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Structure–microwave property relations in $(Sr_xCa_{(1-x)})_{n+1}Ti_nO_{3n+1}$

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Abstract

The microwave dielectric properties of the $(Sr_xCa_{(1-x)})_{n+1}Ti_nO_{3n+1}$ series have been measured. When $n=\infty$, a linear decrease in TCF from +1647 ($SrTiO_3$) to 859 ($CaTiO_3$) MK^{-1} was observed as Ca content increased. This trend in TCF was attributed to the onset of octahedral tilt transitions brought about by decreasing tolerance factor. Additions of excess SrO to $SrTiO_3$ formed the $Sr_{n+1}Ti_nO_{3n+1}$ series with Q a maximum for $Sr_3Ti_2O_7$. Ca substitutions to $Sr_3Ti_2O_7$ resulted in a solid solution limited to the Sr and Ca rich ends of the $(Sr_xCa_{1-x})_3Ti_2O_7$ series with Q a maximum of 10 250 at 2.5 GHz for $Sr_{2.4}Ca_{0.6}Ti_2O_7$ and TCF a minimum of 50 MK^{-1} for $Ca_3Ti_2O_7$. The variation of TCF for the $(Sr_xCa_{1-x})_3Ti_2O_7$ series was also attributed to the onset of octahedral tilt transitions.

Keywords: Alkaline earth oxides; Dielectric properties; Electron microscopy; Perovskites; X-ray methods

1. Introduction

Commercial microwave dielectrics with dielectric constants (ε_r) from 30 to 45, quality factors (Q) > 20 000 at 1 GHz and temperature coefficients of dielectric constant (TCF) ±5 MK^{-1} are currently fabricated from perovskite-structured Ca and Sr titanate doped with lanthanide aluminates. However, little attention has been paid to the properties of the $Sr_xCa_{1-x}TiO_3$ solid solution and even less to the effect of AO (SrO/CaO) excess.

The following sequence of transitions has recently been suggested for $Sr_xCa_{1-x}TiO_3$: $Pm\bar{3}m$ $1 \geqslant x \geqslant 0.95$–0.92, 14/mcm $0.92 \geqslant x \geqslant 0.65$, Bmmb $0.6 \geqslant x \geqslant 0.45$ and Pbnm $x < 0.4$.[1,2] The order parameter for these phase transitions is the amplitude of rotation (tilting) of the oxygen octahedra and the symmetries of the crystal structures can be predicted according to Glazer.[3]

Additions of excess SrO to $SrTiO_3$ form a homologous series with the general formula $Sr_{n+1}Ti_nO_{3n+1}$ (n indicates the number of layers of $SrTiO_3$) and are known as Ruddlesden–Popper (RP) phases.[4,5] RP phases consist of SrO layers, which separate and shear by 1/2 [111] $SrTiO_3$ perovskite blocks. The phases Sr_2TiO_4, $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$ have been reported, but the latter requires long heat treatments at high temperatures to form a single phase.[6] Ceh and Kolar[7] observed that excess CaO additions to $CaTiO_3$ also formed a homologous series with the general formula $Ca_{n+1}Ti_nO_{3n+1}$. The $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$ compounds have been reported, but Elcombe et al.[8] demonstrated that the Ca_2TiO_4 phase could not form.

Tolerance factor (t), given by Eq. (1) where R_A, R_B, and R_O are the radii of the A-, B-site and O^{-2}-ions, respectively, is a measure of the stability of the perovskite phase,

$$t = (R_A + R_O)/\sqrt{2}(R_B + R_O) \quad (1)$$

Compounds with $t > 0.98$ are untilted whereas compounds with $t < 0.98$ have undergone at least one octahedral tilt transition on cooling.[9] Sr based RP phases are tetragonal whereas the Ca analogues are orthorhombic. The orthorhombic distortion arises because of an octahedral tilt transition driven by the low t of the perovskite blocks. Reaney et al.[9] demonstrated the relationship of t with temperature coefficient of dielectric constant, TCε, (TC$\varepsilon = -2$(TCF + α_L) where α_L is the linear thermal expansion coefficient) for Sr and Ba based complex perovskites. Decreasing t from 1.01 to 0.98 in complex

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perovskites will induce octahedral tilt transitions and force TCF/TCε towards zero, an important industrial criterion for a dielectric resonator.

The aim of this paper is to relate the microwave dielectric properties of the $Sr_xCa_{1-x}TiO_3$, $Sr_{n+1}Ti_nO_{3n+1}$ and $(Sr_xCa_{1-x})_3Ti_2O_7$ series to changes in crystal structure determined using X-ray diffraction (XRD) and transmission electron microscopy (TEM).

2. Experimental

High purity (>99.95%) $SrCO_3$, $CaCO_3$ and TiO_2 powders were processed using the conventional mixed oxide route to form compounds in the $Sr_xCa_{1-x}TiO_3$, $Sr_{n+1}Ti_nO_{3n+1}$ and $(Sr_xCa_{1-x})_3Ti_2O_7$ series. Starting mixtures were wet milled for 16 h, calcined (double calcined for higher Ca content) for 4 h at 1150–1350°C in air and re-milled in propan-2-ol with 2 wt.% PEG binder. Twenty millimetre diameter pellets were uniaxially pressed at 110 MPa into discs and sintered for 4 h at various temperatures in air until the highest density was achieved. A Philips X-ray diffractometer was used to characterise the phases formed and a Jeol 3010 TEM was used to verify the phase assemblage of each sample and examine the stacking sequences of these compounds. Microwave measurements were performed using an aluminium cavity ~4 times the diameter of the test resonator, (this ensured an "isolated" but shielded resonator) and a vector network analyser operating in the $TE_{01\delta}$ resonance mode in reflectance.

3. Results and discussion

3.1. X-ray diffraction (XRD)

XRD patterns for the $Sr_xCa_{1-x}TiO_3$ series are shown in Fig. 1a. The following sequence of phase transitions was observed as a function of composition: $x=1$ ($SrTiO_3$) cubic $Pm\bar{3}m$, $x=0.8$ tetragonal I4/mcm, $x=0.5$ orthorhombic Bmmb/Pbnm, $0.4 \geqslant x \geqslant 0$ ($CaTiO_3$) orthorhombic Pbnm.

These results, are in agreement with Qin et al.[2] who also suggested that I4/mcm symmetry does not persist in the $Sr_{0.5}Ca_{0.5}TiO_3$ phase. However, it is unclear whether the compound has transformed to Bmmb or Pbnm. XRD from a conventional source could not reveal some of the weak superlattice reflections characteristic of Bmmb observed by Ball et al.[1] using synchrotron radiation. $Sr_{0.5}Ca_{0.5}TiO_3$ is, however, close to the Bmmb/Pbnm phase boundary[1] and hence phases may coexist.

Fig. 1b shows XRD traces obtained for members of the $Sr_{n+1}Ti_nO_{3n+1}$ series. $Sr_3Ti_2O_7$ appears in all samples as either the major ($n \geqslant 2$) or as a second phase ($n=1$). Ab initio calculations by Udayakumar and Cormack[10] have

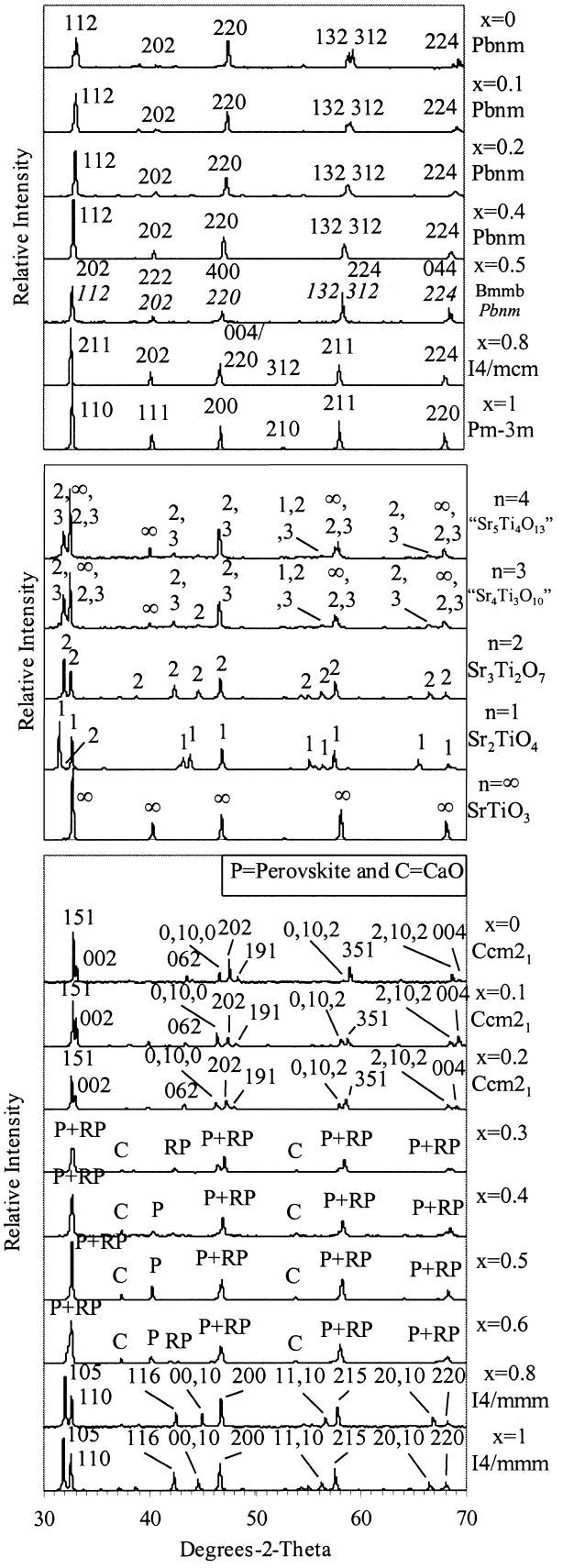

Fig. 1. XRD of the (a) $Sr_xCa_{1-x}TiO_3$, (b) $Sr_{n+1}Ti_nO_{3n+1}$ and (c) $(Sr_xCa_{1-x})_3Ti_2O_7$ series.

suggested that $Sr_3Ti_2O_7$ is the most stable of the RP compounds in agreement with the above observations.

Fig. 1c shows the XRD patterns from the $(Sr_xCa_{1-x})_3Ti_2O_7$ series. Compositions where $x=1$ and 0.8 may be indexed as tetragonal I4/mmm, consistent with the presence of an RP phase whereas $x=0.6$, 0.5, 0.4 and 0.3 are mixtures of perovskite, CaO and RP compounds. Samples where $x=0.2$, 0.1 and 0 could be indexed as orthorhombic $Ccm2_1$, consistent with the presence of a distorted RP phase.

3.2. Transmission electron microscopy (TEM)

Fig. 2 is a bright-field image of a planar defect in a grain of $Ca_3Ti_2O_7$; in the inserted electron diffraction patterns the electron beam is aligned parallel with the pseudotetragonal (a) [110] and (b) [$\bar{1}$10] directions (c is the long axis). These two directions are identical in $Sr_3Ti_2O_7$ [11] but in the Ca analogue a systematic row of superlattice reflections is observed in the [110] but not in [$\bar{1}$10] direction. Reaney et al.[9] have shown that these reflections arise from antiphase rotations of oxygen octahedra around the *c* (long) axis. Moving across the defect results in the appearance and disappearance of the superlattice reflections, identifying it as an orientation domain wall. The presence of superstructure arising from octahedral tilting is consistent with structural refinements of this compound.[8]

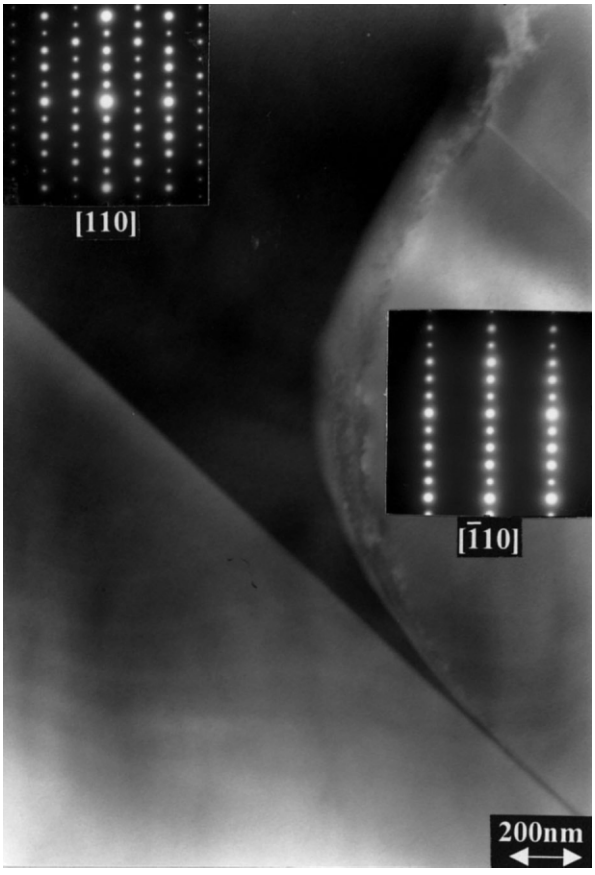

Fig. 2. Planar fault in $Ca_3Ti_2O_7$ with inserted [110] and [$\bar{1}$10] electron diffraction patterns.

3.3. Microwave dielectric properties

Table 1 shows Q, ε_r and TCF for the $Sr_xCa_{1-x}TiO_3$, $Sr_{n+1}Ti_nO_{3n+1}$ and $(Sr_xCa_{1-x})_3Ti_2O_7$ series. The converted TCε data of the single phase members of the $Sr_xCa_{1-x}TiO_3$ and $(Sr_xCa_{1-x})_3Ti_2O_7$ series, of this study, are compared with the tolerance factor curve of Reaney et al.[9], for Sr and Ba based complex perovskites, in Fig. 3.

These two systems undergo octahedral tilt transitions upon the substitution of Ca for Sr. Furthermore, TCε increases in a manner consistent with the results of Reaney et al.[9] For $Sr_xCa_{1-x}TiO_3$, the increment is from -3294 to -1718 MK^{-1} and for $(Sr_xCa_{1-x})_3Ti_2O_7$ from -718 to -100 MK^{-1}. The trend is the same in each case but the magnitude of TCε is different. As there is essentially little change in dielectric constant between the end members of each series, it is proposed that the main mechanism for tuning TCε is tilting of the octahedra.

Members of the $Sr_{n+1}Ti_nO_{3n+1}$ series can all be described by the same tetragonal space group, I4/mmm, so there are no rotations of octahedra or changes in t of the perovskite blocks as excess SrO is added. Table 1 reveals a decreased TCF as the amount of excess SrO increases. As SrO content increases the average ionic polarisability decreases, decreasing ε_r and TCε and therefore TCF.[11]

The values of Q throughout all the series are more difficult to interpret than TCF/TCε and ε_r. There are few systematic changes but Sr rich compositions where $n=2$ seem to show highest values. This phase has been

Table 1
Microwave dielectric properties of the $Sr_{n+1}Ti_nO_{3n+1}$ series

	Q	fo/GHz	ε_r	TCF/MK^{-1}
$Sr_xCa_{1-x}TiO_3$				
$SrTiO_3$[a]	2460	1.22	190	1647
$x=0.8$	2446	1.62	145	1534
$x=0.5$	3300	1.25	236	1234
$x=0.4$	5700	1.26	218	1164
$x=0.2$	6100	1.36	181	991
$x=0.1$	5900	1.41	170	931
$x=0$	8700	1.49	162	859
$Sr_{n+1}Ti_nO_{3n+1}$				
$n=1$	2616	3.14	37.4	137
$Sr_3Ti_2O_7$[b]	7450	2.53	57.9	317
$n=3$	5700	2.23	76.1	576
n=4	2030	1.95	99.8	801
$(Sr_xCa_{1-x})_3Ti_2O_7$				
$x=0.8$	10250	2.51	58	359
$x=0.2$	1070	2.46	60	232
$x=0.1$	1197	2.52	56	141
$x=0$	970	2.69	46	50

[a] $SrTiO_3$ is also the $n=\infty$ member of $Sr_{n+1}Ti_nO_{3n+1}$.
[b] $Sr_3Ti_2O_7$ is also the $x=1$ member of $(Sr_xCa_{1-x})_3Ti_2O_7$.

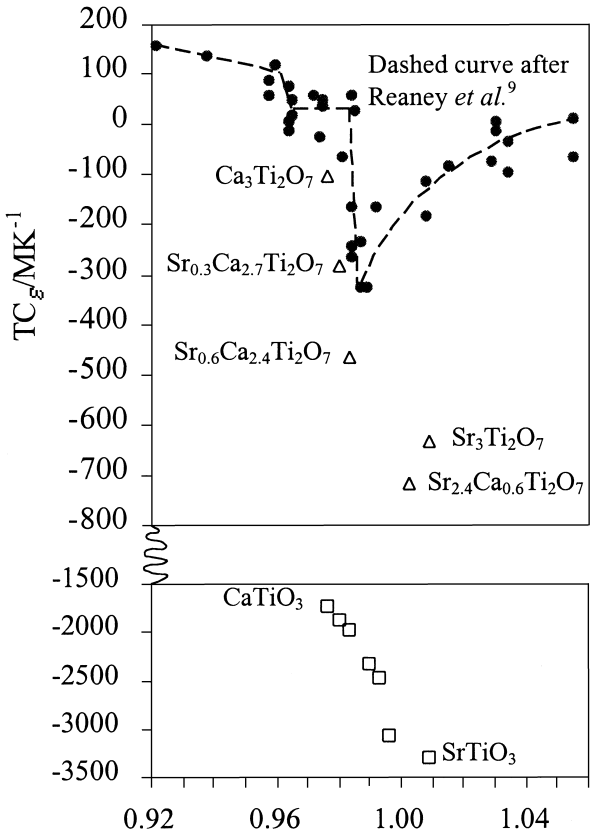

Fig. 3. TCε compared with the tolerance factor curve after Reaney et al.[9] for the $Sr_xCa_{1-x}TiO_3$ and $Sr_xCa_{3-x}Ti_2O_7$ series.

shown by ab initio calculation to be energetically the most stable.[10]

4. Conclusion

Changes in TCF/TCε in the $Sr_xCa_{1-x}TiO_3$ and $(Sr_xCa_{1-x})_3Ti_2O_7$ can be attributed to the onset of octahedral tilt transitions induced by decreasing tolerance factor. For the $Sr_{n+1}Ti_nO_{3n+1}$ series, TCF decreases with ε_r, implying that dilution of the average ionic polarisability is the mechanism for tuning. The largest Q values were reported for Sr rich members of $(Sr_xCa_{1-x})_3Ti_2O_7$ with $x=1$ (7450 at 2.5 GHz) and 0.8 (10250 at 2.5 GHz).

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