Effect of ionic radii on the Curie temperature in Ba$_{1-x-y}$Sr$_x$Ca$_y$TiO$_3$ compounds

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A series of Ba$_{1-x-y}$Sr$_x$Ca$_y$TiO$_3$ compounds were prepared with varying average ionic radii and cation disorder on A-site. All samples showed typical ferroelectric behavior. A simple empirical equation correlated Curie temperature, $T_C$, with the values of ionic radii of A-site cations. This correlation was related to the distortion of TiO$_6$ octahedra observed during neutron diffraction studies. The equation was used for the selection of compounds with predetermined values of $T_C$. The effects of A-site ionic radii on the temperatures of phase transitions in Ba$_{1-x-y}$Sr$_x$Ca$_y$TiO$_3$ were discussed.

Perovskites with the general formula: Ba$_{1-x}$Sr$_x$TiO$_3$ (BSCT) show enhancement of several properties (e.g. dielectric, piezoelectric\cite{1}, electrocaloric\cite{2} response) in the vicinity of Curie temperature, $T_C$, where a cubic to tetragonal phase transition occurs and could be strong contenders for Pb-free ferroelectric materials\cite{3}. As a result, the ability to optimize chemical composition of BSCT compounds in order to shift $T_C$ to the desired operating temperature range is important from a practical point of view. Several decades of research have established some of the key parameters that influence the $T_C$ in perovskites: chemical composition of A- and B-sites in ABO$_3$ perovskites\cite{4}, A to B nonstoichiometry ratio\cite{5}, average mass of A-site ions\cite{6}, O$_{18}$/O$_{16}$ isotope ratio\cite{7}, grain size\cite{8}, annealing temperature\cite{9}, hydrostatic pressure\cite{10}, strain in thin film\cite{11}. Nevertheless there is still a lack of simple guidelines for the selection of the materials compositions with predetermined value of $T_C$.

The average ionic radius, $\langle r_{\text{A-site}} \rangle$, of A-site ions has a strong effect on the $T_C$ especially in Ba$_{1-x}$Sr$_x$TiO$_3$ compounds where $T_C$ decreases linearly with Sr doping. This decrease is usually explained by the substitution of Ba ions by smaller Sr ions resulting in the observed linear decrease of the $T_C$ with lattice parameter in Ba$_{1-x}$Sr$_x$TiO$_3$ ($a$ or $\sqrt{2}a$ for cubic or tetragonal phases, respectively)\cite{6}. Similarly, the decrease $T_C$ with applied hydrostatic pressure\cite{12} was explained by the pressure induced decrease of the unit cell volume\cite{14}.

Another parameter affecting $T_C$ is the A-site cation disorder which can be quantified by variance, $\sigma^2$, as follows\cite{15}

$$\sigma^2 = \sum y_i r_i^2 - \langle r_{\text{A-site}} \rangle^2 \quad (1)$$

where $r_i$ and $y_i$—ionic radii and occupancy of A-site of element $i$, respectively. The linear increase of the $T_C$ with $\sigma^2$ in BSCT has been observed when the average ionic radius was kept constant\cite{16}. In other perovskite or perovskite related structures, the increase of $\sigma^2$ was shown to decrease the metal-insulator transition temperature in manganites\cite{15} and decrease critical current in YBCO-type superconductors\cite{17}. In this work we evaluated the effects of average ionic radius (ionic radii in 12 fold coordination were used\cite{18}) and ionic radii variance of A-site ions in the perovskite lattice on the phase transitions in BSCT compounds.

A series of compounds (see Table 1) were prepared by a conventional solid-state reaction synthesis with starting chemicals BaCO$_3$ (Alfa Aesar, 99.95%), CaCO$_3$ (Alfa Aesar, 99.95%), SrCO$_3$ (Alfa Aesar, 99.99%) and TiO$_2$ (PI-KEM Ltd., 99.9%) calcined at 1300°C for 10h. Three series of compounds were prepared: series A where $\langle r_{\text{A-site}} \rangle$ was fixed at 1.551 Å and $\sigma^2$ was varied from 0.0066 to 0.0125 Å$^2$, series B where both $\langle r_{\text{A-site}} \rangle$ and $\sigma^2$ were varied, series C where both $\langle r_{\text{A-site}} \rangle$ and $\sigma^2$ were varied in order to maintain constant $T_C$ as described below. Chemical composition was confirmed by ICP-OES analysis (DV 200 OES, Perkin Elmer). XRD (XPERT MPD, PANalytical) showed that all specimens were single phase tetragonal perovskites (4 mm s.g.) at room temperature except for Ba$_{0.78}$Ca$_{0.22}$TiO$_3$ where a weak peak belonging to CaTiO$_3$ was observed (see Supplementary Fig. S1). This composition is close to the temperature dependent Ca solubility limit of 16% at 1300°C\cite{19}, 25% at 1430°C\cite{20}.

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and 1549 °C. A good agreement between the values of the lattice parameters of Ba1-xSrTiO3 with those reported in the literature was observed. For the series A the increase of variance resulted in a slight decrease of the a lattice parameter and increase of the c lattice parameter whereas the c/a ratio showed an increase. Dense pellets (>92% dense) were prepared by sintering at 1450 °C. The average grain size was 30–65 μm as observed by SEM (JSM 6400, JEOL) and shown in Supplementary Fig. S2. DSC measurements (DSC200 F3, Netzch) during 5 K/min heating showed well defined peaks at TR-O, TO-T and TC which correspond to consecutive phase transitions during heating from rhombohedral (3m) to orthorhombic (mm2) to tetragonal (4mm) and, finally, to cubic (m3m) structures, respectively (see Supplementary Fig. S3 and Supplementary Table S4).

The dielectric properties were evaluated by HP 4263B LCR with 0.3 V/mm ac signal at 0.1–100 kHz. The thermal hysteresis observed between heating and cooling runs was less than 3 K. Dielectric permittivity, $\varepsilon_r$, peaked at $T_C$ and showed humps at $T_{R-O}$ and $T_{O-T}$ (Fig. 1). No frequency dependence of $\varepsilon_r$ was observed. The tanδ showed clear peaks positioned slightly below (by less than 10 K) the temperatures of the corresponding phase transitions. The estimated error in the determination of temperatures of phase transitions is 1.5 K and a good agreement was observed between the values of $T_R$, $T_{R-O}$ and $T_{O-T}$ determined from DSC and LCR measurements. Both $T_{R-O}$ and $T_{O-T}$ decreased with Ca doping and no $T_{R-O}$ and $T_{O-T}$ were observed in the samples with more than 20 and 15% of Ca doping, respectively, in agreement with the literature. $T_C$ increases linearly with the tetragonal distortions in the lattice (expressed as c/a ratio) regardless of the chemical composition of samples (Supplementary Fig. S5). The $\varepsilon_r$ data located 10–20 K above $T_C$ were fitted to the Curie-Weiss law (Table 2). The value of $T_C$ determined from the fitting, was smaller than $T_C$ suggesting a first order phase transition in all studied samples.

It has been shown that the increase of cation disorder results in the formation of relaxor type behavior. As a result a modified Curie-Weiss law was used to fit the data

| Composition | $\langle r_{rளr} \rangle$ (Å) | $\delta^2$ (Å²) | $a$ (Å) | $c$ (Å) | c/a |
|-------------|------------------------|-------------|--------|--------|-----|
| Series A    |                        |             |        |        |     |
| Ba0.65Sr0.35TiO3 | 1.5505              | 0.0066     | 3.9657(1) | 3.9739(1) | 1.0021 |
| Ba0.69Sr0.24Ca0.07TiO3 | 1.5505              | 0.0085     | 3.9655(4) | 3.9831(8) | 1.0044 |
| Ba0.74Sr0.12Ca0.15TiO3 | 1.5506              | 0.0105     | 3.9633(6) | 3.9938(8) | 1.0077 |
| Ba0.78Ca0.22TiO3 | 1.5506              | 0.0125     | 3.9631(7) | 4.0066(9) | 1.0110 |
| Series B    |                        |             |        |        |     |
| Ba0.65Sr0.35TiO3 | 1.5760              | 0.0046     | 3.9804(1) | 4.0045(4) | 1.0061 |
| Ba0.69Sr0.24Ca0.07TiO3 | 1.5220              | 0.0126     | 3.9500(1) | 3.9640(5) | 1.0036 |
| Ba0.74Sr0.12Ca0.15TiO3 | 1.5830              | 0.0066     | 3.9784(1) | 4.0236(1) | 1.0114 |
| Ba0.78Ca0.22TiO3 | 1.5795              | 0.0056     | 3.9783(2) | 4.0149(2) | 1.0089 |
| Series C    |                        |             |        |        |     |
| Ba0.65Sr0.35TiO3 | 1.5559              | 0.0063     | 3.9688(1) | 3.9795(3) | 1.0027 |
| Ba0.62Sr0.28Ca0.1TiO3 | 1.5359              | 0.0098     | 3.9580(1) | 3.9683(4) | 1.0026 |

Table 1. Crystalllographic parameters of studied samples.

![Figure 1. Temperature dependence of permittivity and loss tangent of Ba0.69Sr0.24Ca0.07TiO3 at 0.1, 1, 10 and 100 kHz. Measurements were performed during 1 K min⁻¹ heating. Inset shows temperatures of phase transitions in BSCT compounds (series A) as a function of $\sigma^2$.](image-url)
As iteA site

no shift of Ti ions from the centrosymmetric positions were possible (Fig. 2(a)). An increase of

σ
introduction of larger A-site ions (respectively. An empirical hard sphere ionic model has been proposed 28 where the increase in

atom-atom distance (distance between non-distorted tetragonal and cubic phases). The linear increase of the

TC, suggested 4 site distribution of Ti ions in tetragonal and 8 site distribution in cubic phases with the site

distribution (Fig. 2(b)) or an increase of

ε
function was observed in a large number of manganites 28 .

0

ε
0

TT-O

and

TR-O

showed a monotonic decrease with

σ
Recently a combined effect of the average ionic radii and cation variance on the phase transition temperature

in perovskite (alkaline earth doped rare earth manganites) and perovskite related (cuprate superconductors)

compounds was proposed 27 . For example, a linear decrease of the metal-insulator transition temperature with the

in alkaline earth doped manganites and perovskite superconductors 27 , 33 , 34 , 35 , 36 , 37 . Additionally, it has been shown that the temperature splitting (see inset Fig. 1), shown to be a function of

δ
A

and (assuming

1/2(2τA-site + 2τO))2 ≡ σ2

for the former (Fig. 2(b)) and later (Fig. 2(c)) cases, respectively. It has been shown both empirically 31 and theo-

retically 32,33 that

Tc

depends on the atomic displacement of B-site cations, d, as

Tc ≈ d2.

A

A

 tackle distortions caused by ion size mismatch relieved not by BO\textsubscript{6} octahedra tilting but by shifting of oxygen ions leading to the distortion of BO\textsubscript{6} octahedra 29 . In the model the ferroelectricity was assumed to be caused by the shift of Ti ions in the direction of equatorial oxygen in TiO\textsubscript{6} octahedra however the results of local-structure refinements in Sr doped BaTiO\textsubscript{3} suggested 4 site distribution of Ti ions in tetragonal and 8 site distribution in cubic phases with the site splitting of ≈ 0.2 Å 29,30 . In the ideal non-distorted cubic perovskite (t = 1) Ti and O ions were closely packed and no shift of Ti ions from the centrosymmetric positions were possible (Fig. 2(a)). An increase of

< rB-site >

by the introduction of larger A-site ions (σ\textsuperscript{2} = 0 Fig. 2(b)) or an increase of σ\textsuperscript{2} by the introduction of cation disorder

< rA-site >

was likely to enlarge TiO\textsubscript{6} octahedra and allowed Ti ions to shift from the centrosymmetric position at

T < Tc by the distance d. From the geometrical considerations:

\[ d^2 = \frac{1}{2} (\langle r_{A-site} \rangle - \tau_{A-site})^2 \]

and

\[ d^2 \approx \frac{1}{4} \sigma^2 \]

for the former (Fig. 2(b)) and later (Fig. 2(c)) cases, respectively. It has been shown both empirically 31 and theo-

retically 32,33 that

Tc depends on the atomic displacement of B-site cations, d, as

Tc ≈ d^2.

As a result an increase of the

Tc with both

\[ \langle r_{A-site} \rangle - \tau_{A-site} \]

and

\[ \sigma^2 \]

was expected. However a poor correlation of values of

Tc with

\[ \sigma^2 + (\langle r_{A-site} \rangle - \tau_{A-site})^2 \]

function was observed for the samples studied in this work (Supplementary Fig. S6) presumably due to the assumptions used in the suggested simple model (spherical

| Composition | \( T_{BO} (K) \) | \( T_{TO} (K) \) | \( T_C (K) \) | \( \delta_{rr} \) | \( T_2 (K) \) | \( \gamma \) |
|-------------|-----------------|-----------------|-----------------|--------------|-----------------|--------------|
| Series A    |                 |                 |                 |              |                 |              |
| Ba\textsubscript{0.65}Sr\textsubscript{0.35}TiO\textsubscript{3} | 174             | 222             | 294             | 2566         | 271             | 1.09         |
| Ba\textsubscript{0.62}Sr\textsubscript{0.28}Ca\textsubscript{0.1}TiO\textsubscript{3} | 146             | 208             | 328             | 2635         | 289             | 1.03         |
| Ba\textsubscript{0.7Sr0.1Ca0.2}TiO\textsubscript{3} | 104             | 167             | 363             | 6132         | 351             | 1.12         |
| Ba\textsubscript{0.6Sr0.2Ca0.2}TiO\textsubscript{3} | NA              | NA              | 397             | 4049         | 373             | 1.19         |
| Series B    |                 |                 |                 |              |                 |              |
| Ba\textsubscript{0.6Sr0.2Ca0.2}TiO\textsubscript{3} | 187             | 253             | 343             | 4483         | 322             | 1.11         |
| Ba\textsubscript{0.62Sr0.28}Ca\textsubscript{0.1}TiO\textsubscript{3} | 148             | 231             | 411             | 2994         | 385             | 1.27         |
| Ba\textsubscript{0.7Sr0.1Ca0.2}TiO\textsubscript{3} | 172             | 250             | 378             | 4251         | 365             | 1.15         |
| Ba\textsubscript{0.62Sr0.28}Ca\textsubscript{0.1}TiO\textsubscript{3} | 134             | 206             | 375             | 3697         | 360             | 1.21         |
| Ba\textsubscript{0.7Sr0.1Ca0.2}TiO\textsubscript{3} | NA              | 170             | 373             | 3161         | 357             | 1.25         |
| Ba\textsubscript{0.62Sr0.28}Ca\textsubscript{0.1}TiO\textsubscript{3} | 94              | 363             | 3826            | 353          | 353             | 1.24         |
| Series C    |                 |                 |                 |              |                 |              |
| Ba\textsubscript{0.68Sr0.32}TiO\textsubscript{3} | 176             | 229             | 304             | 3737         | 269             | 1.08         |
| Ba\textsubscript{0.68Sr0.32}Ca\textsubscript{0.12}TiO\textsubscript{3} | 124             | 184             | 311             | 9564         | 309             | 1.18         |

Table 2. The results of dielectric measurements of studied compounds.
non polarizing ions, cubic perovskite structure in the ferroelectric phase, neglect of off centered Ca ions, etc.) and a modified empirical function

\[ \sigma = \frac{1}{\sqrt{2}} (2r_{A-site}^0 + 2r_A) \]

As it was suggested. The TC of all studied samples showed a linear correlation with the modified function regardless of the cation composition on A-site (Fig. 3) as follows:

\[ T_C[K] = 17252 \times \left( \sigma^2 + \left( \frac{r_{A-site}^0}{<r_{A-site}^0>} \right)^2 \right) (2\sigma_A - r_{A-site}^0) \]

Although the proposed simple model appeared to qualitatively explain the empirical relationship of \( \sigma^2 \) and \( <r_{A-site}^0> \) with \( T_C \), a detailed model is required to relate ionic radii of individual ions with the following factors influencing ferroelectricity in titanate perovskites: magnitude of Ti off centering in TiO\(_6\) octahedra, the direction

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**Figure 2.** Schematic representation of (110) planes in the ideal cubic perovskite with \( <r_{A-site}^0> = r_{A-site}^0 \) and \( \sigma^2 = 0 \) (a), in the cubic perovskite with \( <r_{A-site}^0> > r_{A-site}^0 \) and \( \sigma^2 = 0 \) (b) and in the cubic perovskite with \( <r_{A-site}^0> = r_{A-site}^0 \) and \( \sigma^2 > 0 \) (c). Grey, white, and patterned circles represent A-site ions, O and Ti ions, respectively.

**Figure 3.** \( T_C \) as a function of \( \sigma^2 + \left( \frac{r_{A-site}^0}{<r_{A-site}^0>} \right)^2 \) \( (2\sigma_A - r_{A-site}^0)^2 \). Solid line is a fit to equation 3. Inset shows \( \gamma \) as function of \( \sigma^2 + \left( \frac{r_{A-site}^0}{<r_{A-site}^0>} \right)^2 \) \( (2\sigma_A - r_{A-site}^0)^2 \).
of the Ti off centering and contributions from A-site ions displacements. Recent studies of local structure provided vital information on the influence of Ca and Sr substitution in BaTiO$_3$ on the above mentioned parameters$^{29,30,34}$. The magnitude of Ti off centering was found to decrease monotonically with Sr doping in BaTiO$_3$ as TiO$_6$ octahedra became more regular and reduced in volume$^{29,30,35}$. This effect is usually associated with the observed decrease of $T_C$ upon Sr doping. The effect of Ca doping on TiO$_6$ octahedra remains controversial. It was shown that Ca doping decreased the average volume of TiO$_6$ octahedra whereas the degree of distortions in TiO$_6$ network increased$^{35}$. The volume of some TiO$_6$ octahedra was found to be close to the one of BaTiO$_3$ even when 30% Ca was introduced on A-site. On the other hand the increase of the volume of TiO$_6$ octahedra with the increasing number of neighboring Ca ions and concurrent increase of the Ti displacement was reported$^{30}$. The direction of Ti ions displacement was found to be aligned at $\approx 33^\circ$ with respect to the c axis in BaTiO$_3$\textsuperscript{29}. Sr doping increased this angle of alignment to 39° in Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ and 54° (Ti displacement along (111) direction) in Ba$_{0.5}$Sr$_{0.5}$TiO$_3$. As a result the c-axis component of polarization diminished lowering the value of $T_C$. Ca doping appeared to induce an opposite effect as the direction of Ti ions displacement was closely aligned with c axis in Ba$_{0.7}$Ca$_{0.3}$TiO$_3$\textsuperscript{30}. No Sr off-centering was observed in Ba$_{1-x}$Sr$_x$TiO$_3$ materials resulting in an isotropic relaxation of oxygen ions around the A-site thus providing no additional contribution to specimen polarisation$^{29,30}$. Ca off-centering was experimentally observed by EXAFS in CaTiO$_3$\textsuperscript{34} and Ba$_{1-x}$Ca$_x$TiO$_3$ (0 $<$ x $<$ 0.5)$^{30}$, by XANES in

| Parameter | Series A | Series B | Series C |
|-----------|---------|---------|---------|
| z (Å)     | 3.96435(3) | 3.96279(3) | 3.96231(7) |
| c (Å)     | 3.98716(5) | 3.99661(4) | 4.00921(9) |
| z (A-site) | 0.514(2) | 0.512(14) | 0.509(2) |
| Uiso(A-site) (Å$^2$) | 0.0056(2) | 0.0097(2) | 0.0073(3) |
| Uiso(Ti) (Å$^2$) | 0.0033(4) | 0.0071(3) | 0.0050(4) |
| z (O1)    | 0.530(2) | 0.5332(1) | 0.536(1) |
| Uiso(O1) (Å$^2$) | 0.0079(6) | 0.0115(4) | 0.0100(5) |
| z (O2)    | 0.029(1) | 0.030(1) | 0.031(1) |
| Uiso(O2) (Å$^2$) | 0.0058(3) | 0.0101(2) | 0.0080(3) |
| wRp      | 4.11 | 4.34 | 5.90 |
| Ti-O1 (Å) | 1.876(6) | 1.866(4) | 1.861(5) |
| Ti-O1 (Å) | 2.111(6) | 2.131(4) | 2.148(5) |
| Ti-O2 (Å) | 1.9856(3) | 1.9851(2) | 1.9850(3) |
| Ti-O-Ti (°) | 173.2(3) | 173.0(2) | 172.9(3) |
| A-O1 (Å) | 2.8039(1) | 2.8034(1) | 2.8039(2) |
| A-O2 (Å) | 2.767(3) | 2.762(3) | 2.756(3) |
| A-O2 (Å) | 2.857(4) | 2.862(3) | 2.882(4) |

Figure 4. Ti-O bond lengths as a function of $\sigma^2 + \left(\frac{r_{A-site}}{<r_{A-site}>}\right)^2 - r_{A-site}^0)^2$. Inset shows $d^2$ as function of $\sigma^2 + \left(\frac{r_{A-site}}{<r_{A-site}>}\right)^2 - r_{A-site}^0)^2$. 

Table 3. Refined parameters obtained from Rietveld refinements on neutron data.
Ba$_{1-x}$Ca$_x$TiO$_3$ (x = 0.02, 0.05) compounds and theoretically predicted in Ba$_{0.875}$Ca$_{0.125}$TiO$_3$ and Ba$_{1-x}$Ca$_x$TiO$_3$. If Ca off-center displacements occur in the same direction as TiO$_6$ distortions this additional contribution to polarization results in the increased values of $T_C$. The direction of Ca off-centering were reported along [111], [001], or [113] directions. Furthermore Ca displacements were shown to facilitate Ti displacements inside TiO$_6$ octahedra further enhancing ferroelectric behaviour. It is possible to speculate that the increase of A-site cation disorder (expressed as $\sigma^2$) could facilitate the shift of smaller A-site cations from the centrosymmetric positions in order to relieve an associated bond strain. A model was proposed that assumed two competitive effects active during Ca doping in Ba$_{1-x}$Ca$_x$TiO$_3$: the shrinkage of TiO$_6$ octahedra resulting in smaller Ti displacements (and possibly away from the c-axis direction) and the increase of the number of off-centered Ca ions. This mode described experimentally observed $T_C$ dependence reasonably well. Similar A-site driven ferroelectricity was found in perovskites with the $t < 1$ where the introduction of smaller ions (e.g. Li in K$_{0.5}$Li$_{0.5}$NbO$_3$ and Lu in (La,Lu)MnNiO$_6$ stabilized off-centering of A-site ion (thus inducing ferroelectric state) over tilting of BO$_6$ octahedra.

The observed increase of $T_C$ with $\sigma^2$ and decrease of $T_C$ with $<r_{A-site}>$ are in agreement with previous results. A weak increase of $\gamma$ with $\sigma^2 + \frac{r_{A-site}^0}{<r_{A-site}>}$ was observed (inset Fig. 3) presumably due to the increased degree of cation disorder. In order to evaluate whether this simple empirical equation (5) consisting of tabulated values of ionic radii, could be used for the selection of compositions with specific values of $T_C$, two compounds (series C) were prepared with an intended $T_C$ of 35 °C. The Ca doping on A site, y, in Ba$_{1-x}$Sr$_x$Ca$_y$TiO$_3$ was fixed at y = 0 and 0.1, respectively. A good agreement between the intended and measured values of $T_C$ were observed (31 °C for 0 and 37 °C for 0.1 Ca doped samples).
Neutron diffraction data were collected at room temperature on several samples using the high resolution powder diffractometer, HRPD, at the ISIS neutron facility, Rutherford Appleton Laboratories, UK. Diffraction patterns were recorded over the time-of-flight range 31–125 ms, corresponding to a $d$-spacing range 0.65–2.58 Å, or 0.85–3.89 Å, for patterns collected in the back-scattering and 90 degree detector banks, respectively. The patterns were recorded to a total incident proton beam of about 60 $\mu$A h. The neutron patterns from back scattered and 90 degree banks were fitted simultaneously by Rietveld profile refinement method using Gsas II software. The data were refined in P4 mm space group with the following atomic positions: Ti (0, 0, 0), Ba/Sr/Ca (0.5, 0.5, z), O1 (0, 0, z), O2 (0, 0.5, z). Due to strong correlation, atomic positions and isotropic thermal factors for A-site cations were not refined independently. As a result we were unable to model Ca ion off-centering ions as discussed above. The cation occupancies were fixed according to the results of the chemical analysis and the full oxygen occupancy was assumed. The following parameters were refined: background coefficients, scale factors, diffractometer constant, peak shape, anisotropic strain, atomic positions and isotropic displacement parameters. The results of the refinements are given in the Table 3. As a function of $\sigma^2 \left[ \frac{r_{A-site}^0}{<r_{A-site}^0>} \right] \left( <r_{A-site}^0> - r_{A-site}^0 \right)^2$, the temperature deviation, $\Delta T$, of Ca containing samples (Ba$_{1-x}$Sr$_x$Ca$_y$TiO$_3$, open symbols) from line for only Ba, Sr containing compounds (Ba$_{1-x}$Sr$_x$TiO$_3$, solid symbols). Insets show $\Delta T$ as a function of Ca doping, $y$. Solid lines are guides to eye.

Figure 7. Temperatures of orthorhombic to tetragonal transition, $T_{O-T}$ (a) and rhombohedral to orthorhombic transition, $T_{R-O}$ (b) as function of $\sigma^2 \left[ \frac{r_{A-site}^0}{<r_{A-site}^0>} \right] \left( <r_{A-site}^0> - r_{A-site}^0 \right)^2$. The temperature deviation, $\Delta T$, of Ca containing samples (Ba$_{1-x}$Sr$_x$Ca$_y$TiO$_3$, open symbols) from line for only Ba, Sr containing compounds (Ba$_{1-x}$Sr$_x$TiO$_3$, solid symbols). Insets show $\Delta T$ as a function of Ca doping, $y$. Solid lines are guides to eye.
one Ti-O1 bond monotonically increased whereas another Ti-O1 bond decreased leading to the distortion of TiO$_6$ octahedra (Fig. 4). As a result a linear increase of the squared atomic displacement of Ti ions from the center-symmetry position, $d^2$, is observed (inset Fig. 4).

Figure 5 shows the $T_C$ as a function of $\sigma^2 + \frac{r^2_{A-site}}{r^2_{A-site}} \left( <r_{A-site}^2> - r^2_{A-site} \right)^2$ in a large number of Ba$_{1-x}$Sr$_x$Ca$_y$TiO$_3$ with the tolerance factor greater than 1 reported in the literature over the last 60 years$^{12,20,40-59}$. A strong linear correlation is observed with some scatter of data presumably due to compositional inhomogeneity (including partial substitution of Ca on B site$^{20}$), annealing conditions$^5$, thermal hysteresis during the measurements$^9$, etc. In datasets$^{44,46}$ that showed a deviation from the observed empirical trend, frequency dependences of $\epsilon$ was observed in heavily doped Ca samples. As a result we suggest that the observed empirical equation (5) is valid for typical ferroelectrics.

It is interesting to consider the effect of Ca doping on $T_C$ in Ba$_{1-x}$Ca$_x$TiO$_3$ compounds. It has been shown that Ca doping on A-site results in first slight increase of $T_C$ with up to 8% Ca doping followed by a decrease$^{20,30,44,51}$, whereas even small extend of Ca doping on B site resulted in a drastic decrease of $T_C$ (Fig. 6). From the proposed model the introduction of smaller Ca ions in BaTiO$_3$ resulted in the increase of $\sigma^2$ and the decrease of $<r_{A-site}^2> - r^2_{A-site}$, thus exhibiting opposite effects on the values of $T_C$. As a result $T_C$ is expected to show the maximum with Ca doping. When the $T_C$ data was replotted as a function of $\sigma^2 + \frac{r^2_{A-site}}{r^2_{A-site}} \left( <r_{A-site}^2> - r^2_{A-site} \right)^2$ a monotonic increase of $T_C$ was observed (inset to Fig. 6) regardless of Ca doping on A- or B-sites ($r^2_{A-site}$ increased with Ca doping on the Ti-site). Furthermore our preliminary results showed that the correlation similar to (5) exists in Zr and Sn doped titanates. As a result it is possible that the observed empirical correlation (5) is valid for the families of titanates with A- and B-sites doped by isoelectronic ions. At the same time the proposed model is expected to break down when the ion shape cannot be considered spherical, for example when the stereochemically active electron lone pairs (Pb$^{2+}$, Bi$^{3+}$) or partially filled orbitals (La$^{3+}$) are present as shown in Supplementary Fig. 7.

The temperatures for rhombohedral to orthorhombic, $T_{R\rightarrow O}$, and orthorhombic to tetragonal, $T_{O\rightarrow T}$, transitions in BSCT are shown in Fig. 7(a,b), respectively. For compounds containing only Ba and Sr on the A-site, a linear increase of the transition temperatures with $\sigma^2 + \frac{r^2_{A-site}}{r^2_{A-site}} \left( <r_{A-site}^2> - r^2_{A-site} \right)^2$ was observed. The Ca containing samples showed negative deviation of $T_{R\rightarrow O}$ and $T_{O\rightarrow T}$ from the linear trends of Ba$_{1-x}$Sr$_x$TiO$_3$ compounds (marked as $\Delta T$ on Fig. 7(a,b)). $\Delta T$ increased linearly with Ca doping, $y$, regardless of Sr and Ba content (insets to Fig. 7(a,b)). The following empirical equations were proposed:

for orthorhombic to tetragonal transition ($y < 0.2$)

$$T_{O\rightarrow T}[K] = 9010 \times \sigma^2 + \frac{r^2_{A-site}}{r^2_{A-site}} \left( <r_{A-site}^2> - r^2_{A-site} \right)^2 - 521 \times y - 61.4$$  \hspace{1cm} (6)

for rhombohedral to orthorhombic transition ($y < 0.15$)

$$T_{R\rightarrow O}[K] = 4046 \times \sigma^2 + \frac{r^2_{A-site}}{r^2_{A-site}} \left( <r_{A-site}^2> - r^2_{A-site} \right)^2 - 519 \times y - 100.0$$  \hspace{1cm} (7)

In conclusion we demonstrated a combined effect of average ionic radii and cation variance on $T_C$ a Ba$_{1-x}$Sr$_x$Ca$_y$TiO$_3$ ferroelectric perovskites. $T_C$ increased linearly with $\sigma^2$ and $<r_{A-site}^2>$. A set of empirical equations was proposed which allowed the estimation of temperature of phase transitions in alkaline-earth titanates based on the tabulated values of ionic radii. This provides simple guidelines for a selection of compounds with required values phase transitions temperatures ($T_{O\rightarrow T}$, $T_{R\rightarrow O}$, and $T_{O\rightarrow T}$) in Ba$_{1-x}$Sr$_x$Ca$_y$TiO$_3$ perovskites.

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A.B. prepared samples, collected and analysed X-ray diffraction, ICP, DSC and dielectric data, performed Rietveld refinements and F.L.G. performed neutron measurements. N.A. supervised the project. All authors contributed in writing of the manuscript.

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