslant 0.40$. As x approaches 0.12, T_C tends towards zero, suggesting that the strength of the sublattice coupling parameter (g) decreases with decreasing Ca^{2+} content. An ideally zero Curie–Weiss temperature would mean a system with non-interacting (independent) dipoles (Weiss term is zero) which follows the Curie law in the paraelectric phase. Thus with decreasing Ca^{2+} content, T_C becomes less negative until it passes through zero for $x \approx 0.12$ and then shows positive values for still lower Ca^{2+} content characteristic of a ferroelectric or relaxor ferroelectric/dipole glass transition. The fact that at lower calcium concentrations, i.e. $x \leqslant 0.10$, non-linear P–E response and a P–E hysteresis loop have been reported by Mitsui and Westphal [2] suggests that ferroelectric or relaxor ferroelectric-like ordering exists in this composition range. The smearing of the $\varepsilon'(T)$ response in the classical regime $0.016 \leqslant x \leqslant 0.12$ is due to the competition between the antiferroelectric interactions mentioned above and the incipient ferroelectric interactions of the $SrTiO_3$ matrix. As a result of this competition, the order parameter is frustrated [25], leading to glassy features in $\varepsilon'(\omega, T)$ and $\varepsilon''(\omega, T)$ for $x \leqslant 0.12$.

7. Conclusions

We have investigated the temperature variation of real $\varepsilon'(T)$ and imaginary $\varepsilon''(T)$ parts of the dielectric constant of $Sr_{1-x}Ca_xTiO_3$ in the composition range $0.18 \leqslant x \leqslant 0.40$. The equality of the peak temperatures T_m' and T_m'' in the $\varepsilon'(T)$ and $\varepsilon''(T)$ data and their frequency independence suggests that the dielectric peaks are due to a thermodynamic phase transition and not a relaxor ferroelectric or dipole glass transition. The Curie–Weiss temperature for the composition range $0.18 \leqslant x \leqslant 0.40$. is found to be negative. In Kittel's phenomenological theory, negative Curie–Weiss temperature is possible for antiferroelectric transition. The antiferroelectric interactions dominate for $x > 0.12$ but compete with ferroelectric interactions of the $SrTiO_3$ matrix for $x < 0.12$ leading to frustration and glassy features in $\varepsilon'(T)$, $\varepsilon''(T)$ and $P_r(T)$ data observed by earlier workers.

Acknowledgments

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