# Electrical and Optical Properties of Dielectric BaTiO₃ Single Crystals Prepared by Flux Technique

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## Abstract

Single-crystal plates of $BaTiO_3$ have been prepared for the first time by flux technique. Both smooth and highly porous crystals were grown depending on growth temperature and rate of cooling. Grown crystals contained an unidentified, low-symmetry barium titanate modification. Annealing at 500-900 °C converted the crystals to the cubic phase, while annealing at 1000 °C produced the tetragonal phase and an increase in the grain size. Grown and annealed crystals were highly dielectric with DC resistivity in the $10^{10}$-$10^{12}$ $\Omega$.cm range. AC resistivity decreased with frequency following a power-law dependence with an exponent of -0.6 to -0.7. Both resistivity and capacitance remained stable at temperatures to 400 °C. The effective dielectric constant (20-25 at 10 kHz) was possibly determined by amorphous grain-boundary region with high density of traps.

## الخلاصة

تم تحضير رقائق لأول مرة من تيتانيت الباريوم $BaTiO_3$ بطريقة المذيب. تم الحصول على بلورات صقيلة وأخرى مسامية إعتمادا على درجة حرارة الأنماء البلوري ومعدل التبريد. البلورات الناتجة كانت قليلة التماثل لذلك تمت عملية التلدين للبلورات. التلدين في درجات حرارة بين 500-900 درجة مئوية يحول البلورات الى طور المكعب, بينما التلدين عند 1000 درجة مئوية ينتج الطور الرباعي مع زيادة في الحجم الحبيبي. البلورات المحضرة والملدنة أظهرت مقاومة عالية للتيار المستمر في حدود $10^{10}$-$10^{12}$ أوم.سنتمتر. تنخفض المقاومة للتيار المتناوب مع التردد إعتمادا على قانون القدرة بقيمة أسية عند 0.6- إلى 0.7-. المقومية والسعة بقيت مستقرة عند 400 درجة مئوية. ثابت العزل الفعال (20-25 عند 10 كيلو هرتز) حدد في منطقة الحدود الحبيبية العشوائية مع الكثافة العلية للمصائد.

## Introduction

Barium titanate, $BaTiO_3$, is considered an attractive advanced material. Considerable research has focused on single-crystal and ceramic $BaTiO_3$ which have found many applications, such as dielectric layers, ferroelectrics, sensors, capacitors (Liu *et al.,* 1993), waveguides,(Gill, 1996) and luminescent materials.(Block & Wessels, 1994). The interest in the $BaTiO_3$ has increased recently due to the need for high-dielectric-constant materials for ferroelectric RAM and bypass capacitors(Golego *et al.,* 1998). The paraelectric cubic phase of $BaTiO_3$ is generally preferred for such applications because it has greater temperature stability than the ferroelectric phase and lacks sharp changes in structure and dielectric constant associated with the phase transitions in the latter. In addition, the paraelectric phase is thermodynamically favored for submicrometer polycrystalline $BaTiO_3$ due to grain-size effect.(Takeuchi *et al.,* 1997)

Much effort has gone into obtaining high-quality dielectric single crystal barium titanate by several methods; including melt growth, flux technique technique, electrochemical and electro hydrothermal methods. In the present paper, an alternative method, flux technique, is proposed for the growth of single crystal barium titanate. We have successfully employed flux technique for growing single crystals of $BaTiO_3$. It was shown elsewhere (Mohammed, 2005), that when an access of the $LiF-BaF_2$ was used, the growth temperature could be lowered significantly as compared to commonly used fluxes. This allows for growth of $BaTiO_3$ single crystal at low temperature, which is attractive if the processing of the material is to be integrated into the electrical and optical applications.

## Experimental Section

The flux growth setup and solid state preparation of $BaTiO_3$ have been reported in detail elsewhere. (Mohammed, 2005) The powder of $BaTiO_3$ was prepared by using equimolar mixture of $BaCO_3$ and $TiO_2$. The starting powder has been heated to 1100 °C for 24 hours in air in platinum crucible. Several kinds of combinations could be used as a solvent

of $BaTiO_3$ in their melt phase. The "KF" type is the preferred flux to obtain high quality single crystal of $BaTiO_3$ (Sekiya *et al.,* 1984). In this project, two types of fluxes were selected. The first one was an equimolar mixture of $LiCl-BaCl_2$, which required $1300^oC$ heating temperature to change it to the liquid phase. The second flux selected, successfully, to grow a single crystal of $BaTiO_3$ was a mixture of KF and $BaF_2$ which has physical and chemical properties suited and simplified Remaika's method for $BaTiO_3$ crystal growth. The melting point of the mixture is lower than 1200 $^oC$, that no chemical reaction with $BaTiO_{3,}$ which occurs after 1200 $^oC$ point.

A powder of $BaTiO_3$ has been introduced in a platinum crucible and covered by a flux with different weight ratio of $BaTiO_3$: flux and then, the crucible covered with platinum lid. The reaction was carried out in the electric furnace at a temperature of about 1200-1300 $^oC$ for 24 hours. The mixture was cooled down to 850 $^oC$ with cooling rate of 4-8 $^oC/hr$. At the point 850 $^oC$, the crucible was tilted in order to drain the melt flux. The crucible in an upside-down position was held in the furnace at 850 $^oC$ for 10 hours. Finally, it is cooled to room temperature at a rate of 10 $^oC/hr$. The temperature of melt was measured for each flux. The weight ratio of $BaTiO_3$: flux mixture depends on temperature point of melt. The yield was a multy-layer of thin plates (1-5 mm) thickness.

The crystals were investigated using scanning electron microscopy (SEM) on a Hitachi S-570 microscope equipped with energy-dispersive spectroscopy (EDS) microanalysis system. Structural analysis of the crystals was done using X-ray diffraction (XRD) on a Siemens Kristalloflex diffractometer with Cu KR radiation. The resolution in the whole studied $2\theta$ range, 20-60°, was high enough to resolve the KR1-KR2 doublet. The R2 lines were subtracted from the experimental diffraction data. UV-vis optical absorption spectra were recorded on a Shimadzu UV-160U double-beam spectrophotometer from 200 to 1100 nm. Some of the crystals were annealed in a quartz reactor for 2-5 h at temperatures from 500 to 1000 °C in different ambients (argon, hydrogen, air).

Aluminum and platinum contacts (100-400 nm thick) were RF-sputtered in argon at 10 mTorr. A mask was used to deposit several circular electrodes 1 mm in diameter. In some cases, conductive ITO or aluminum was used as a back contact. Conductivity measurements were performed on a homemade high-impedance setup in a constant voltage mode using a Hewlett-Packard E3612A voltage source (0-120 V DC) and Keithley 485 autoranging picoammeter ($10^{-13}$ A sensitivity). A solid metal Faraday cell was used to reduce electromagnetic interference noise. Carrier mobility and concentration were determined from Hall effect experiments on a homemade apparatus[8,9] in a magnetic field of 0.8 T using Keithley 220 programmable current source ($10^{-1}-(5x10^{-13})A$) and Keithley 197 autoranging digital multimeter. In all cases, the contacts were verified to be ohmic by a current-voltage sweep.

Current-voltage characteristics were recorded on a digital recording oscilloscope (Nicolet Instrument Co., model 2090- IIIA) connected to a computer and a sweep generator-potentiostat assembly. Dielectric parameters of the material were obtained with blocking electrodes from complex impedance measurements using a Solartron 1173 frequency response analyzer with a 1186 interface in the 10 Hz to 1 MHz range in a planarcapacitor geometry.

**Table 1: Flux Technique Growing Conditions for $BaTiO_3$ Single Crystals Shown in the Corresponding Figures**

| figure | Flux type | weight ratio $BaTiO_3$: flux | initial temperature ($^{o}$C) | cooling rate ($^{o}$C/h) |
|--------|-----------|------------------|------------------|-----------|
| 1a,b | $KF-BaF_2$ | 40 : 60 | 1200 | 4 |
| 2a,b | $LiCl-BaCl_2$ | 25 : 75 | 1200 | 6 |
| 2c,d | $LiCl-BaCl_2$ | 20 : 80 | 1260 | 7 |
| 2e,f | $LiCl-BaCl_2$ | 15 : 85 | 1300 | 8 |

## Results and Discussion

Depending on the growth rate and flux temperature point, $BaTiO_3$ single crystals were grown with a variety of morphologies. The growth conditions of several crystals are shown in Table 1. Generally, the temperature and growth rate dependence followed that previously observed and reported in detail for KF flux. (Mohammed, 2005) 1Using low growth rates (below 5 $^{o}$C/h), smooth, optical-quality crystals were obtained (Figure 1a). They were thin (under 2 mm) and transparent below the intrinsic absorption edge. A small number of round particles less than 300 nm in diameter were present on the surface. The cross-section images indicated that these particles sat on top of the crystal and did not penetrate it. It is possible that these particles served as nucleation centers for further crystal growth. They almost entirely disappeared after annealing at 900 °C (Figure 1b). No cracking or peeling was observed for annealed samples (Figure 1b). A different type of crystal was grown from more weight ratios at higher growth rates (6-8 $^{o}$C/h). These crystals were thick (2-5 mm) and opaque, and SEM revealed a high degree of porosity, as seen in Figure 2. Surface roughness increased in comparison to the optical quality crystals. Low melt temperature, around 1200 °C, gave thick, highly porous crystals (Figure 2a). Annealing caused crystallization and significant changes in surface morphology (Figure 2b), which may indicate that the grown material was amorphous. Crystals grown at higher temperatures (1200-1300 °C) had a less porous structure (Figure 2c) that was not affected by annealing (Figure 2d). It is interesting that distinctly crystalline crystals can be prepared at very high growth rates. In Figure 2e, one can see finely faced crystallites several micrometers in size. These crystallites did not appear to change their shape upon annealing (Figure 2f), although this treatment caused dramatic changes in the crystalline structure as discussed below. Again, both grown and annealed crystals were cracking free (Figure 2).

All grown crystals belonged to a phase that could not be identified. This phase could be a BaO-TiO2 compound such as barium tetratitanate or other complex titanates. Other likely impurities, such as titanium dioxide, barium carbonate, oxide, or hydroxide, are excluded. None of these compounds was identified from the XRD patterns. In addition, the grown crystals did not change their mass after prolonged treatment with hot water; hence, no water-soluble compounds were present. The analytical balance that was used in the mass change experiments was capable of recording changes as low as 0.1 mg. The mass of a typical 5 mm-thick crystal is on the order of 10 mg, assuming an ideal density of 6 g/cm$^{3}$.
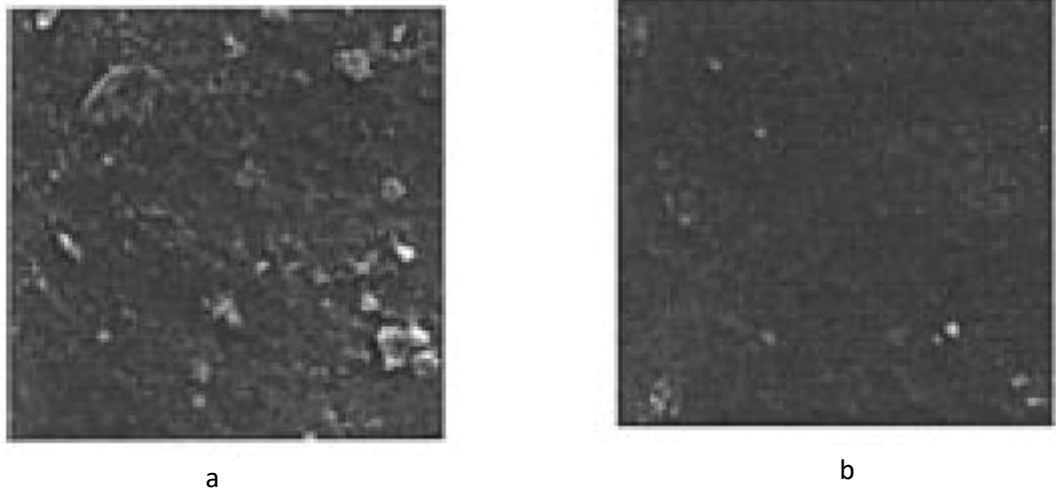
**Figure 1:** SEM images of smooth single-crystal BaTiO$_3$ grown by KF-BaF$_2$

flux at low growing rates, image size 4 × 4 μm.

e                                              f
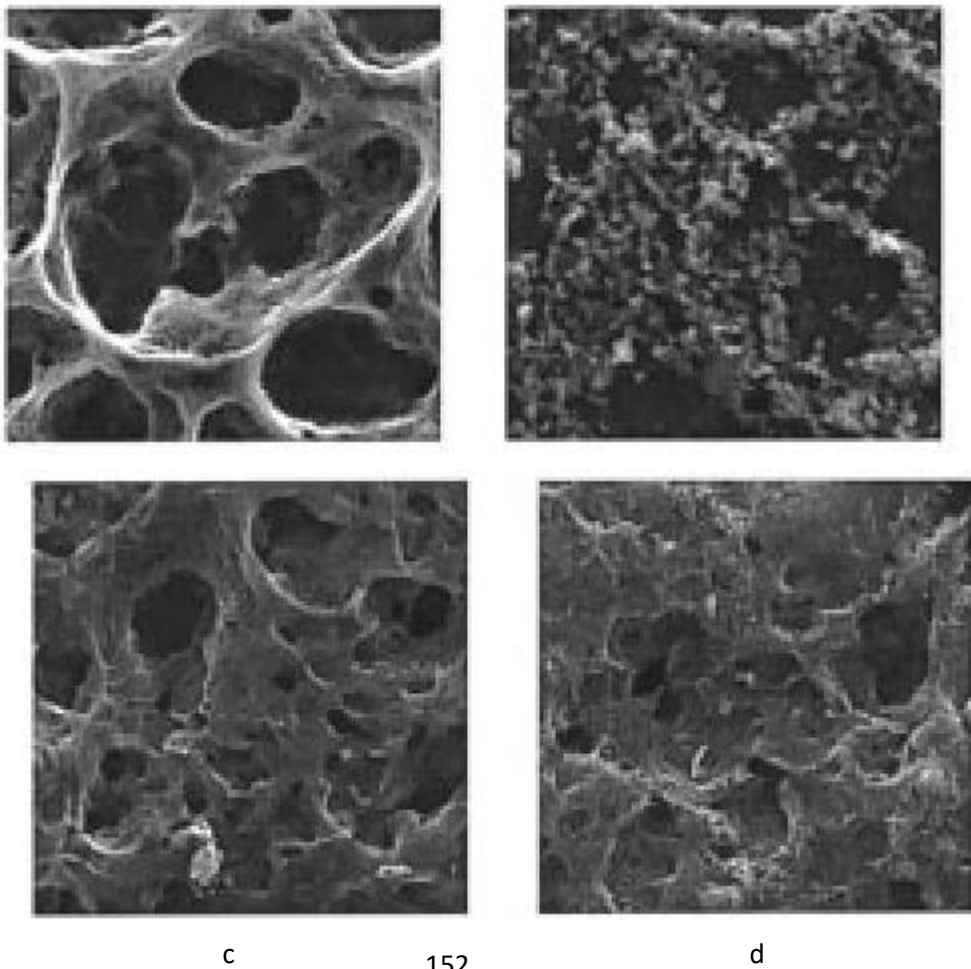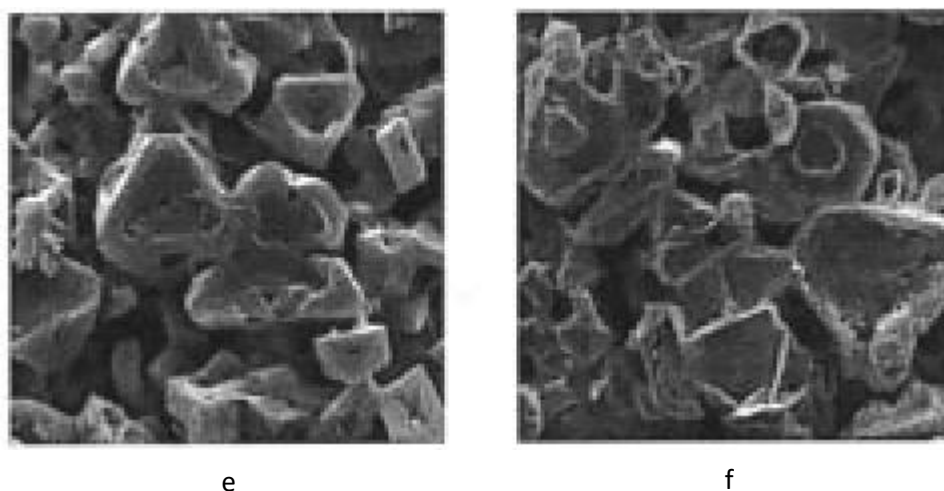
**Figure 2:** SEM images of single-crystal $BaTiO_3$ grown byLiCl-$BaCl_2$ flux at high grown rates (shown in Table 1), image size $20 \times 20$ µm.

(a) grown at 1200 °C.        (b) annealed in air at 600 °C.

(c) grown at 1260 °C.        (d) annealed in argon at 500 °C.

No change was observed in all crystals, although XRD gave low-symmetry peaks of magnitude comparable to that of cubic barium titanate. If this had been an impurity to the latter, its mass should have been a large fraction of the crystal mass.

The presence of non-crystalline material is excluded. Although, as has been shown previously,(Sekiya, 1984; Mohammed, 2005) flux growth at low temperatures can produce crystals that are not fully crystalline, the growth temperature in the present work was not less than 1200 °C. The KF flux has been shown(Mohammed, 2005) to decompose fully at 1200 °C; therefore, it could not have been present in the crystals. While barium carbonate is a more stable compound, it was not identified on XRD. Besides, its decomposition during annealing would have changed the mass of the crystal, but no change was observed.

It is proposed that the grown crystals contained a low-symmetry barium titanate phase, possibly a complex barium titanate. Indeed, as seen in Figure 3b, the diffraction pattern of the grown crystals is an extension of that of cubic barium titanate (Figure 3a). SEM investigation provided additional support. As seen in Figure 2e,f, the phase transition from grown phase to cubic barium titanate associated with mild annealing at 500 °C (Figure 3c) did not affect the morphology and crystallite shape of the crystalline crystals. No change in mass or crystal thickness was observed also. Because these results are characteristic of a disorder-order transition, the grown crystal is likely a low-symmetry phase.

Because several samples of ceramic $BaTiO_3$ that were used as reference had the same XRD pattern as the annealed crystals, these crystals were unambiguously identified as cubic barium titanate. Annealing at 500-900 °C did not change the crystalline structure of the material (Figure 3c-e). However, a 1000 °C anneal caused partial phase transformation into the ferroelectric tetragonal barium titanate (Figure 3g) as illustrated more clearly in Figure 4.
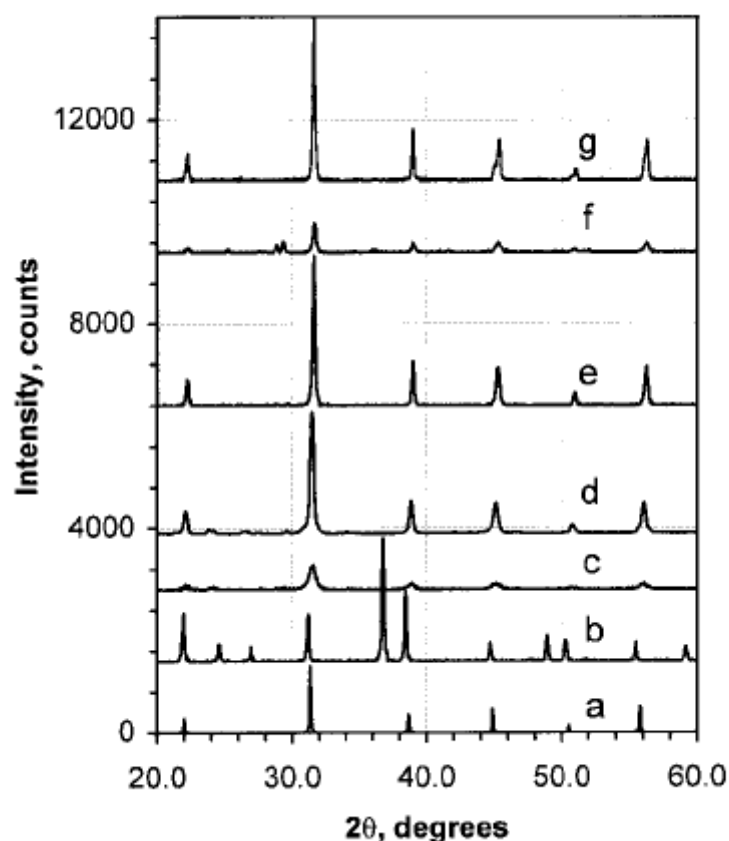
**Figure 3:** XRD pattern of single-crystal BaTiO₃ grown byLiCl-BaCl₂ flux and annealed at different temperatures in different ambient:

(a) theoretical cubic.

(b) grown at 1250 °C.

(c) annealed at 500 °C in argon.

(d) annealed at 600 °C in air.

The XRD peak positions in Figure 4 also indicate that annealing caused a small decrease in crystal lattice parameters. Similar behavior was observed for barium titanate crystals prepared by solgel growth((Nishizawa & Katsube, 1997; Takeuchi *et al.,* 1997) and ion-beam evaporation. (Sonegawa *et al.,* 1996) It is typically associated with temperature-induced grain growth that removes grain size effects and permits formation of the tetragonal phase. This behavior was confirmed in the present study: a distinctly granular structure is evident in the crystals annealed at 1000 °C (Figure 5c,d) as compared to grown crystals (Figure 5a,b).
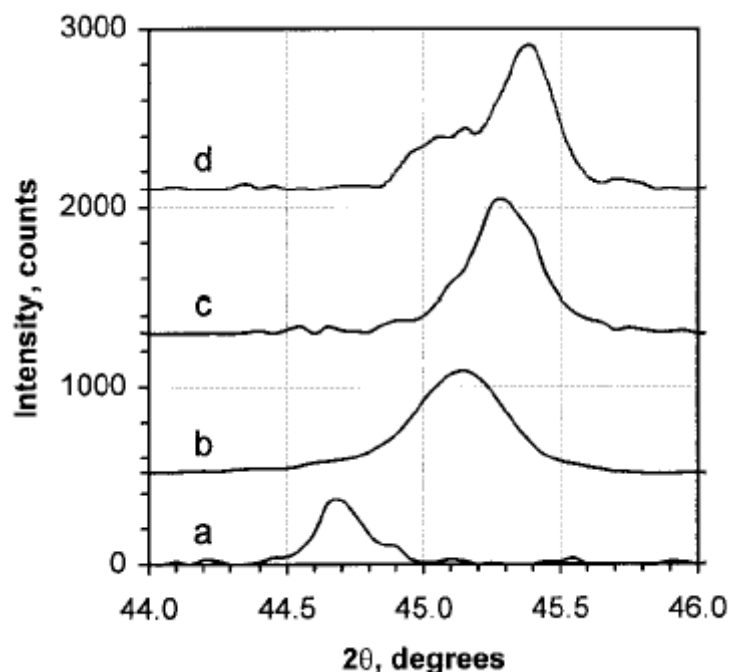
**Figure 4:** Enlarged XRD pattern of single-crystal BaTiO$_3$ grown by LiCl-BaCl$_2$ flux and annealed at different temperatures in air:

(a) grown at 1250 °C. (b) 600 °C.   (c) 900 °C.   (d) 1000 °C.

The cross-section images of both crystals (Figure 5b,d) showed that the crystals were dense and that the thickness did not change after annealing. The difference in annealing ambient (hydrogen, argon, or air) had no effect on the crystal morphology. However, annealing at 900°C in hydrogen caused crystals to become more conductive. In addition, new peaks appeared on the XRD pattern of the hydrogen-annealed crystals (Figure 3f).

One should keep in mind that the identity of the crystals was additionally confirmed by other analytical methods such as XRD and UV-vis absorption spectroscopy.
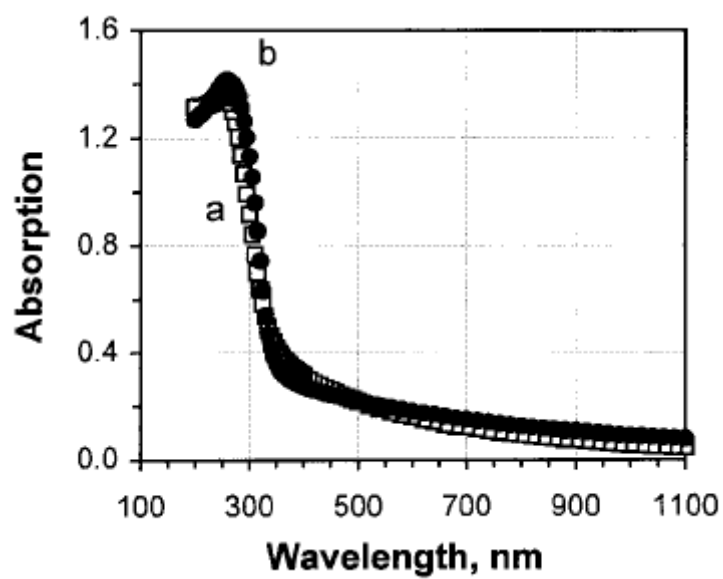
UV-vis optical absorption spectra of the crystals showed that they were transparent below the band gap (Figure 6). Annealing did not change the spectra (Figure 6b vs a), even for hydrogen-annealed crystals, although the band edge sharpened somewhat for crystals annealed at high temperatures, 900-1000 °C, probably resulting from crystal crystallization. Earlier reports of the optical band gap for single-crystal BaTiO$_3$ varied considerably from 2.95(Lu, 1996) to 3.95 eV.(Kamalasnan, 1994) Most of these values were calculated from optical absorption spectra using a parabolic conduction band approximation. Although it appears valid for certain well-studied semiconductors, this approach may not be as precise for wide-band gap, perovskite materials such as BaTiO$_3$. Calculations of band structure[15,16] indicate that perovskite materials cannot be easily identified as either direct or indirect band gap semiconductors. Large conduction zone anisotropy and nearly flat zone regions that lead to two-dimensional conduction bands[16] may render the parabolic conduction band approximation invalid. Optical band gap values obtained in this way may not be precise and may only be useful for comparison of relative values.

For comparison with previous data, indirect and direct band gap values were calculated from the optical absorption spectra using the above-mentioned model. As shown previously, (Ali, 2007) a better fit is obtained by including the dependence of the refractive index on the photon energy. Values of 3.1- 3.2 and 3.7-3.8 eV were obtained for indirect (Figure7) and direct (Figure 8) band gap extrapolation, respectively. As evident from Figures 7 and 8, annealing did not affect the band gap values. Since the crystals did not show any appreciable photoconductivity with 365 nm (3.4 eV) light, the direct band gap value seemed to be the preferred one.
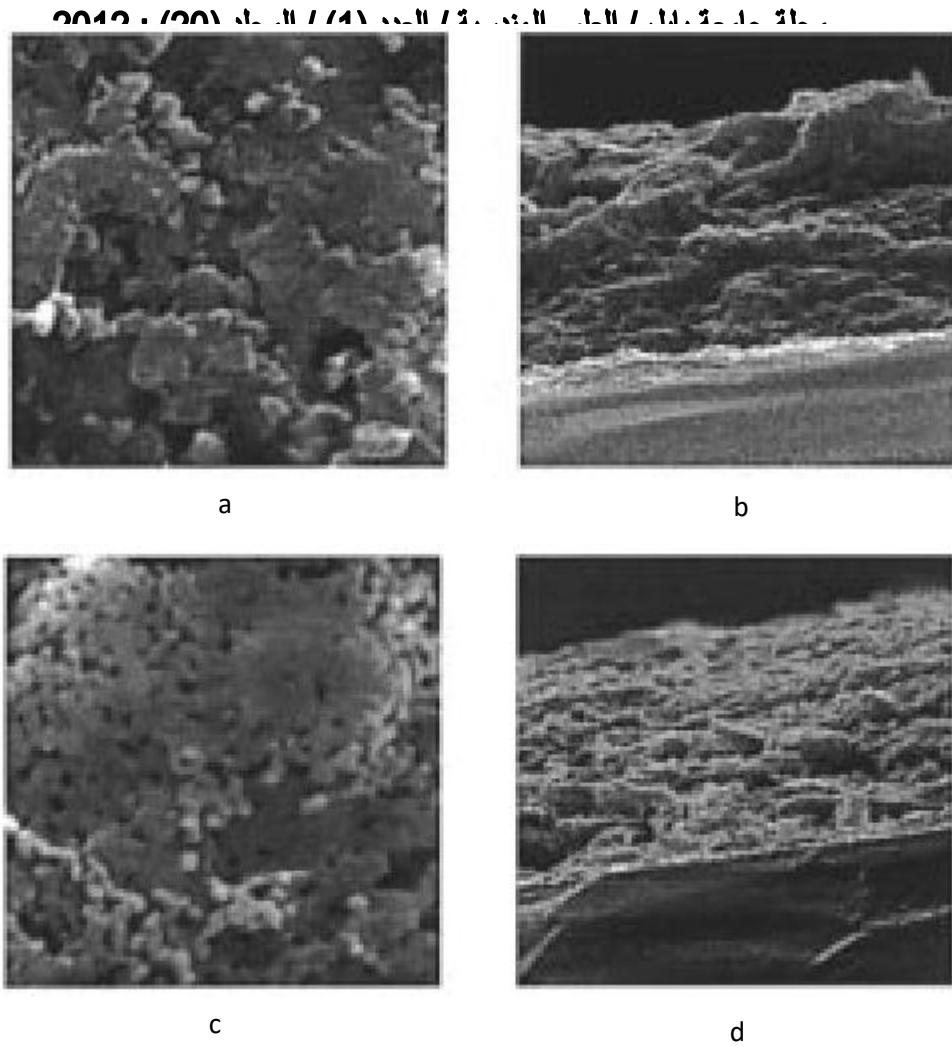
**Figure 5:** SEM images of single-crystal BaTiO$_3$ grown by LiCl-BaCl$_2$ flux (a, c, top view, image size 4 × 4 μm, b, d, cross-section, image size 10× 10 μm):

(a, b) grown at 1250 °C.      (c, d) annealed in air at 1000 °C.



**Figure 6:** Optical absorption spectra of single-crystal BaTiO$_3$ grown by KF-BaF$_2$ flux:

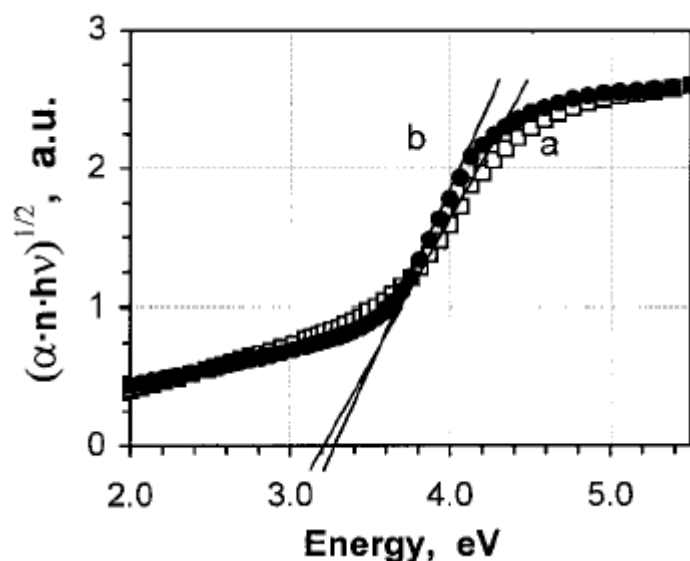(a) grown at 1200 °C.      (b) annealed in air at 1000 °C.

The crystals were very resistive: $10^{10}$ Ω.cm grown and more than $10^{12}$ Ω.cm after annealing. Similar resistivity values were reported previously for crystals prepared by other techniques. (Kuwabara *et al.,* 1993;Mohammed *et al.,* 1996). This large resistivity caused high shot noise in the Hall experiments and dictated the limit of detection of the Hall voltage, which was around 200 μV. Using this limit, the following parameters were estimated: carrier mobility of less than 0.5 $cm^2$/(V.s) and carrier concentration of more than $10^{12}$ $cm^{-3}$. The conductivity type was not determined. Up to 400 °C, the temperature dependence of the conductivity was very weak, implying that neither sub-band-gap states nor band-gap transitions were thermally excited at these temperatures. It is evident from these results that the crystals possessed good dielectric properties.

Complex impedance measurements were performed on Al/$BaTiO_3$/Al and ITO/$BaTiO_3$/Al planar capacitance structures and interpreted in terms of a parallel RC circuit. The real part of impedance, or AC resistivity, was frequency-dependent (Figure 9) and could be fitted to a power law dependence $R \approx \omega^{\alpha}$, with α about -0.6 to -0.7. A similar decrease in resistivity of the crystals with the increase in frequency was observed for solgel prepared crystals,(Kamalasanan *et al.,* 1993) and the authors suggested it was due to trapped charge carriers. In polycrystalline $BaTiO_3$, these traps may be localized at oxygen-related grain-boundary states(Zhu *et al.,* 1996; Russell *et al.,*1996) that were found to dominate electron transport in many polycrystalline oxides such as $TiO_2$ (Golego, *et al.,* 1998) and ZnO.(Studenikin *et al.,* 1998) This model is consistent with the increase in resistance at lower frequency because grain boundaries are very thin and, therefore, have a much larger capacitance, which manifests itself in the lower frequency region. As a result, the resistivity of grown crystals obeyed the power-law dependence in the whole range of the frequency (Figure 9b). On the other hand, the resistance of annealed crystals leveled off at 10 kHz (Figure 9a), indicating that grain bulk states began to make a contribution at higher frequencies as crystal size increased.

Both resistance and capacitance were stable with temperature. This agrees with the proposed model in which capacitance is determined by temperature independent grain-boundary capacitance.[21,25,26] The bulk capacitance, which presumably follows the Curie-Weiss law, is expected to show up at a much higher frequency than we were able to attain with our setup. The effective dielectric constant of the crystals showed a characteristic dispersion with frequency (Figure 10) and was equal to 20-25 at 10 kHz, consistent with the values reported previously Chen *et al.,* 1985; Liu, *et al.,* 1993; Sonegawa *et al.,* 1996; Cho *et al.,* 1997) Crystals annealed at 1000 °C had the tetragonal structure suitable for ferroelectric behavior. Unfortunately, this behavior could not be studied because the high-temperature destroyed the back-contact.



**Figure 7.** Indirect band gap extrapolation for single-crystal $BaTiO_3$ grown by KF-$BaF_2$ flux:
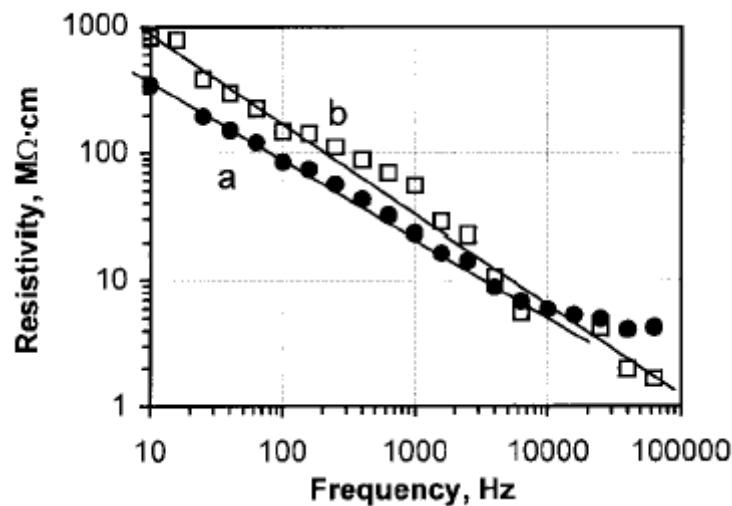
(a) grown at 1200 °C.          (b) annealed in air at 1000 °C.
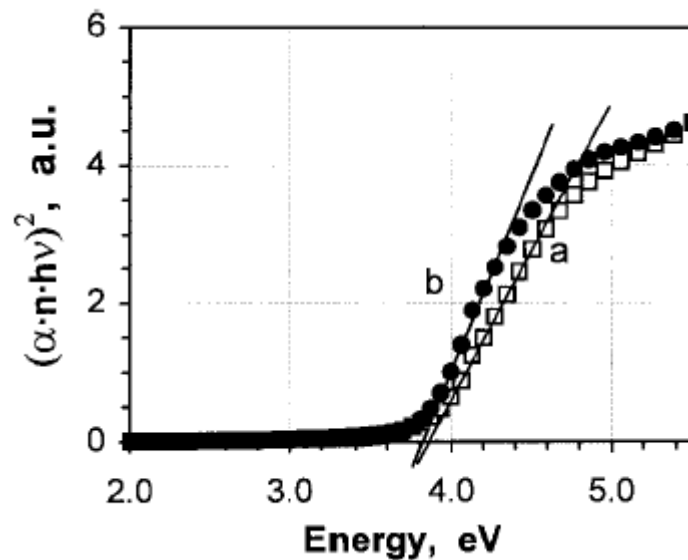
**Figure 8.** Direct band gap extrapolation for single-crystal $BaTiO_3$ grown by $KF$-$BaF_2$ flux:

(a) grown at 1200 °C,        (b) annealed in air at 1000 °C
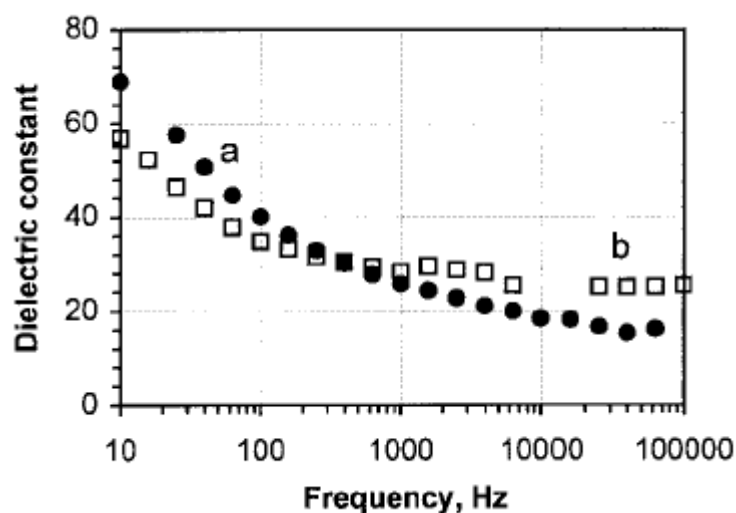


**Figure 9.** Frequency dependence of resistivity for single-crystal $BaTiO_3$ grown by $LiCl$-$BaCl_2$ flux:

(a) annealed in argon at 500 °C,        (b) grown at 1300 °C

## Conclusions

Stoichiometric single-crystal $BaTiO_3$ has been prepared for the first time by flux technique. Either closely packed or highly porous crystals could be grown by regulating the growth temperature and cooling rate. Grown crystals contained an unidentified, low-symmetry barium titanate phase. Annealing at 500-900 °C converted the crystals to the cubic phase, while annealing at 1000 °C caused formation of the tetragonal phase and a corresponding increase in the grain size. Grown and annealed crystals were dielectric with DC resistivity in the $10^{10}$-$10^{12}$ Ω.cm range. The AC resistivity decreased with increased frequency and followed a power-law dependence that may be due to grain-boundary traps. Both resistivity and capacitance remained stable at temperatures up to 400 °C. The effective dielectric constant was 20-25 at 10 kHz.

**Figure 10.** Frequency dependence of dielectric constant for single-crystal BaTiO$_3$ grown by LiCl-BaCl$_2$ flux:

(a) grown at 1300 °C      (b) annealed in argon at 500 °C

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