RELAXOR PROPERTIES OF “BUTTERFLY WING” BARIUM TITANATE CRYSTALS

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ABSTRACT

Barium titanate (BaTiO$_3$, BT) crystals have been grown by the Remeika method using both the regular KF and mixed KF-NaF (0.6-0.4) solvents. Typical acute angle “butterfly wing” crystals are obtained and characterized using x-ray diffraction, scanning electron microscopy (including energy dispersive spectroscopy), conventional dielectric and acoustic emission methods. A typical wing has a triangular plate shape, up to 0.5 mm thick with a 10-15 mm$^2$ area, and a (001) habit with an atomically smooth outer surface. Both K$^+$ and F$^-$ solvent ions are incorporated as dopants into the crystal lattice during growth substituting for Ba$^{2+}$ and O$^{2-}$ ions respectively. The dopants’ distribution is found to be inhomogeneous, their content being almost an order of magnitude higher (up to 2 mol%) at out surface of the plate relatively to the bulk. A few µm thick surface layer is formed where a multidomain ferroelectric net is confined between two ≤ 1 µm thick dopant-rich surfaces. The layer exhibits relaxor ferroelectric properties, which is apparent from the appearance of a broad maximum ($T_m$) in the temperature dependence of the dielectric permittivity. Intense acoustic emission responses detected near $T_m$ allow to observe the $T_m$ shift to lower temperatures at higher frequencies, or dispersion, typical for relaxor ferroelectrics. The outer surface of the BT wing can thus serve as a relaxor thin film for various electronic applications, such as capacitors, or as a substrate for BT-based multiferroic structure.

1. INTRODUCTION

The barium titanate, BaTiO$_3$ (BT), crystal is known as a classical ferroelectric oxide material with a Curie temperature, $T_c$, in the 120-130 °C temperature range corresponding to the ferroelectric (tetragonal) to paraelectric (cubic) phase transition on heating (1). BT single crystals belong to the ABO$_3$ perovskite structure where the B-site cations have octahedral coordination and the A-site cations are at the centers of cavities formed by eight BO$_6$ octahedra (2). The ferroelectric property in tetragonal BT is due to the average relative displacement of titanium ions from their centrosymmetric positions in the unit cells and thus creation of a permanent electric polarization. Such displacive mechanism of ferroelectric distortion is facilitated by the large size of the Ba cation. In fact, replacement of Ba by the smaller Sr leads to a perovskite with a cubic structure (3) at room temperature. Therefore, cationic homovalent and heterovalent as well as anionic substitutions in the BT system are apt to lead to appreciable variations in the material properties. The crystal structure can be then described by a general formula $(\text{Ba}_{1-x}\text{A}_x)(\text{Ti}_{1-y}\text{B}_y)\text{O}_{1-z}\text{X}_z$, where A = {Ca, Sr, La, Bi, K, Na or Li}, B = {Zr, Sn, Ce, Nb, Ta or Mg} and X = {F} (4,5). Different substitution types and levels have been shown to promote a continuous crossover from the ferroelectric state of pure BT to the relaxor state of the above solid solutions.
Some relaxor features have been revealed also in nominally pure BT crystals (6-9); they may be related to incorporation of uncontrolled impurities and the associated emergence of local stresses.

The relaxor state differs qualitatively in several features of its dielectric response (10,11). In relaxor ferroelectrics [RFEs], or relaxors, the temperature dependences of real and imaginary parts of the complex dielectric permittivity show high and broad maxima ($T_m$) with a dispersive shift to higher temperatures with increasing the measurement frequency. Relaxors exist in a number of crystal structures, including tungsten bronzes and disordered perovskites (11). In perovskites, compositional disorder (also called chemical, ionic or substitutional disorder), i.e. the disorder in the arrangement of A-, B- or X-type ions on the crystallographically equivalent sites, is a common feature at high enough temperatures in the paraelectric phase. It is generally accepted that the strong dielectric dispersion of $T_m$ is a consequence of the dynamics of polar nanoregions (PNRs). The latter form at the chemically ordered domain length scale without long range polar order (ferroelectricity) below some temperature, $T_d$ (Burns temperature) several hundred of degrees above the $T_m$ (12,13). In addition to the compositional disorder, the knowledge of random fields and random bonds (9) as well as local strains and stresses is needed to understand the formation of PNRs influencing the peculiar phase transitions in RFEs. An important insight into this subject gives the fact that the PNRs themselves undergo local phase transitions below an intermediate temperature, $T^* (T_m < T^* < T_d)$, which we have studied mainly in lead-containing pervskite crystals (14,15). The latter are already implemented in modern technological applications because they exhibit large dielectric constants and giant piezoelectric coefficients (16,17).

Presently, much effort is being put into developing environmentally friendly lead-free RFEs lacking the drawbacks associated with the volatility and toxicity of PbO. The BT-based relaxors are an important class of such materials (4,18). Of special interest is the KF-doped BT, usually expressed by the chemical formula Ba$_{1-x}$K$_x$TiO$_3$-$_x$F$_x$ (KF-BT/x), where K$^+$ ions substitute for Ba$^{2+}$ ions and F$^-$ ions substitute for O$^{2-}$ ions. Single crystals of KF-BT/x exhibit outstanding piezoelectric properties at certain values of x (19), and they can be readily grown from KF fluxes by the Remeika method (20-24). This method yields twinned, so called “butterfly-wing” crystals, consisting of two triangular planes joined along the hypotenuse at either acute ~39° or obtuse 109.5° reentrant angles (25). Crystallographically, twinning on {111} type planes is combined with a {100} habit. The topology of the crystal surfaces on opposite sides of the thin plate-like wings of the twinned crystal is noticeably different. On the reentrant angle side, growth layers spread upward along the wings from the reentrant angle generating a heavily stepped surface. The reentrant angle serves as a source from which growth layers originate and spread over the crystal surface (17). Therefore, the kinetics of incorporation of impurities, including the flux forming K$^+$ and F$^-$ ions, is expected to be different on the opposite wing sides. The difference in potassium incorporation profiles on both such sides has been indeed observed by X-ray microanalysis (26).

KF substitution is known to affect markedly the physical properties of BT crystals, e.g. their $T_c$ values (20), magnitude of the piezoelectric coefficients (19,27) and the phase diagrams under zero and applied bias (24,29). The variation in $T_c$ with composition, $dT_c/dx = -14$ K/mol % for x ≥ 0.12 is reported for KF-BT/x ceramics, with obvious relaxor properties for the KF-BT/0.15 composition (28). Reduction of $T_c$ is attributed to decrease in covalency of the Ti-O bond when highly electronegative
F⁻ ions replaces an O²⁻ ion as well as to the random electric fields (RFs) induced by KF doping. Anomalies in the behavior of longitudinal acoustic (LA) phonon of KF-BT/x crystals measured by micro-Brillouin scattering has been also explained in terms of the existence of RFs (30). The LA phonon correlates with the relaxation of dipoles via piezoelectric coupling inside the PNRs, and the relaxation is linked to hopping of Ti⁴⁺ ions between off-center sites in the high-symmetry paraelectric phase. The RFs are obviously known to be the reason for frequency dispersion of \( T_m \) in RFEs (13). Recently, we have reported on the ferroelectric phase transition properties of KF-BT/x crystals using the combination of dielectric and acoustic emission (AE) methods (31) and found that the transition has rather diffusive than relaxor properties. However, the samples used had an ambiguous processing history, which might have affected the results. In the present work, we have studied the ferroelectric to paraelectric (FE-PE) phase transition of BT crystals grown in-house from KF fluxes by the Remeika method. The obtained "butterfly-wing" crystals were fully characterized both crystallographically and compositionally, which allowed to clarify some peculiarities of their relaxor-type features. Preliminary results on the BT crystal properties obtained using a mixed KF/NaF flux are also discussed.

2. CRYSTAL GROWTH

Single crystals of BT were grown by the “Remeika method” (20) from supersaturated solutions using mainly KF as a flux. A single experiment with a mixed 0.6KF-0.4NaF flux was carried out as well. The starting materials were Alfa Aesar (99.9% metal basis) BaTiO₃ and Merck extra pure grade KF and NaF (<0.005 wt% Fe) powders. In a standard procedure, a 100 g mixture of BaTiO₃ and KF corresponding to a typically 10-11% molar ratio was loaded into a 90 cm³ platinum crucible, covered with a platinum lid and heated to temperatures just below 1200 °C in a muffle furnace. The batch compositions were usually chosen such as to correspond to solidification temperatures in the 1125-1150 °C range based on the published BT-KF solubility data (32). No charge compensating additions of ferric oxide (20) were employed. After a 10 h soaking period growth was initiated by slow cooling, at 8-12 °/h rates, down to the 900 °C temperature. The flux still liquid at this temperature was quickly decanted; the crucible with the crystals was cooled down to room temperature at variable rates from 25 to 50 °/h. An abundance of 5-7 mm size lightly brownish colored twinned crystals with a nearly 39° splay between their “butterfly wings” were routinely obtained (see Fig. 1).

Fig. 1. BaTiO₃ “butterfly wing” single crystals grown by the Remeika method.
The “butterfly wings” grew out upwards into the solution from a mass of chunky crystals at the bottom of the crucible, but the latter were not studied in this work. Based on some interrupted growth experiments the spine of a butterfly twin was observed to advance ahead of the remainder of the crystal at a fast rate, and its length was limited by the solution depth and local temperature gradient. It was already suggested in the past (21) that the wings of the twinned crystal developed by concurrent rapid growth away from the spine partly by rapid growth in directions parallel to the wings and partly as a result of the spreading of additional growth layers on the re-entrant-angle side of the plates forming the wings of the twinned crystals. Due to fragility, the “butterfly-wing” crystals were carefully mechanically removed from the crucible. The wings had a triangular plate shape with thicknesses of up to 0.5 mm, and they could be easily split apart. The yield and size of BT twinned crystals grown from the mixed KF-NaF fluxes was considerably smaller, in part because of the lower growth temperatures, due to the KF-NaF solution eutectics at 710 °C (33).

3. RESULTS AND DISCUSSION

3.1 Phase and Morphological Analysis

The phase analysis of the grown BT crystals was carried out by X-ray diffraction measurements, performed on the D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) with a goniometer radius of 217.5 mm, secondary Graphite monochromator, 2° Sollers slits and 0.2 mm receiving slit. XRD patterns within the range 20 to 108° 2θ were recorded at room temperature using CuKα radiation (\( \lambda = 1.5418 \) Å) with following measurement conditions: tube voltage of 40 kV, tube current of 40 mA, step-scan mode with a step size of 0.02° 2θ and counting time of 1 s/step. Examination of an XRD pattern obtained from a powder specimen reveals that grown BT has tetragonal structure belonging to the P4mm (99) space group (PDF-04-002-9077). The refined with using Rietveld procedure values of unit cell parameters were \( a = b = 3.9936(1) \) Å and \( c = 4.0322(2) \) Å, and the c/a ratio was thus very close to the 1.01 value typical for a single domain crystal (25).

![Fig. 2. XRD patterns of an as-grown KF-BT crystal showing reflections from (100) and (001) facets. Inset: photograph of the crystal with facet assignment.](image-url)
The crystal morphology results are summarized in Fig. 2. The ideally developed so-called acute-angle BT twin is shown in the figure’s inset. It is usually described as a double \{111\} twin consisting of two right isosceles triangles each joined along its hypotenuse to two sides of a common prism, or spine, which terminates in a well developed narrow facet of the \{111\} or \{110\} type (21). In the present study, we were interested in verifying the morphology of a single twin plate. Therefore, XRD reflection patterns were taken from oriented single crystalline samples so as to determine the crystallographic planes associated with plate’s large surface and the narrow edge facet. The XRD traces shown in Fig. 1 demonstrate that the former is a (001)-type plane, while the latter is a (100)-type plane. This finding is in contradiction with earlier reports claiming that the large twin faces are \{100\}, and it may be important for many physical studies of twinned BT crystals, especially where the knowledge of the direction of the electric field application is essential.

3.2 Compositional Analysis

Based on the foregoing a double twin of BT with two (111) twin planes (25) grows from a KF-BT solution acquiring the (001) habit. The observed morphological features of the twinned crystal imply that the crystal grows from a low-micron size BT nucleus containing all the twinning elements, such as (111) faces, and serving as twinning sites. The fast growth directions are along the spine (effectively [110]) and <100> (perpendicular to the edge) while growth in the <001> directions is markedly suppressed. The presence of KF in the solution is assumed to stabilize the hexagonal barium titanate phase facilitating the \{111\} twinning (21). However, only small amounts of \(+K\) and \(-F\) ions, from 0.1 to 1.5 at\%, are incorporated on the average into the crystals (23,26), and some workers report that their distribution is inhomogeneous (26). We have verified this claim in the case of our as-grown BT crystals. Compositional analysis was carried out by using energy dispersive X-ray spectroscopy (EDS) in a scanning electron microscope (SEM). The SEM used was a MagellanT XHR 400L (Nanolab Technologies, USA) equipped with high sensitive and ultrafast electron detectors (including scanning-transmission 14-segments BF/DF/HAADF detector). Microanalysis was available with the large area EDS silicon drift detector Oxford X-Max (Oxford Instruments, UK) working on INCA 450 platform.

EDS spectra taken on a number of samples show that in addition to the major constituent atoms of the BT crystals, namely Ba, Ti and O in close to their stoichiometric ratios in BaTiO$_3$, traces of K and F atoms are present. It is known that \(+K\) and \(-F\) ions may readily substitute for the respective Ba$^{2+}$ and O$^{2-}$ ions in BaTiO$_3$, which is frequently named as KF-substitution (24). Appreciable concentrations of K and F atoms are found on the outer (001) surfaces, in the 1 to 2 at\% range. Yet, < 1 at\% of K and even less F (sometimes below the detection limit of 0.1 at\%) are detected at the inner (001) surfaces, on the re-entrant-angle side of the plate. We have, therefore, studied the distribution of the K and F atoms near the outer (001) surface. As-grown BT plates were cleaved perpendicularly to the (001) plane, and the cleaved surfaces near the end of the (100) edge facet were subjected to chemical analysis. Fig. 3 shows the SEM secondary electron image of a crystal area probed, together with the compositional profiles and the corresponding elemental distribution maps.
Fig. 3. SEM secondary electron image of an edge of a KF-BT crystal with elemental compositional profiles (left) and corresponding elemental distribution maps (right).

The analysis extends approximately 15 µm from the edge into the crystal depth. A distinct 3.5 µm thick layer differing in appearance from the bulk crystal is revealed. From studying a great variety of samples, the layer may be up to 10 µm thick. The proportional variations of the major atom concentrations (Ba, Ti and O) are attributed to the topographical roughness of the cleaved surfaces. An intriguing feature is the K and F atoms’ distributions. Their concentrations are maximal at the layer outer surfaces with 4-5 higher peak values than in the bulk. In thicker layers, additional K and F concentration peaks may emerge in-between. These peculiarities can be explained by considering the kinetics of both the “butterfly wing” crystals growth and the FE-PE phase transformation.

We recall that the wings of the twinned crystal develop by concurrent rapid growth away from the spine initially by rapid growth in a [100] direction and furthermore as a result of the spreading of additional growth layers which are found on the re-entrant-angle side of the (001)-plates forming the wings of the twinned crystal. This implies that a few microns thick plate forms at the first stage, at the highest growth temperature, and eventually it does not grow outwards, but rather inwards. We presume that the re-entrant angle which results from the combination of (001) habit and (111) composition plane appears to provide permanent steps for nucleation of growth layers which thicken the crystal as the growth proceeds at lower temperatures. This may explain the appearance of the double KF-layer (Fig. 3) forming at the initial high-temperature stage of growth. Such layer is prone to affect the ferroelectric structure of the BT crystal on cooling through the PE-FE phase transition temperature, the Curie point. The clearly inhomogeneous distribution of the KF impurities causes local lattice mismatches and, therefore, mechanical strains which induces the formation of a square-net ferroelectric multi-domain structure, the “Forsbergh net”, that lowers the total energy of the lattice (34). The impurities at the layer borders (see Fig. 3) pin the domains and confine them to the layer. The latter may become slightly additionally strained and bended when the concentrations of impurities at its opposite side are unequal, like in a bimetallic. When looked at in the electron backscattering mode, the layer appears as a material with a density distinctly different from the bulk. Also, one of us had observed earlier the “Forsbergh net”
domin structure in the Remeika-grown BT crystals by means of polarized optics (35). Earlier work on ferroelectric domain switching and electron-mirror microscopy in such crystals revealed the existence of 0.7 to 12.5 µm surface layers as well (36).

3.3 Relaxor Properties

The ferroelectric properties of the FE-PE phase transition in butterfly twin BT crystals have been studied using a combination of the complex dielectric permittivity (\( \varepsilon = \varepsilon' + \varepsilon'' \)) measurements and the AE method. The experimental details are described elsewhere (14). In the present study, typically single wing 5×7 mm² area and 0.5 mm thick samples have been used. Electrical contacts were applied to the triangular surfaces, and the samples were mounted in resistance furnaces equipped with the peripheral systems allowing for simultaneous capacitance and acoustic response measurements. The AE signals in the form of acoustic count rate, \( \partial N/\partial t \), are generally attributed to bursts of radiation related to the stored elastic energy, although the details of the mechanism are generally system specific. In particular, the formation of a ferroelectric domain structure due to relaxation of mechanical stresses on the boundary between paraelectric and ferroelectric phases has been evidenced through the appearance of AE responses both in normal and relaxor ferroelectrics (14,37).

Fig. 4. Temperature dependences of the real and imaginary parts of dielectric permittivity (left scale) and AE count rate (right scale) of a KF-BT crystal at 0.1, 1.0 and 10.0 kHz frequencies. Notes for AE: squares - 0.1 kHz, triangles - 1.0 kHz, circles - 10. kHz, bottom - AE noise.

The cumulative results obtained with BT crystals grown from KF fluxes are presented in Fig. 4. Temperature dependences of both the real and imaginary parts of the permittivity, \( \varepsilon' (T) \) and \( \varepsilon'' (T) \) have been measured at 0.1, 1.0 and 10.0 KHz frequencies on heating from room temperature. However, only a relatively narrow temperature interval, 100-130°C, associated with the tetragonal to cubic (FE-PE)
phase transitions is featured in the figure. The 0.1 kHz $\varepsilon' (T)$ curve contains two quite well resolved peaks, $T'_c$ and $T''_c$, at about 116 and 122 °C respectively. As the measurement frequency is increased to 1.0 KHz, the low-temperature peak moves to higher temperatures and diminishes in size, and it turns into a barely distinguishable shoulder under the high-temperature peak at 10.0 KHz. This constitutes a typical relaxor-type behavior in ferroelectrics (10,11), and we assign the $T''_c$ dispersion to the surface layer relatively rich in KF impurities. In contrast, the high-temperature peak practically does not shift from the $T'_c = 122$ °C value typical for the classical BaTiO$_3$ ferroelectric, and we attribute it to be the diffuse ferroelectric Curie point in the crystal bulk. Indeed, the bulk contains almost an order of magnitude lower concentration of KF, which is too small to produce an RFE. However, the presence of a certain amount of $\text{K}^+$ and $\text{F}^-$ ions randomly distributed in the crystal matrix broadens the $T_c$ peak without dispersion (31).

The temperature dependence of the imaginary part of the dielectric permittivity is quite remarkable. The $\varepsilon'' (T)$ peaks shift to the right as the measurement frequency increases, like $\varepsilon' (T)$, showing clear dispersion, or an RFE behavior. The $\varepsilon'' (T)$ bands are broad reflecting the broad distribution of relaxation times associated with the presence of a large number of small ferroelectric domains, the intersecting groups of multiple laminar domains forming the “Forsbergh net” during the cool down through the Curie point. However, the shoulder at about 120 °C related to the bulk ferroelectric phase transition and appearing at the right sides of all three $\varepsilon'' (T)$ curves does not show any sign of dispersion, as expected. Most importantly, the peak temperatures of the $\varepsilon'' (T)$ curves can be readily determined, unlike the peaks of the $\varepsilon' (T)$ curves that are obscured by the more intense and broad $T'_c$ band. Concurrently, the AE activity has been monitored on heating the sample in course of dielectric measurements at all three frequencies. Sharp acoustic responses have been detected exactly at temperatures corresponding to the $\varepsilon'' (T)$ curves peaks, or maximal losses within the “Forsbergh net” layer, and a less intense count rate at the bulk $T_c$. Indeed, strong AE is induced by the movement of ferroelectric domain walls (37). The maximum velocity of the ferroelectric domain growth is also known to be of the order of the velocity of sound (38). We can now compare the $\varepsilon''$ and AE peak temperature of 110 °C taken at 0.1 kHz with the phase diagram of KF-doped BT crystals (39) based on dielectric measurements carried out at a close to our frequency of 0.3 KHz. We deduce from the phase diagram that the 110 °C tetragonal to cubic phase transition corresponds roughly to a KF concentration of 1.5 at%, which is excellent agreement with our experimental EDS measurements indicating that the K and F concentrations on the impurity-rich surfaces of our samples is in the 1-2 at% range.

We can also studied twinned BT crystals grown from mixed KF-NaF fluxes, but obtained negative results in terms of their relaxor properties. The dielectric permittivity curves show no visible dispersion, although the $T_c$ peak is broad and shifted to a higher temperature of 130 °C. This resembles the diffusive transition character observed also in Ba$_{1-x}$Na$_x$Ti$_{1-x}$Nb$_x$O$_3$ ceramics at low $x$-values. Therefore, addition of NaF to the flux does not yield crystals with useful relaxor properties. On the contrary, BT crystals grown from pure KF-fluxes reveal tangible relaxor behavior in the surface layer. Fig. 2 shows that the latter typically has a complex double-layer structure in terms of the enhanced KF concentration. The outer layer is, in fact, less than 1 µm thick and can be considered as a naturally grown thin film. Therefore, the Remeika-grown BT “butterfly wings” can be used for developing relaxor ferroelectric thin films as capacitors (40) or as substrates for depositing additional films and
producing complex, e.g. multiferroic, structures for numerous thin film electronic applications (41). Higher dielectric constants, piezoelectric coefficients and electromechanical coupling factors can be obtained with increased KF-dopant concentrations of 9-10 mol% (19,27), which presumably can be achieved by modifying the parameters of the Remeika growth process. The appropriate experiments are currently underway.

4. CONCLUSIONS

BT single crystals grown from KF fluxes by the Remeika method in the form of “butterfly wings” exhibit interesting morphological, compositional and dielectric properties. Both constituent flux ions, K+ substituting for Ba2+ and F− for O2−, are incorporated into the BT matrix in course of growth, but the KF distribution is highly inhomogeneous. The outer (001) surfaces of the wings contain almost an order of magnitude higher concentrations of K+ and F− relatively to the crystal bulk, close to 2 at% each. Moreover, the impurity ions typically form a double-wall layer (see Fig. 2) enveloping and pinning to the surface a few microns thick ferroelectric domain net. This layer is found to display dielectric properties different from the normal ferroelectric BT bulk. It shows a typical RFE behavior which is manifested in clearly diffuse FE-PE phase transition with broad and dispersive dielectric permittivity maxima, $T_m$. The real part of the layer’s dielectric permittivity appears as a weak shoulder under the strong $T_c$ peak belonging to the bulk at measurement frequencies $\geq 1.0$ kHz. However, the broad imaginary permittivity peaks, together with the sharp AE responses, allow to determine accurately the phase transition temperatures at each frequency. The outer surface of the layer is less than 1 µm thick, and it can serve as an element in thin film ferroelectric and multiferroic devices as well as a substrate for additional complex perovskite structure thin films.

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