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The ferroelectric Curie temperature T_C in $ATiO_3$ perovskites is shown to increase linearly with the size variance of the A-site cation mixture [A = (Ba, Sr, Ca)] and this effect accounts for the unusual T_C variation in the $Ba_{1-x}Ca_xTiO_3$ system.

$BaTiO_3$ is a ferroelectric perovskite widely used in capacitors, thermistors and piezoelectric devices. The Curie temperature above which $BaTiO_3$ changes from being tetragonal and ferroelectric to cubic and paraelectric is T_C = 403 K.[1] The ferroelectricity arises from displacements of the Ti atoms towards one of the octahedrally coordinating oxygen atoms along the c-axis. A complete solubility exists between $BaTiO_3$ and $SrTiO_3$, and T_C decreases across the series to a value of 110 K for $SrTiO_3$.[2] This trend was ascribed to a cation size effect, in which the smaller Sr ion causes a reduction in the average radius of the A cation site and stabilises the cubic $ATiO_3$ structure to lower temperatures. By contrast, in the $Ba_{1-x}Ca_xTiO_3$ system, T_C rises from 403 K to a maximum value of 410 K at x = 0.08 before dropping to 391 K at the solid solution limit of x = 0.24.[3] This variation is not consistent with the above size effect.

It has recently been shown that the electronic and structural phase transition temperatures of several perovskite-type materials vary with the mean size and the size mismatch of the cations on the A-site.[4,5] Size is parameterised by the mean A-cation radius, $<r_A>$, and A-site size mismatch is described by the statistical variance in the distribution of the radii, σ^2:

$$\sigma^2 = <r_A^2> - <r_A>^2$$

σ^2 is defined for a mixture of many cations, but in a binary system such as A = ($Ba_{1-x}M_x$), it reduces to:

$$\sigma^2 = x(1 - x)(r_{Ba} - r_M)^2$$

and hence σ^2 varies quadratically with x. At a constant $<r_A>$, the temperatures of the ferromagnetic metal to paramagnetic insulator transition in $AMnO_3$ perovskites (at which colossal magnetoresistances are observed),[6] and the superconducting critical transitions in A_2CuO_4 and ABa_2CuO_7 decrease linearly with increasing σ^2.[5,7] However, the orthorhombic–tetragonal structural transition in the A_2CuO_4 materials shows a strong linear increase with σ^2.[5] Here, we present the first systematic study of the influence of A site disorder on the properties of $BaTiO_3$-based ferroelectric perovskites.

Six (Ba, Sr, Ca)TiO₃ compositions (Table 1) were chosen to give a constant $<r_A>$ = 1.454 Å but variable σ^2. $<r_A>$ and σ^2 were calculated using standard values of nine-coordinate ionic radii.[8] 10 g samples were prepared by mixing appropriate quantities of $BaCO_3$, $SrCO_3$, $CaCO_3$ and TiO_2 (all 99.99+% pure) which were ground in an agate mortar and pestle with acetone for 15 min, fired in Pt foil boats at 1000 °C for 12 h, then reground for 15 min before refiring at 1200 and 1350 °C. Regrinding and refiring at 1350 °C for 12 h was repeated six times. The powders were milled in a planetary ball mill for 5 min rather than a mortar and pestle for the final three cycles. This lengthy preparative procedure was necessary as it is known to be difficult to homogenise low levels of alkaline earth dopants in $BaTiO_3$ powders.[9]

Table 1 Starting and EPMA analysed compositions for six $(Ba_{0.90+0.45x}Sr_{0.1-x}Ca_{0.55x})TiO_3$ samples and their A site cation size variances

Starting composition	Analysed formula[a]	σ^2/Å²
$Ba_{0.900}Sr_{0.100}TiO_3$	$Ba_{0.91(3)}Sr_{0.09(3)}Ti_{1.0(4)}O_3$	0.0023
$Ba_{0.909}Sr_{0.080}Ca_{0.011}TiO_3$	$Ba_{0.90(2)}Sr_{0.09(2)}Ca_{0.01(2)}Ti_{1.02(2)}O_3$	0.0028
$Ba_{0.918}Sr_{0.060}Ca_{0.022}TiO_3$	$Ba_{0.92(1)}Sr_{0.06(1)}Ca_{0.02(1)}Ti_{1.02(2)}O_3$	0.0032
$Ba_{0.927}Sr_{0.040}Ca_{0.033}TiO_3$	$Ba_{0.93(1)}Sr_{0.04(1)}Ca_{0.03(1)}Ti_{1.02(2)}O_3$	0.0037
$Ba_{0.936}Sr_{0.020}Ca_{0.044}TiO_3$	$Ba_{0.94(1)}Sr_{0.02(1)}Ca_{0.04(1)}Ti_{1.02(2)}O_3$	0.0041
$Ba_{0.945}Ca_{0.055}TiO_3$	$Ba_{0.95(1)}Ca_{0.05(1)}Ti_{1.03(1)}O_3$	0.0047

[a] Formulae were calculated by normalising to Ba + Sr + Ca = 1.

The samples were characterised by electron probe microanalysis (EPMA), using a Cameca SX51 microprobe, and powder X-ray diffraction on a Stoe STADI/P diffractometer. The $L\alpha$ line of Ba and the $K\alpha$ line of Sr, Ti and Ca were used for the cation analysis, by employing calibration standards of $BaTiSi_3O_9$, $SrTiO_3$ and $CaSiO_3$ and the oxygen contents were calculated by difference. The EPMA showed the samples to be homogeneous with compositions consistent with the starting formulae (Table 1). The room temperature diffraction patterns were obtained with monochromated Cu-Kα_1 radiation and were all fully indexed in the tetragonal space group $P4mm$. A linear variation of lattice parameters with σ^2 is observed (Fig. 1), however, the cell volumes for all samples (64.10 ± 0.09 Å³) were the same within error and showed no significant variation with σ^2.

The ferroelectric Curie temperatures, T_C, were found from permittivity and calorimetric measurements. Pellets for the permittivity experiments were cold pressed and fired overnight at 1350 °C in air. Impedance was measured between 25 and 180 °C over the frequency range 10–10⁷ Hz with an applied voltage of 100 mV using a 4192 Hewlett Packard impedance analyser. Data obtained at fixed frequency of 1 kHz showed sharp permittivity vs. temperature profiles for all the samples, with no apparent broadening of the ferroelectric transition, T_C values were extracted from the permittivity maximum obtained
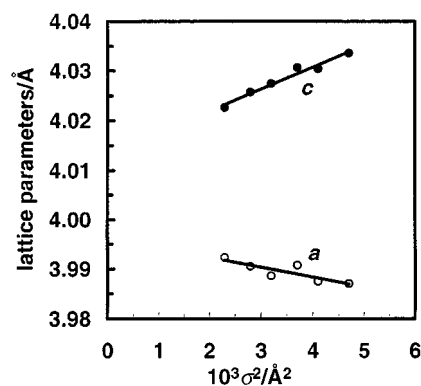

Fig. 1 Variation in the tetragonal lattice parameters of the $ATiO_3$ samples with σ^2 at 300 K.

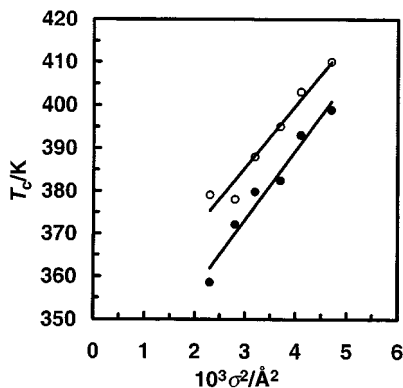*Chem. Commun.*, 1999, 1497–1498 **1497**

Fig. 2 Variation in T_C with σ^2. Open and filled circles correspond to data obtained from permittivity and DSC measurements, respectively.

on a heating cycle. Such values are dependent on the thermal history of the sample, as BaTiO$_3$-based materials show hysteresis on thermal cycling, so calorimetric measurements were used to confirm the T_C variation. Powdered samples were thermally cycled between 0 and 180 °C in a Polymers Lab differential scanning calorimeter at a heating rate of 10 °C min^{-1} and T_C values were extracted from the peak maximum associated with the endotherm in the cooling cycle. The two sets of T_C values are plotted vs. σ^2 in Fig. 2. A detailed analysis of the microstructure and electrical properties of the samples, which are sensitive to microstructural effects such as grain size and pellet density,[9] will be reported elsewhere.

The two sets of T_C values both show a strong linear increase with increasing A-cation size variance, σ^2, although the calorimetric values are systematically lower than those obtained from permittivity measurements. Linear fits to the permittivity and DSC results give slopes of $dT_C/d\sigma^2$ = 14500(400) and 16000(300) K Å^{-2}, and T_C^0 values (by extrapolation to $\sigma^2 = 0$) of 341(3) and 325(3) K, respectively, with fitting errors in parentheses. To estimate the contribution of cation size disorder to T_C in the Ba$_{1-x}$Ca$_x$Ca$_x$TiO$_3$ series, the reported T_C values are shown together with disorder-corrected T_C^0 values in Fig. 3. These were calculated in the first approximation by extrapolating from T_C to $\sigma^2 = 0$ assuming a constant $dT_C/d\sigma^2$ = 15 000 K Å^{-2}, although a slight variation in $dT_C/d\sigma^2$ is expected across the series by comparison with other systems.[4] The resulting T_C^0 values show a near-linear fall with x comparable to the behaviour of T_C in the Ba$_{1-x}$Sr$_x$TiO$_3$ series.[2]

These results show that the ferroelectric transition temperature in doped BaTiO$_3$ materials is strongly influenced by
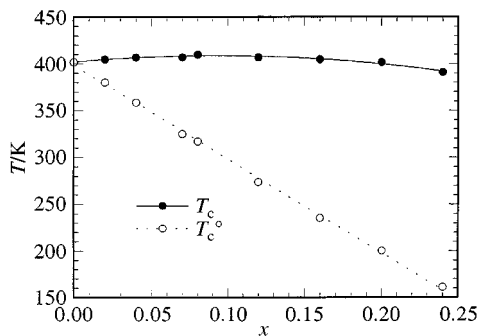
both the average A cation size $<r_A>$ and the size variance σ^2. These effects initially oppose one another in substituted (Ba$_{1-x}$M$_x$)TiO$_3$ series where Ba is replaced by smaller M = Sr or Ca cations. As x increases, the decreasing $<r_A>$ reduces T_c but the increasing σ^2 raises T_C. The former reduction is essentially linear with $<r_A>$, as evidenced by the T_C^0 variation in Fig. 3, in apparent contrast to the size dependence of the previously studied electronic transitions, which decrease quadratically with $<r_A>$.[4,6] The linear increase of T_C with σ^2 is in keeping with the observed variation of the structural transition in A$_2$CuO$_4$ materials. Reducing $<r_A>$ in the ATiO$_3$ perovskites leads to tilts and rotations of the TiO$_6$ octahedra that destabilise the ferroelectrically ordered phase, whereas the local disorder associated with increasing σ^2 enables the ferroelectric distortions in the TiO$_3$ network to occur more easily and thereby stabilises the ferroelectric phase. This is supported by the data in Fig. 1, which show a divergence of the tetragonal a and c parameters as σ^2 increases.

The observed $dT_C/d\sigma^2 \approx 15\,000$ K Å^{-2} in our ATiO$_3$ series is smaller than the value of $\approx 50\,000$ K Å^{-2} found for the A$_2$CuO$_4$ structural transition,[5] which involves rotations but not distortions of the CuO$_6$ octahedra. However, $dT_C/d\sigma^2$ is comparable to the reported magnitudes of $\approx 20\,000$ K Å^{-2} for the metal–insulator transition in AMnO$_3$ perovskites.[4,6] This is accompanied by the formation of Jahn–Teller distortions of the MnO$_6$ octahedra *above* the transition,[10] whereas Ti displacements of comparable magnitude occur within the TiO$_6$ octahedra *below* the ferroelectric transition in ATiO$_3$ materials. Hence, the magnitude of $dT_C/d\sigma^2$ appears to be related to the degree of structural distortion occurring at the transition.

In conclusion, the ferroelectric–paraelectric transition temperature of ATiO$_3$ materials shows a strong linear increase with A-cation size variance. The σ^2 effect opposes the influence of the average A cation size and may be useful in stabilising ferroelectric phases to higher temperatures. In the (Ba$_{1-x}$Sr$_x$)-TiO$_3$ series, the size effect dominates, so T_C falls with increasing x. However, Fig. 3 shows that the much greater σ^2 contribution in the (Ba$_{1-x}$Ca$_x$)TiO$_3$ series effectively cancels out the $<r_A>$ effect, leading to almost constant T_C values up to the observed maximum $x = 0.24$.

Fig. 3 The variation of T_C (from ref. 3) and the disorder corrected T_C^0 in the (Ba$_{1-x}$Ca$_x$)TiO$_3$ series.

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