

Effect of oxygenation on the structural and dielectric properties of $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ with $0.20 \leq x \leq 0.40$

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(Received 20 February 2008; accepted 2 May 2008; published online 27 May 2008)

Effects of oxygenation on the structural and dielectric properties of $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ ($0.20 \leq x \leq 0.40$) ceramics, prepared through solid-state reaction, have been studied employing x-ray diffraction, transmission electron microscopy, and temperature dependent dielectric permittivity measurements. It has been found that oxygenation has drastic effects on the ceramics' dielectric properties, but their crystal structure remains least affected. The effect of oxygenation on the sharpening of the first order antiferroelectric phase transition has been studied. © 2008 American Institute of Physics.

[DOI: 10.1063/1.2936293]

CaTiO_3 and its substituted perovskites have received intense attention due to their importance in a variety of fields like synrocs, for radioactive waste¹ management, in which CaTiO_3 has been proven to be an efficient host for Sr90 (Ref. 2) and in phase and frequency agile electronics with tunable high- Q devices due to its nonlinear optical and electric-field-dependent dielectric properties.³ Therefore, there has been considerable interest in knowing the correct crystallographic structure of Sr substituted CaTiO_3 in its various forms ranging from bulk to nanophases.⁴ Attempts carried out regarding the structural characterization of $\text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3$ (SCT) solid solutions are full of controversies.⁵⁻⁹ The knowledge of the correct phase, as a function of the Sr:Ca ratio, is very much needed for control on the above mentioned physical properties. However, there has been almost no attempt to know the root cause of the discrepancies. Few probable reasons appear to be different routes of structural investigations and sample processing methods, which do not provide proper oxygenation. The effect of oxygenation has been realized for TiO_2 .¹⁰ In the following, we investigate the effect of oxygenation on the structural and dielectric properties of a wide composition range of SCT ($0.20 \leq x \leq 0.40$) ceramics. The present report is important from the point of view of processing method, which can produce SCT ceramics with definite reproducible structural and dielectric properties. We also investigate and discuss the composition (Ca) dependent competing antiferroelectric (AFE) and ferroelectric (FE) interactions in these high quality SCT samples.

The SCT ceramic pellets with $0.20 \leq x \leq 0.40$ were prepared using SrCO_3 , CaCO_3 , and TiO_2 after sintering at 1300°C following⁸ the solid-state reaction route. The sintered pellets were crushed and grounded to fine powders. Two sets of pellets were prepared out of these powders. For the first set, we directly used the as crushed powders, but for the second one, the crushed powders were first annealed in high purity (99.99%) oxygen atmosphere at 950°C for 24 h. The two sets of the pelletized ceramics were then sintered at 1350°C for 12 h. The final sintered samples were subjected to x-ray diffraction (XRD), transmission electron microscopy (TEM), and temperature dependent dielectric characterizations.¹¹ Details of TEM and the dielectric mea-

surement are given elsewhere.^{8,11} All the pellets were found to be similarly dense, $\sim 95\%$ of their corresponding x-ray density.

Figure 1(a) shows the XRD data of oxygenated SCT ceramics, which were Rietveld refined using space groups

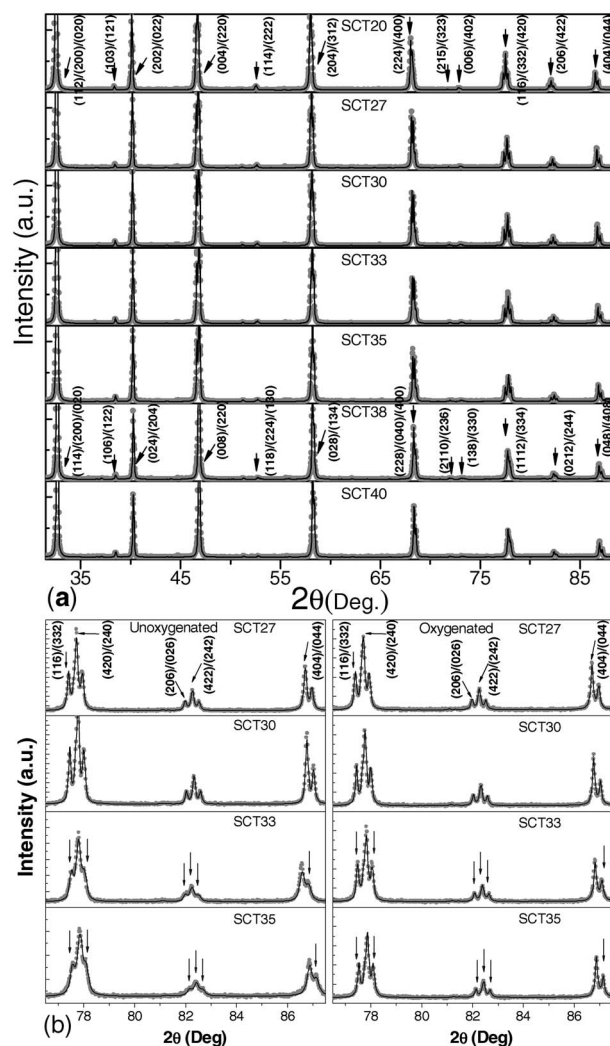


FIG. 1. (a) Reitveld refined XRD data of oxygenated SCT ceramics. (b) Comparison of XRD data for $0.20 \leq x \leq 0.35$ showing no structural change but oxygenation induced decrease in half-widths of the XRD peaks. This can be realized by comparing the extent of splitting of XRD peaks for SCT with $x > 0.33$.

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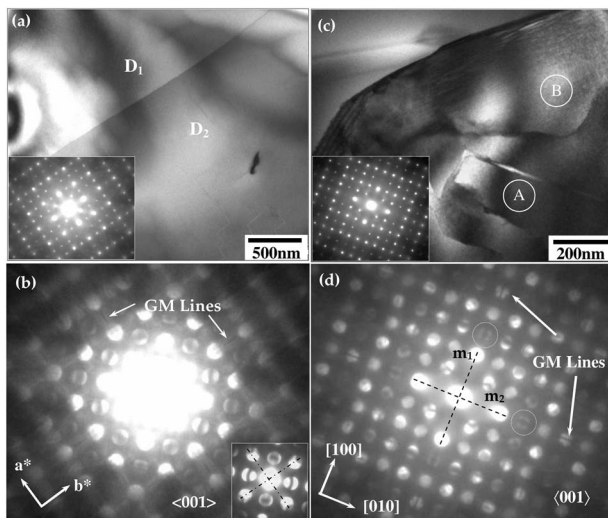


FIG. 2. TEM results of SCT30 and SCT40 ceramics. Electron micrographs exhibit 90° twin domains of (a) $P2_12_12$ and (c) $Pbcm$ phases. Corresponding insets show the $\langle 001 \rangle$ zone SAD patterns from respective domains. (b) and (d) show the low-angle CBEDs. The presence of Gjønnnes and Moodie (GM) lines (Ref. 8) has been indicated by arrows in (500) and (050) forbidden disks of CBEDs in (b) and (d). The absence of the mirror about these GM lines along a^* and b^* in (b) has been indicated by dashed lines in the corresponding inset. The absence of the mirror along GM lines indicate the presence of mutually perpendicular screw axes confirming the $P2_12_12$ phase. (Ref. 8) On the contrary, the presence of mirrors in (d) confirm the presence of mutually perpendicular glide planes in the $Pbcm/Pbcm$ phase.⁸

$P2_12_12$ (Ref. 8) for $0.20 \leq x \leq 0.35$ and $Pbcm$ for $x=0.38$ and 0.40. The absence of any unaccounted peak revealed the formation of single phase SCT ceramics. Figure 1(b) shows a comparison of few high-angle peaks of the XRD patterns of some oxygenated and unoxygenated SCT samples. Although no structural change was found after oxygenation, it was a bit effective in improving the structural order of the SCT ceramics with $x \geq 0.33$. This was inferred from better split peaks at $\sim 77.8^\circ$, $\sim 82.3^\circ$, and $\sim 87^\circ 2\theta$ in Fig. 1(b), as indicated by arrows. The observed splitting is due to decreased linewidth after oxygenation. However, oxygenation was ineffective for the already structurally ordered SCT with $x \leq 0.30$.

Figures 2(a)–2(d) show the electron micrographs, selected area electron diffraction (SAD), and convergent beam electron diffraction (CBED) patterns from the typical SCT samples studied in the present investigation. The presence of 90° twin domains D_1 and D_2 of the $P2_12_12$ phase⁸ in Fig. 2(a), a representative for $0.20 \leq x \leq 0.35$, and the presence of $Pbcm/Pbcm$ domains in Fig. 2(c), a representative for $0.38 \leq x \leq 0.40$, can be seen. Microstructural and diffraction features, as shown in Fig. 2, were found to be the same for unoxygenated and oxygenated SCTs.

Figure 3 presents temperature variation of the real part of the dielectric permittivity (ϵ' - T) for the whole set of unoxygenated and oxygenated SCT samples carried out during both heating and cooling cycles. The presence of hysteresis in ϵ' - T and the negative Curie–Weiss temperature (see insets) show the occurrence of a first order AFE phase transition. It can be seen that oxygenated SCT samples have drastically different hysteresis loops. No such change was observed for samples that which were simply sintered, even for 72 h at 1350°C , but not oxygenated. The dielectric loss ($\tan \delta$) for oxygenated samples at 300 K ranged from ~ 0.002 to ~ 0.0002 . $\tan \delta$ was found to decrease on

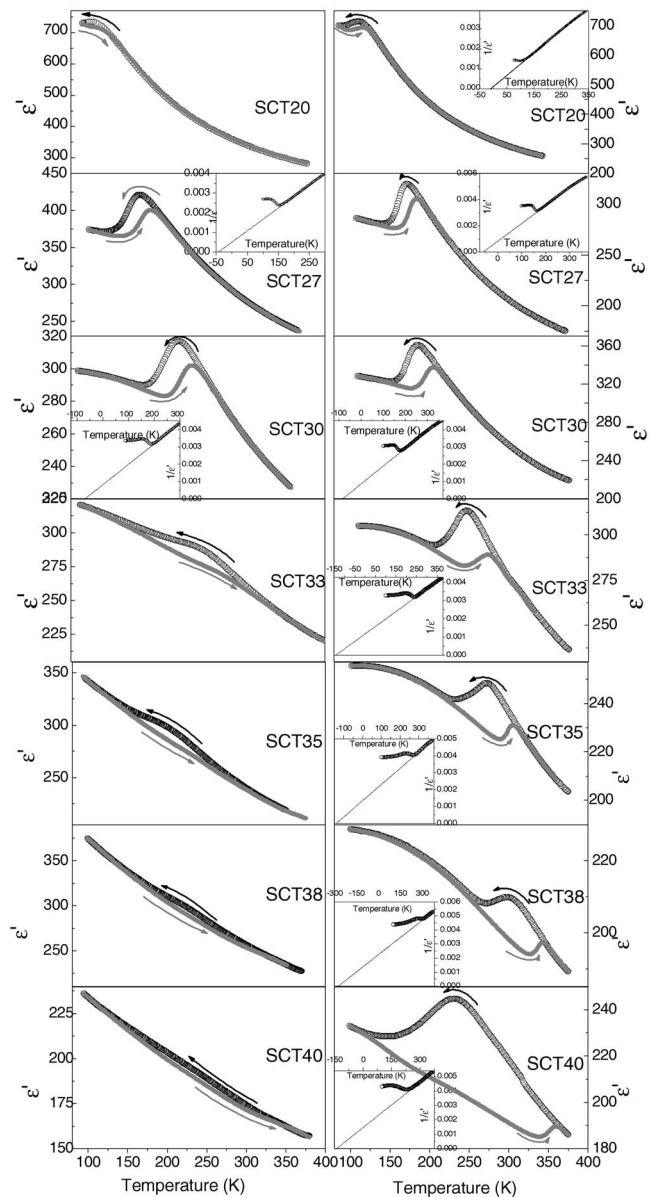


FIG. 3. ϵ' - T curves for the unoxygenated (left column) and oxygenated (right column) SCTs measured at 1 kHz. Insets show the Curie–Weiss fit to the PE regime of the cooling curves.

oxygenation¹⁰ by factors of 0.6–0.1, roughly decreasing with Ca concentration. Thus, keeping in view the above observations and the difference in the methods of preparation, it becomes obvious that it is the oxygenation which has brought drastic effects on the nature of the first order phase transition (FOPT). On oxygenation, the ill-defined and slim hysteresis loops became much sharper with well-behaved widths. It should be noted that the area under the hysteresis loop increases for oxygenated samples, indicating a many-fold increase in the volume fraction of the SCT ceramics undergoing AFE phase transition. A comparison of XRD and TEM results with those of the ϵ' - T hysteresis curves directly reveals that oxygenated and unoxygenated samples look structurally similar but have drastically different dielectric properties. The observed broadening of the AFE FOPT for unoxygenated samples is due to oxygen deficiency. It can be noticed that the ratio of the areas under the hysteresis loops corresponding to the unoxygenated sample to that of the oxygenated sample decreases with increasing Ca concentration.

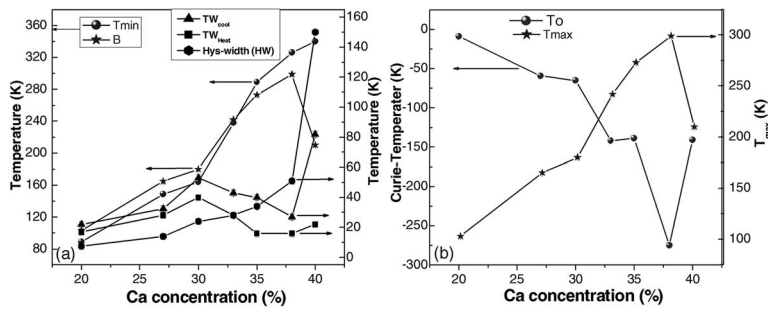


FIG. 4. Graphical comparison of the Ca concentration dependence of the parameters T_0 , T_{max} , T_{min} , HW, TW_{cool} , and TW_{heat} extracted from the hysteresis loops.

This indicates that the effect of oxygen deficiency is rather drastic in SCT samples with higher Ca concentrations. In a defect free system, the transition will be sharp with well-defined hysteresis widths, but with the presence of defects, such as local strain or oxygen inhomogeneity the transition widths will broaden, whereas the hysteresis widths will remain the same.

Various parameters, extracted out of the observed hysteresis loops of the AFE transition, are shown in Figs. 4(a) and 4(b). T_0 , T_{max} , and T_{min} are the Curie-Weiss temperature, ϵ' -maxima temperature during cooling, and ϵ' -minima temperature during heating, respectively. HW is the hysteresis width and TW_{cool} and TW_{heat} are the respective transition widths during cooling and heating cycles. The parameters T_{max} and T_{min} were determined directly from the ϵ' - T curves, whereas HW, TW_{cool} , and TW_{heat} were determined using $d\epsilon'/dT$ of the ϵ' - T variation. Usually, for a FOPT, the T_{min} should be higher than T_{max} , but experimentally we find that for $0.20 \leq x \leq 0.30$, T_{min} is lower than T_{max} , indicating that the transformation from AFE to paraelectric (PE) during heating starts at a temperature before the PE to AFE transformation temperature during cooling. This is probably due to a wide distribution in the transition temperature (T_C) arising due to disorder. In cases when HW is smaller than TWs, such apparent discrepancies may arise. In such situations, T_{max} will be defined by the phase fraction with the highest T_C , whereas during heating, the T_{min} will be defined by the phase fraction with the lowest T_C . If the width of hysteresis is narrower than the width of T_C distribution, T_{min} will be lower than T_{max} . In Fig. 4(a), it can be seen that T_{min} undergoes a crossover with T_{max} at $x=0.33$. Up to $x=0.33$, the HWs are smaller than the TW_{heat} but for $x>0.33$, the HWs become larger than TW_{heat} . Therefore, the corresponding T_{min} also becomes larger than T_{max} , which is generally expected in a FOPT. It can be noticed that HW is a slowly increasing function of (x) up to $x \sim 0.38$ but rises abruptly, together with TW_{cool} , for $x>0.38$. This abrupt rise appears to be related to the change in the AFE interaction with increasing Ca. Figure 4(b) shows a plot of T_{max} and T_0 . The sudden rise in T_0 has been accompanied by a decrease in T_{max} . This correlated change occurs exactly at the same Ca concentration at which HW diverges.

The occurrence of AFE interaction in SCT has been attributed to the Ca substitution.¹² It increases with Ca content up to a certain level.^{9,12} The physical significance of the Curie temperature (T_0) is related to the strength of interaction.¹³ The more negative the value of T_0 , the higher the corresponding AFE interaction and the transition temperature. Thus, an abrupt decrease in the negative value of T_0 indicates an abrupt decrease of the AFE interaction strength followed

by a decrease in T_{max} . It so appears that with increasing Ca, SCT undergoes an interaction phase change. The increasing AFE interaction starts getting suppressed at $x \sim 0.38$. The extreme member of SCT, i.e., the CaTiO_3 , is PE.¹⁴ The PE behavior starts^{6,9,12} in SCT for $x \geq 0.41$. The occurrence of PE behavior in SCT indicates suppression of the AFE interaction. The sudden increase in HW and TW at $x \sim 0.38$ also indicates some change in the interaction. The occurrence of diffuse phase transition has been attributed to the presence of some random field.¹⁵ The sudden increase in TW_{cool} for $x=0.40$ appears to indicate the emergence of some random field, in the present case also. Looking into the decreasing AFE interaction, it appears that a random field may be a result of slowly appearing FE interaction. A broad humplike feature below T_{max} in the ϵ' - T curves for oxygenated SCT samples has been observed for nearly all the compositions. This hump also shows a narrow hysteresis, whose area increases with Ca content. The presence of hysteresis in the broad ϵ' - T feature is rather clear for $x=0.38$. For $x=0.40$, this has been masked by the abrupt increase of the hysteresis width of the AFE transition.

Thus, we conclude that simple calcinations followed by sintering, produce SCT ceramics, which have structurally all the signatures of a good sample, but it is only after a proper oxygenation that the correct phases of SCT with reproducible dielectric properties are formed. Following this process, we have prepared SCT ceramics exhibiting reproducible and systematic effects of Ca substitution on its dielectric properties so that we could detect the occurrence of a different competing interaction between AFE and FE for $x>0.38$.

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