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# Structure–property relationships in $BaTiO_3$–$BiFeO_3$–$BiYbO_3$ ceramics

Giorgio Schileo[a,f], Luke Luisman[a,f], Antonio Feteira[a,b,∗,f], Marco Deluca[c,d], Klaus Reichmann[e]

[a] *Christian Doppler Laboratory for Advanced Ferroic Oxides, School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom*
[b] *Department of Physics, The University of Warwick, Gibbet Hill Road, CV4 7AL Coventry, United Kingdom*
[c] *Institut für Struktur- und Funktionskeramik, Montanuniversitaet Leoben, Peter Tunner Str. 5, 8700 Leoben, Austria*
[d] *Materials Center Leoben Forschung GmbH, Roseggerstr. 12, 8700 Leoben, Austria*
[e] *Christian Doppler Laboratory for Advanced Ferroic Oxides, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria*

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## Abstract

$Ba_{1-x}Bi_xTi_{1-x}Yb_{x/2}Fe_{x/2}O_3$ ceramics were fabricated by the solid state reaction method. X-ray diffraction analyses show $0 \leq x \leq 0.04$ ceramics to have an average crystal structure described by the non-centrosymmetric tetragonal P4 mm space group, whereas $x \geq 0.08$ ceramics are consistent with a centrosymmetric cubic perovskite (space group Pm-3 m). Coexistence of both tetragonal and cubic symmetries is observed for $x = 0.06$. Raman spectroscopy analysis corroborate a change in average structure with increasing $x$, but also show the local crystal symmetry for $x \geq 0.08$ ceramics to deviate from the idealized cubic perovskite structure. Dielectric data show a ferroelectric-to-relaxor crossover, which occurs in conjunction with the change in both the average and local crystal symmetry as indicated by X-ray and Raman data. For $x \geq 0.08$, ceramics exhibit relaxor behavior, which is also accompanied by a shift of the permittivity maxima towards higher temperatures with increasing $x$.

*Keywords:* $BaTiO_3$ and titanates; Ferroelectrics; Relaxors; Raman spectroscopy; $BiFeO_3$

## 1. Introduction

$BaTiO_3$ (BT) is one the most studied lead-free ferroelectric perovskites ($ABO_3$) and certainly the most commercially successful. Indeed, more than 3 billion multilayer ceramic capacitors (MLCCs) based on BT are annually fabricated.[1] The discovery of BT in 1941 during World War II was surrounded by considerable secrecy, mainly due to its extraordinarily large room-temperature relative permittivity, $\varepsilon_r$, which exceeds 1000.[2] At that time, this $\varepsilon_r$ value was ten times larger than the values exhibited by any other known ceramic. This unusually high $\varepsilon_r$ was understood to be associated with the ferroelectric nature of BT. Moreover, early crystallographic studies suggested a correlated displacement of $Ti^{4+}$ away from a centrosymmetric position within $TiO_6$ octahedra chains to be at the origin of the large spontaneous polarization (~16 μC/cm$^2$) in BT. Von Hippel[2] proposed this displacement to be driven by the hybridization of empty $Ti^{4+}$ 3d orbitals and $O^{2-}$ p orbitals. In 1949, Kay and Vousden[3] showed that on heating BT undergoes three consecutive ferroelectric structural phase transitions. Hence, its crystal structure changes from rhombohedral to orthorhombic at ~−80 °C, from orthorhombic to tetragonal at ~0 °C and from tetragonal to cubic at ~130 °C. These phase transitions are accompanied by large anomalies in $\varepsilon_r$. For example, $\varepsilon_r$ values as high as 10,000 are observed around 130 °C. Above this temperature, known as the Curie Temperature, $T_c$, BT is no longer ferroelectric and its $\varepsilon_r$ decreases according to the empirical Curie–Weiss law. The temperature dependence of $\varepsilon_r$ imparted by the structural phase transitions is undesirable for most technological applications and especially for MLCCs. Chemical doping has been successfully employed to reduce the temperature dependence of $\varepsilon_r$ in BT-based ceramics.[4,5] Nevertheless, most of the dopants added or substituted into the BT lattice tend to lower $T_c$, limiting the temperature range of its use. Fortunately, some dopants such as $Pb^{2+}$ and $Ca^{2+}$ were found to increase $T_c$.[6] This result prompted the exploration of A-site non-centrosymmetry as an alternative route for ferroelectricity. In the case of $Pb^{2+}$, the non-centrosymmetry is due

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[∗] Corresponding author at: Tel.: +44 0114 225 2650; fax: +44 0114 225 4249.
*E-mail address:* a.feteira@shu.ac.uk (A. Feteira).

[f] Now at Christian Doppler Laboratory for Advanced Ferroic Oxides, Materials Engineering Research Institute, Sheffield Hallam University, Sheffield S1 1WB, United Kingdom.

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to the presence of stereochemically active lone-pair electrons.[7] Obviously, this observation also lead to the investigation of the doping effects induced in BT by cations such as $Bi^{3+}$, $Te^{4+}$ and $Sn^{2+}$, all showing a lone-pair of electrons due to the $ns^2$ electron configuration.[8–10]

The solubility limit of Bi into the BT lattice according to the electronic compensated $Ba_{1-x}Bi_xTiO_3$ mechanism was reported to be $x \leq 0.03$.[10] On the other hand, the solubility limit according to the A-site vacancy $Ba_{1-x}Bi_{2x/3}TiO_3$ mechanism was reported by Bahri et al.[8] to extend up to $x = 0.15$. These authors observed ceramics with $x \leq 0.09$ to exhibit a typical classical ferroelectric response marked by sharp permittivity maxima, whereas above this concentration the ceramics exhibit a relaxor-type ferroelectric response. Moreover, in contrast with $Ba_{1-x}Pb_xTiO_3$, $T_c$ for $Ba_{1-x}Bi_{2x/3}TiO_3$ ceramics remained virtually unaltered up to $x = 0.09$ and above this concentration the permittivity maximum decreased at 20 °C/mol%. This result shows that the simple presence of a lone-pair of electrons is insufficient to cause an increase in $T_c$.

Previously Eitel et al.[11] postulated that the $T_c$ of $PbTiO_3$ could be increased to temperatures greater than 600 °C by chemical doping according to a double doped self-compensated $Pb_{1-x}Bi_xTi_{1-x}Yb_xO_3$ mechanism. In this solid solution, the A-site of the perovskite structure is occupied by both $Bi^{3+}$ and $Pb^{2+}$, each having a lone-pair of electrons. Nevertheless, according to Eitel et al.[11] the enhancement of $T_c$ is strongly determined by the large ionic radii of $Yb^{3+}$ (0.868 Å) in comparison with $Ti^{4+}$(0.605 Å). It is worth mentioning that, while $PbTiO_3$ adopts the perovskite structure, $BiYbO_3$ exists as a triclinic structure with symmetry described by the P-1 space group, and can it be regarded as a distorted fluorite.[12] Therefore, the simultaneous incorporation of $Bi^{3+}$ and $Yb^{3+}$ into the $PbTiO_3$ lattice is to certain extent constrained by the dissimilar structures between $PbTiO_3$ and $BiYbO_3$.

More recently, a double doping mechanism based on the replacement of $Ba^{2+}$ by $Bi^{3+}$ and $Ti^{4+}$ by trivalent cations such as $Me^{3+} = Sc^{3+}$, $Al^{3+}$ or $Yb^{3+}$ according to $Ba_{1-x}Bi_xTi_{1-x}Me_xO_3$ has been investigated.[13,14] For example, Ogihara et al.[13] found that the co-solubility of $Bi^{3+}$ and $Sc^{3+}$ into the BT lattice according to the $Ba_{1-x}Bi_xTi_{1-x}Sc_xO_3$ can be as high as $x = 0.30$. A weak-relaxor type behavior was reported to occur for $x = 0.20$ and 0.30. This type of behavior was also observed by Luisman et al.[15] in the $K_{1-x}Bi_xTi_{1-x}Yb_xO_3$ system for $x = 0.20$ and 0.30, who postulated that this peculiar dielectric response is ultimately associated to the presence of $Bi^{3+}$.

Later, Strathdee et al.[14] investigated the $Ba_{1-x}Bi_xTi_{1-x}Yb_xO_3$ (BBTYb) system and observed that $T_c$ remained virtually unchanged at low doping levels ($x = 0.02$), whereas a continuous reduction in $T_c$ accompanied by a ferroelectric-to-relaxor crossover was observed for $0.02 < x \leq 0.04$. For $x \geq 0.06$ relaxor behavior was observed, however interesting for $x \geq 0.08$ the temperature of the permittivity maxima shifts towards higher temperature with increasing $x$. The emergence of relaxor behavior coincided with the structural change from tetragonal to cubic as determined by XRD. A clear change in the Raman spectra of these ceramics with increasing $x$ was detected, which supported the structural changes determined from XRD analysis. However, the spectra also showed the 'cubic' compositions to have local distortions that were not discernible from XRD. Relaxor behavior in the pseudocubic compositions was attributed to a "subgrain structure encompassing regions of uncorrelated polarization".

The $Ba_{1-x}Bi_xTi_{1-x}Fe_xO_3$ solid solution was also investigated by several researchers.[16–36] In this case, $BaTiO_3$ is combined with $BiFeO_3$, a high Curie temperature (850 °C) ferroelectric, which is also antiferromagnetic up to 370 °C. For $Ba_{1-x}Bi_xTi_{1-x}Fe_xO_3$ the tetragonal symmetry is maintained up to $x = 0.04$. Between $x = 0.08$ and 0.70, the average crystal structure is cubic. Above $x = 0.70$ the crystal structure is rhombohedral. Guo et al.[18] observed the permittivity maxima to shift toward lower temperatures with increasing $x$, and for $x = 0.08$ the permittivity maximum was below room temperature, in contrast to $Ba_{1-x}Bi_xTi_{1-x}Yb_xO_3$, where for $x > 0.06$ the permittivity maxima shift toward higher temperatures.[14]

In the present work the structure-property relationships in $BaTiO_3$–$BiFeO_3$–$BiYbO_3$ ceramics prepared according to the $Ba_{1-x}Bi_xTi_{1-x}Yb_{x/2}Fe_{x/2}O_3$ ($0 \leq x \leq 0.20$) mechanism have been investigated using a combination of XRD, Raman spectroscopy, electron probe microanalysis (EPMA) and dielectric measurements. The relative impact of the B-site average radii on both the structure and the dielectric properties can be evaluated by comparison with the $Ba_{1-x}Bi_xTi_{1-x}Yb_xO_3$ system. Basically, both systems are characterized by a full occupancy of both the A- and B-sites and an equal concentration of $Bi^{3+}$ on the A-site, but a lower concentration of $Yb^{3+}$ on the B-site due to its partial replacement by $Fe^{3+}$. Hence, this study elucidates the relative role of both $Bi^{3+}$ and B-site ionic radii on the overall dielectric response of self-compensated $BaTiO_3$-Bi(Me)$O_3$.

## 2. Experimental

$Ba_{1-x}Bi_xTi_{1-x}Yb_{x/2}Fe_{x/2}O_3$ (BBTYbFe) powders were synthesized by standard solid-state reactions. The raw materials used were $BaCO_3$ (>99%), $Bi_2O_3$ (>99.9%), $TiO_2$ (>99%), $Yb_2O_3$ (>99.9%), and $Fe_2O_3$ (>99%) (Sigma Aldrich Chemical Co. Milwaukee, USA). Raw materials were weighed to 4 decimal places to correct ratios to satisfy the $Ba_{1-x}Bi_xTi_{1-x}Yb_{x/2}Fe_{x/2}O_3$ stoichiometry. Reagents were mixed in ~250 ml milling bottles, using ~0.5 kg of cylindrical yttria-stabilized zirconia milling media (Dynamic Ceramics, Crewe, UK), together with ~50 ml propan-2-ol to produce a slurry. Slurries were then milled for ~20 h on a roller ball mill. Slurries were dried and the resulting powder was passed through a 500 μm sieve to remove milling media. Mixed powders were packed into closed alumina crucibles and calcined first at 700 °C for 8 h and then at 900 °C for 8 h. Powders were milled between calcinations. Reactions at 900 °C were repeated until no changes in XRD diffraction data were observed between subsequent cycles. The reacted powders were mixed with 5% Poly(ethylene glycol) Bio Ultra 20,000 (Sigma Aldrich Chemical Co, Milwaukee, USA) to act as a binder. These blended powders were then pressed as 13 mm diameter ~1 mm thick pellets using a uniaxial press (Specac, Kent, U.K.). Green pellets were sintered at