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Anomalous Curie temperature behavior of A-site Gd-doped BaTiO₃ ceramics: The influence of strain

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The influence of A-site Gd³⁺ doping on the *c/a* ratio, cell volume and Curie temperature (*T_c*) of ferroelectric BaTiO₃ according to the titanium vacancy mechanism, viz., Ba_{1-x}Gd_xTi_{1-x/4}O₃ has been investigated and compared to that of La³⁺-doping. The *c/a* ratio and cell volume of Gd-doped samples are larger than the equivalent La-doped samples and *T_c* decreases at a rate of only ~8 °C/at. % for Gd³⁺ substitution compared to ~24 °C/at. % for La³⁺ substitution. These trends are opposite to that expected based on ionic-radii and tolerance factor arguments. This anomalous behavior is attributed to an ion-size mismatch (cation variance) effect on the A-site between the Ba²⁺ and Gd³⁺ ions that induces local strain in the lattice that suppresses the reduction in the *c/a* ratio and cell volume, and as a consequence in the rate of decrease in *T_c*. © 2011 American Institute of Physics. [doi:10.1063/1.3563710]

Ferroelectric BaTiO₃ is an important perovskite-type material for many applications including multilayer ceramic capacitors (MLCCs) and positive temperature coefficient of resistance thermistors. The ferroelectric to paraelectric phase transition from tetragonal (space group *P4mm*) to cubic symmetry (space group *Pm-3m*) occurs at ~120–130 °C and is known as the Curie temperature, *T_c*. In many applications, adjustment of *T_c* is required. For example, a simultaneous increase and decrease in *T_c* in grain-cores and grain-shells, respectively, in core-shell type BaTiO₃ ceramics is required to smooth-out and extend the temperature stability range of the capacitance in X8R-rated ceramic capacitors.¹ In other cases, such as PTCR-BaTiO₃ based thermistors, an increase or decrease in *T_c* is required to adjust the switching temperature of the device depending on the required application.

In many cases, the influence of chemical doping on *T_c* in BaTiO₃ can be rationalized by simple ion-size effects and changes in the tolerance factor, *t* where $t = [(R_A + R_O) / \sqrt{2(R_B + R_O)}]$ and *R_A*, *R_B*, and *R_O* are the ionic radii of the A, B, and O ions, respectively. For the ideal cubic perovskite structure such as SrTiO₃ at room temperature (RT), $\sqrt{2(R_B + R_O)} = (R_A + R_O)$ and *t* = 1. For undoped BaTiO₃ at RT, the Ti ions are too small to occupy the centrosymmetric position within the BO₃ octahedra and are displaced ~0.1 Å from this central position. This results in the creation of a dipole moment within individual unit cells, and co-operative dipole-dipole interactions lead to the formation of ferroelectric domains. At RT, BaTiO₃ has tetragonal symmetry with a *c/a* ratio of ~1.01 and $(R_A + R_O) > \sqrt{2(R_B + R_O)}$ with *t* ~ 1.06. It is well known that isovalent doping with a smaller A-site ion (e.g., Sr²⁺) and/or a larger B-site ion (e.g., Zr⁴⁺) reduces *t* of BaTiO₃ toward 1, stabilizes the cubic polymorph to lower temperature² and, therefore reduces *T_c*. In many cases, the cell volume and *T_c* show a linear decrease with the level of dopant, e.g., A-site Sr²⁺ doping decreases *T_c* at a rate of ~3.5 °C/at. % Sr. This type of doping behavior is extremely useful when attempting to fine-tune *T_c* to

<130 °C. In the case of A-site aliovalent doping, it has been shown that La³⁺ doping with the creation of B-site vacancies forms an extensive solid solution according to the formula Ba_{1-x}La_xTi_{1-x/4}O₃ where 0 ≤ *x* < 0.25 with *T_c* decreasing linearly at a rate of -24 °C/at. % La up to *x* = 0.06, where after a switch to ferroelectric relaxor behavior is observed.^{3,4} The dramatic decrease in *T_c* for La-doped ceramics was attributed to a combination of an ion size effect by partial replacement of Ba²⁺ ions with the smaller La³⁺ ions and disruption of the ferroelectric TiO₃ network associated with the creation of Ti-vacancies required for charge compensation.

For applications that require *T_c* > 130 °C, two types of doping mechanisms in ceramics are known to exist. In both cases, A-site isovalent doping occurs, e.g., Pb²⁺ or Ca²⁺ but the dopant has a smaller ionic radius than the Ba²⁺ ion and neither mechanism can, therefore, be explained on the basis of an ion size effect. In the case of Pb²⁺ doping, the presence of a stereochemically active electron lone pair (6s²6p⁰) promotes A-site off-centring of the Pb²⁺ ions in addition to displacement of the Ti ions. As a result, PbTiO₃ is a ferroelectric perovskite with tetragonal symmetry at RT with *c/a* ~ 1.06 and a high Curie temperature of ~490 °C. A complete solid solution forms between BaTiO₃ and PbTiO₃ and *T_c* varies linearly between ~130 and 490 °C depending on the Ba/Pb ratio on the A-site.² Other perovskite titanates containing an A-site cation with an electron lone pair, e.g., Bi³⁺ in Na_{1/2}Bi_{1/2}TiO₃ show similar behavior⁵ when forming a solid solution with BaTiO₃.

In the case of A-site Ca²⁺ doping, more complex behavior is observed.^{6,7} *T_c* initially increases with Ca-doping up to a maximum value of ~138 °C at ~8 at. % doping before decreasing with increasing Ca-content to a lower value of ~118 °C for the solid solution limit of ~24 at. %. The initial rise in *T_c* has been attributed to A-cation size variance due to the large mismatch in ionic radii of the Ba²⁺ and Ca²⁺ ions on the A-site.⁷ This effectively induces strain in the lattice and increases *T_c*. Similar cation variance effects have been observed in structural and electronic phase transitions in other perovskite-related materials.^{8,9} We have suggested the A-cation size variance effect opposes the influence of the

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average A-cation size effect and may be a useful mechanism to stabilize T_c in BaTiO_3 ceramics to higher temperatures.⁷

Trivalent rare earth (RE^{3+}) ions are commonly used at low dopant levels in commercial formulations of BaTiO_3 -based devices to improve reliability.¹ They are an interesting class of aliovalent dopant as they are intermediate in size between Ba^{2+} and Ti^{4+} ions. Depending on their ionic radius they can substitute either exclusively on the A-site ($\text{Ba}_{1-x}\text{RE}_x\text{Ti}_{1-x/4}\text{O}_3$) or B-site ($\text{BaTi}_{1-x}\text{RE}_x\text{O}_{3-x/2}$), e.g., La^{3+} (large RE) and Yb^{3+} (small RE), respectively or for intermediate sized RE^{3+} ions they can substitute on both the A- and B-sites in equal amounts (so called self compensation, $\text{Ba}_{1-x}\text{RE}_x\text{Ti}_{1-x}\text{RE}_x\text{O}_3$) in addition to A-site and/or B-site doping.¹⁰ Recently, we have been investigating the composition-structure-property relationships of Gd^{3+} -doped BaTiO_3 ceramics.¹¹ Gd can dope exclusively on the A-site (up to 5 at. %) or on the B-site (up to ~ 3.75 at. %); however, the largest solid solution is obtained for self-compensation (up to ~ 10 at. % on each site). During this study we have discovered anomalous variations in the tetragonality (c/a ratio), cell volume, and T_c of A-site doped Gd ceramics when compared to La-doped ceramics. We attribute this behavior to A-cation site variance associated with the size mismatch between Gd and Ba compared to La and Ba and propose that a feature of so-called “magic RE^{3+} dopants” such as Gd^{3+} , Ho^{3+} , and Er^{3+} (in addition to their ability to act as self-compensation dopants) in BaTiO_3 is their ability to create lattice strain and therefore limit the reduction in T_c associated with A-site size effects.

All samples were prepared by the mixed oxide route from appropriate quantities of BaCO_3 and TiO_2 and Gd_2O_3 or La_2O_3 . Undoped BaTiO_3 powder was prepared by calcination at 1200°C overnight and ceramics were sintered in air at 1450°C for 6 h. A-site Gd- and La-doped powders were prepared according to the general formula $\text{Ba}_{1-x}\text{RE}_x\text{Ti}_{1-x/4}\text{O}_3$ and calcined overnight at 1200°C . Dense pellets were obtained by sintering in flowing O_2 at 1350°C for 12 h. A-site RE doping can result in semiconducting ceramics for low levels of dopants (especially ≤ 1 at. %) when processed in air but this can be suppressed by processing in O_2 to obtain insulating samples.^{12,13} All pellets were $>95\%$ of the theoretical x-ray density. The microstructure for all doped- BaTiO_3 samples consisted of small and uniform grains, with average grain size $\sim 2\text{--}10\ \mu\text{m}$. For undoped BaTiO_3 sample, exaggerated grain growth with grain size up to $\sim 100\ \mu\text{m}$ was observed. Phase purity was checked and lattice parameters obtained using laboratory x-ray diffraction (XRD). Au-paste electrodes were fired onto the major pellet faces of the ceramics at 800°C prior to electrical characterization. Fixed frequency (1 k to 1 MHz) capacitance measurements were performed using an LCR meter (HP 4284A for measurements from RT to 500 K and Agilent E4980A for measurements from 10 K to RT) with the sample placed inside an in-house impedance rig that was inserted into a computer controlled furnace with the sample temperature accurate to $\pm 1^\circ\text{C}$.

XRD revealed the solid solution limit for A-site doping to be $x=0.05$ for Gd and $x\sim 0.20$ for La. Above these values of x , additional reflections were observed in the XRD patterns that were consistent with $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{Ba}_2\text{La}_4\text{Ti}_5\text{O}_{18}$, respectively. RT XRD patterns for undoped BaTiO_3 (BT) and Gd $x=0.05$ fully indexed on space group $P4mm$ (tetragonal

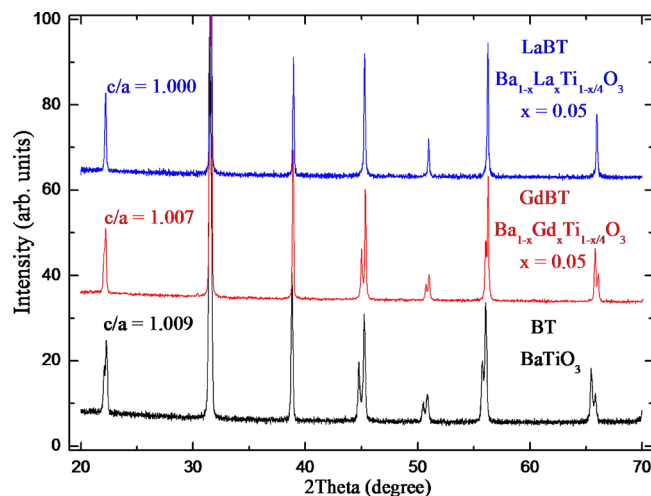


FIG. 1. (Color online) XRD patterns for undoped BaTiO_3 (lower), $\text{Ba}_{0.95}\text{Gd}_{0.05}\text{Ti}_{0.9875}\text{O}_3$ (middle), and $\text{Ba}_{0.95}\text{La}_{0.05}\text{Ti}_{0.9875}\text{O}_3$ (upper).

symmetry) whereas $\text{La } x=0.05$ fully indexed on space group $Pm\text{-}3m$ (cubic symmetry). The difference in RT symmetry of the doped samples can be observed clearly by the splitting of the (200) reflection at $\sim 45^\circ$ 2 theta for the La-doped sample into (002) and (200) reflections with an intensity ratio of $\sim 1:2$ for the Gd-doped sample, Fig. 1. This result demonstrates, for an equivalent 5 at. % doping level on the A-site, RT tetragonality is preserved for the smaller A-site RE dopant ion. RT cell volume for the samples was calculated from the lattice parameters obtained from the RT XRD results and the variation with x is shown in Fig. 2 for A-site La- and Gd-doping. As expected, the replacement of Ba with a smaller RE ion on the A-site results in a decrease in cell volume with increasing x ; however, the decrease is smaller for the Gd-doped samples despite it being a smaller RE-ion than La. For completion, the RT cell volume variation for single-phase Gd-doped B-site and self compensation (A+B) samples is included in Fig. 2. These results will be discussed in detail elsewhere,¹¹ however, they show the expected trend of an increase in cell volume for B-site substitution of the smaller Ti ion with the larger Gd ion and linear behavior for self-compensation samples.

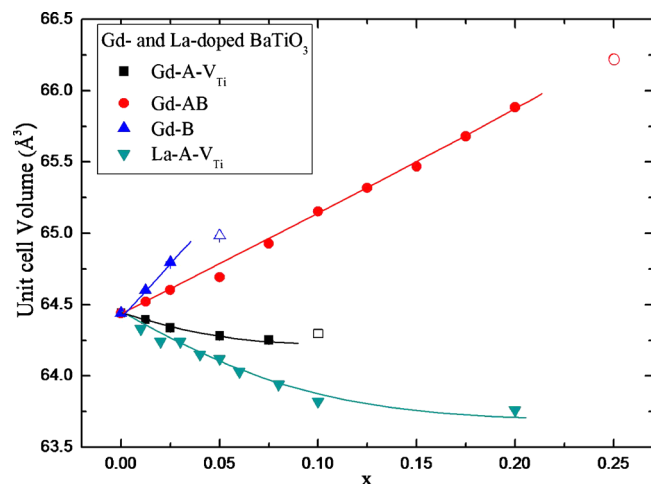


FIG. 2. (Color online) Variation in cell volume vs x for Gd- and La-doped samples. A-site Gd (squares); B-site Gd (dark triangles); A+B-site Gd (circles); and A-site La (light triangles). Filled and open symbols represent single-phase and phase mixtures, respectively.

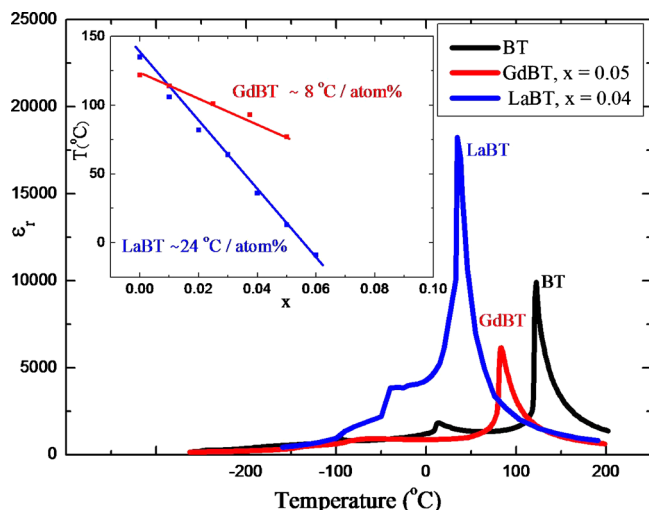


FIG. 3. (Color online) ϵ_r (at 100 kHz) vs temperature for undoped BaTiO_3 (BT), $\text{Ba}_{0.95}\text{Gd}_{0.05}\text{Ti}_{0.9875}\text{O}_3$ (GdBT) and $\text{Ba}_{0.95}\text{La}_{0.04}\text{Ti}_{0.99}\text{O}_3$ (LaBT) ceramics. Inset shows the variation of T_c with x for A-site Gd- and La-doped ceramics.

Impedance spectroscopy results (not shown) showed all samples to be electrically homogeneous and to consist of insulating grains and grain boundaries; there was no evidence of semiconductivity in any of the samples studied. The temperature dependence of ϵ_r (at 100 kHz) for BT, $x=0.05$ Gd and $x=0.04$ La from fixed frequency capacitance measurements is shown in Fig. 3. In each case, the largest peak in ϵ_r is associated with the tetragonal to cubic polymorphic phase transition temperature, T_c . A-site doping with a RE ion results in a suppression of T_c compared to BT; however, there is a more dramatic decrease in T_c for La-doped samples. The ϵ_r data for all A-site Gd-doped samples and for La-doped samples up to $x=0.06$ displayed no frequency dependence (not shown), and therefore the peak in ϵ_r could be used to extract T_c . Consistent with previous studies,⁴ relaxor behavior was observed for La-doped samples with $x > 0.06$. The variation of T_c versus x for the A-site Gd series and La series for $x \leq 0.06$ is shown in the inset of Fig. 3. In both cases, there is a linear decrease in T_c with x , however, the rate ($\Delta T_c/\text{at. \% RE}$) is much larger for the La-doped series ($\sim 24^\circ\text{C}/\text{at. \%}$) compared to that of the Gd-doped series ($\sim 8^\circ\text{C}/\text{at. \%}$).

It is well known that removal of Ti-ions via A-site aliovalent doping with large trivalent RE ions such as La, Ce, or Nd (Refs. 14–16) or removal of oxygen-ions via B-site aliovalent doping with a variety of intermediate-sized divalent or trivalent ions, e.g., Ca^{2+} , Ho^{3+} causes significant disruption to the ferroelectric domain network of BaTiO_3 , and therefore results in considerable suppression of T_c with rates commonly exceeding $10\text{--}20^\circ\text{C}/\text{at. \% dopant}$.^{17,18} In the case of A- or B-site isovalent doping where the creation of Ti- or O-site vacancies is not required for charge balance the rate of change of T_c is $<10^\circ\text{C}/\text{at. \% dopant}$ and can usually be rationalized on the basis of ion-size (tolerance factor) effects. The results presented here for A-site Gd-doped BaTiO_3 contravene both these trends. First, they show an abnormally low rate of change of T_c for a Ti-vacancy mechanism, Fig. 3, and, second, the trend observed for RT tetragonality, cell

volume and change in T_c when compared to La-doped samples is opposite to that expected on the basis of ion-size effects, Figs. 1–3. These trends can be rationalized on the basis of A-site cation variance associated with the size mismatch between the Ba and RE ions. In the case of Gd, the (extrapolated) Shannon ionic radius¹⁹ for 12-fold coordination is $\sim 1.28 \text{ \AA}$ compared to the tabulated values of 1.36 \AA and 1.61 \AA for La and Ba, respectively. The large difference in ionic radius explains the much smaller solid solution limit for A-site Gd doping ($x=0.05$) compared to La-doping ($x \sim 0.20$) and the strain associated with the size-mismatch partially offsets the influence of the average A-site ion size effect and more importantly the detrimental influence of Ti-vacancies on T_c . As a consequence, the rate of decrease in T_c is significantly lower for the Gd-doped series. Unfortunately, the strain effect is not sufficient to result in an overall increase in T_c , as observed for A-site Ca-doped samples (up to 8%) and this is presumably due to the strong influence of Ti-vacancies in suppressing T_c . Nevertheless, this result may partially explain the preference to use intermediate sized RE ions such as Gd to dope BaTiO_3 in commercial applications such as MLCC's, where there is a need to retain close control of the temperature dependence of the permittivity of the core and shells regions of the grains. Although the influence of strain effects on T_c in thin films of perovskite-based ferroelectrics is well documented²⁰ this is a rare example of the influence of bulk strain effects on T_c associated with RE-dopants in ferroelectric BaTiO_3 .

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