



Growth and Properties of CaTiO_3 Single Crystal Fibers

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Abstract. Single crystal fibers of CaTiO_3 have been grown by the Laser Heated Pedestal Growth (LHPG) method up to several cm in length with diameters of 500–700 μm . The crystals, characterized by X-ray diffraction analysis, have the distorted orthorhombic perovskite structure. Dielectric constant, dielectric loss and temperature coefficient of resonant frequency along the $[101]_o$ and $[010]_o$ (o means orthorhombic unit cell) direction of the crystal were investigated over the temperature range from -250°C to 100°C . The results of thermal expansion measurements up to 850°C reveal no unusual behavior associated with phase transitions. One of the modes of twinning reported by Bowman from optical analysis is confirmed by optical microscopy.

Keywords: calcium titanate, single crystal growth, dielectric properties, thermal expansion, twin

1. Introduction

Perovskites belong to an important class of compounds, which have a wide range of useful properties for applied research and technology. The oxides have the general formula ABO_3 where the larger A cation is surrounded by twelve oxygen ions and the smaller B cation is coordinated by an octahedron of anions [1]. Among them, the mineral perovskite CaTiO_3 is an important one, which has given its name to this class of compounds.

There has been a significant amount of research work reported on CaTiO_3 [2–8]. Bulk CaTiO_3 crystals up to millimeters were grown by the flux method [2,3] and flame fusion technique [4]. Single crystal X-ray structure analysis by Kay & Bailey [2] and Sasaki et al. [5] confirmed the orthorhombic cell having space group Pcmn. Phase transition was investigated based upon X-ray powder diffraction at high temperature [6] and Raman spectra vs. temperature and pressure [7]. Electrical and optical properties of synthetic CaTiO_3 crystal were reported by Linz and Herrington [8]. However, to the authors' knowledge, there have been few reports so far on crystal growth methods for growing CaTiO_3 crystals with good quality and on the dielectric properties of CaTiO_3 single crystal with respect to its crystalline orientations.

In recent years, CaTiO_3 has been given much attention because of its potential as microwave dielectric material [9,10]. It has high dielectric permittivity (186, 1 KHz) and large positive temperature coefficient of resonant frequency (TC_f) (800 ppm/ $^\circ\text{C}$), and as solid solution with MgTiO_3 [9,11] and $\text{La}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3$ [10] the compositions yield 0 temperature compensating effect, i.e. $TC_f=0$. It was found in our earlier studies that the $(\text{Mg}_{0.95}\text{Ca}_{0.05})\text{TiO}_3$ crystal grows as the eutectic mixture of CaTiO_3 and MgTiO_3 crystals with MgTiO_3 as the matrix and CaTiO_3 as needle like crystals parallel to the fiber growth direction [11]. Growth of CaTiO_3 single crystal fibers and the study of their anisotropic dielectric properties are of importance for dielectric device applications, especially for 1:3 (CaTiO_3 : MgTiO_3) composite of microwave dielectric materials.

The Laser Heated Pedestal Growth (LHPG) technique is a powerful tool for rapid growth of small diameter single crystals for both property study and fiber devices [12,13]. The LHPG technique has several unique features that are of special importance for growing CaTiO_3 crystals. These advantages include containerless crystal growth, capability of growing high melting temperature oxides, rapid growth rate, and ease of controlling

growth temperature, rate, and orientation to reach good crystal quality.

In the present study, we report the growth of CaTiO_3 single crystal fibers using LHPG technique to demonstrate the micro-scale engineering capability in obtaining one-dimensional dielectric devices. The dielectric and thermal properties of the grown crystals were studied over a wide temperature range. Finally, the twin structure was investigated by the polarizing microscope.

2. Experiment

The ceramic feed rods were prepared using a conventional mixed oxide method. The 99.9% pure CaCO_3 and TiO_2 (Fisher ChemAlert) powders were mixed stoichiometrically in ethanol for 12 hours. After calcining at 1100°C for 3 h, the proper phase formation was confirmed by X-ray powder diffraction. A non-aqueous binder was added and a large circular pellet was pressed and sintered in air at 1300°C for 5 h. The fired pellet was 92% of theoretical density. The feed rods were then cut from the inner portion of the pellet into $0.70\text{ mm} \times 0.70\text{ mm} \times 25\text{ mm}$ square rods. Feed rods without precipitates or inclusions on their surfaces were chosen for LHPG.

The LHPG equipment used in this work consisted of a power source (water-cooled, tunable flowing gas CO_2 180 W laser), an optical layout, and a growth chamber. The circular laser radiation of the TEM_{00} mode was transformed into an annulus by a reflexicon. The annulus was directed onto a parabolic mirror that focused the radiation back to its focal point, forming the hot zone. An optical pyrometer was used to monitor the shape of the molten zone during growth and to measure the molten zone temperature of the composition. Additional details of this LHPG station can be found elsewhere [14,15].

During the growth, an a-axis oriented (in cubic coordinate system) SrTiO_3 single crystal bar was used as a seed. The CaTiO_3 crystal was pulled upward at a rate of 22 to 30 mm/h, and the feed rod was fed in at a rate of 20 mm/h. Neither feed rod nor seed was rotated. The ratios of fiber pulling rate (V_f) to feeding source rod rate (V_s) is determined according to the law of conservation of mass in steady state,

$$V_s/V_f = (D_f/D_s)^2 \quad (1)$$

Where D_f and D_s are the diameter of the fiber and feeding source rod, respectively. By adjusting the pulling rate and the power of the CO_2 laser, the shape and size of the molten zone can be controlled to reach stable and uniform crystal growth. The size of the laser spot was less than 0.8 mm and the height of the molten zone was around 1.2 mm. The crystals were grown in air at atmospheric pressure.

Measurements of dielectric constant and loss tangent as functions of temperature (-100 to 100°C) at discrete frequencies (ranging from 1 KHz to 100 KHz) were made by using an automated dielectric setup equipped with a HP4274 LCR Meter. An HP4192A RF-impedance analyzer was used for measuring dielectric properties ranging from -250 to -100°C .

Thermal expansion measurements were conducted from room temperature to 850°C using a vertical push-rod dilatometer equipped with a high-sensitivity linear variable differential transformer. Expansion measurements were regulated at $2.0^\circ\text{C}/\text{min}$ using a microprocessor based temperature controller.

3. Results and Discussion

With careful alignment of the feed rod and precise control of the shape and temperature of the molten zone, single crystals of CaTiO_3 were grown successfully using the LHPG technique. Figure 1 shows the LHPG grown CaTiO_3 crystal fibers, 20 mm in length and $500\text{--}700\ \mu\text{m}$ in diameter. The as grown crystals were dark brown in color, and changed to light brown and transparent after annealing in air at 1000°C for 10 h. Optical observations show the two clear facets

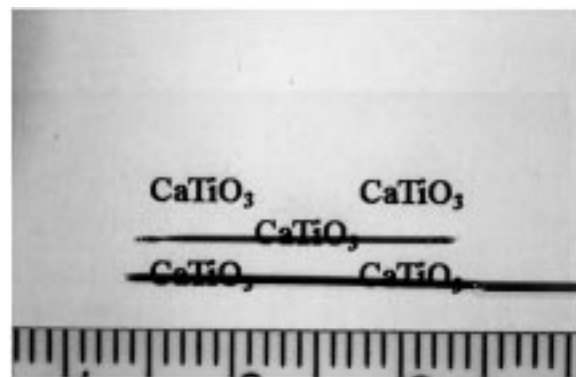


Fig. 1. Photograph of CaTiO_3 single crystal fibers grown by the LHPG technique. Each small division equals 1 mm.

on opposite sides of the fiber, running along the length of the fiber. Parallel to the facets, the crystal fiber can be cleaved along the growth direction with the (010)_o (o means orthorhombic unit cell) surface, which is confirmed by the X-ray Laue diffraction. The crystal fiber growth direction was found to be along [101]_o determined by the Laue back-reflection photograph.

X-ray powder diffraction patterns as shown in Fig. 2, revealed that both the ceramic and crystal fibers contain single CaTiO₃ phase, and have orthorhombic symmetry (based on the Pcmn space group). The crystallographic data for the CaTiO₃ single crystal fibers as determined by X-ray diffraction are: $a = 0.54382$ nm, $b = 0.76371$ nm, $c = 0.53765$ nm, volume = 0.2233 nm³, $Z = 4$, and $\rho = 4.04$ g/cm³. Electron probe micro-analysis (EPMA) of the back-scattered image showed that the as-grown crystal fiber is of single CaTiO₃ phase. No precipitates were found in the crystal fibers. All the samples for property measurement, were cut from the middle section of the fibers.

The dielectric properties of CaTiO₃ single crystals were examined with respect to temperature and crystalline orientations in the rf region. Figure 3 and

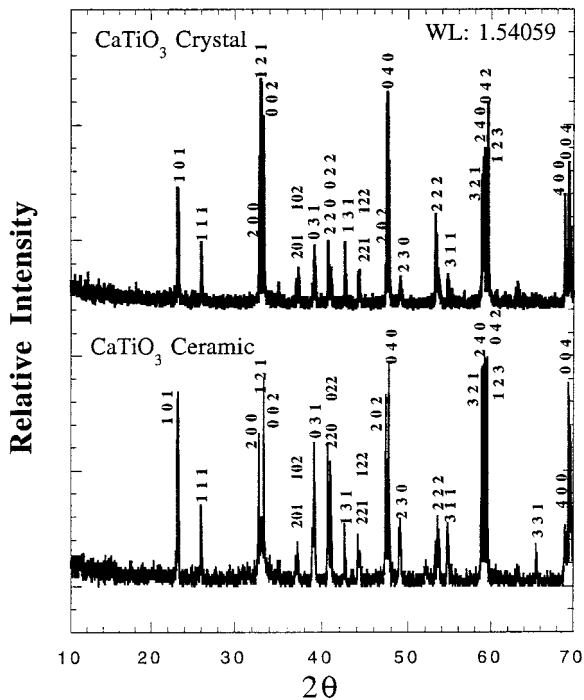


Fig. 2. X-ray diffraction patterns of CaTiO₃ ceramic and single crystal fiber (crushed powder).

Fig. 4 show the temperature dependence of the dielectric permittivity κ and loss factor $\tan \delta$ at 100 KHz. Table 1 summarizes the dielectric permittivity and loss factor at room temperature and temperature coefficient of resonant frequency TC_f between -50°C and 50°C . From Figs. 3, 4 and Table 1, one can see, the dielectric behavior in CaTiO₃ is very similar to that of SrTiO₃ crystals [16], except for the lower dielectric constant and smaller negative temperature coefficient. There is no dielectric anomaly associated with phase transitions in CaTiO₃ crystals present between -250°C and 100°C and the dielectric constant along [101]_o direction is significantly larger than that along [010]_o direction, which is ascribed to the anisotropy of displacement of ions in CaTiO₃ crystal. There is less difference in dielectric loss and TC_f for the [101]_o and [010]_o directions and

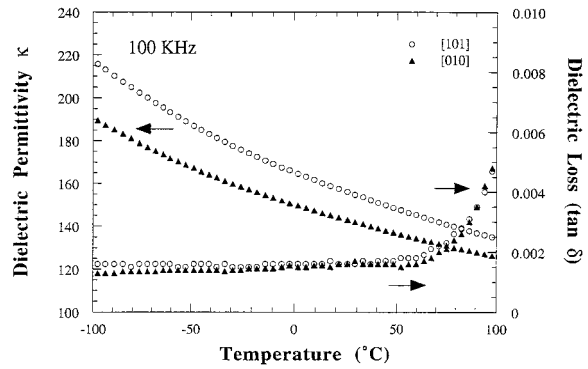


Fig. 3. Temperature dependence of dielectric permittivity and loss factor for CaTiO₃ single crystal fibers along [101]_o and [010]_o directions ranging from -100°C to 100°C .

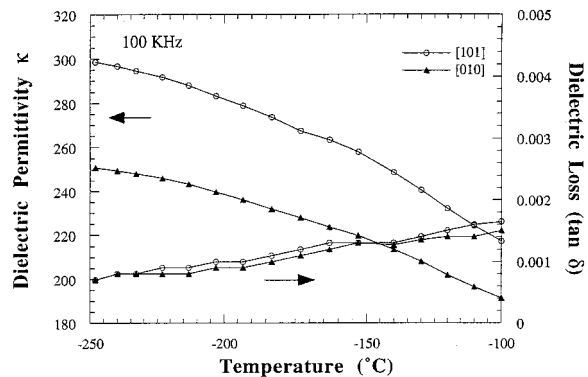


Fig. 4. Temperature dependence of dielectric permittivity and loss factor for CaTiO₃ single crystal fibers along [101]_o and [010]_o directions ranging from -250°C to -100°C .

Table 1. Dielectric properties of CaTiO₃ single crystals

CaTiO ₃ crystal orientation	κ (100 KHz, 25°C)	$\tan \delta$ (100 KHz, 25°C)	TC _r (ppm/°C) (-50°C-50°C, 100 KHz)
[101] _o	155.9	0.0017	1211
[010] _o	142.8	0.0016	1023

no frequency dependence was noted except for the usual space-charge effects.

Thermal expansion analysis was carried out for specimens prepared by cutting crystal fibers perpendicular to the growth direction, with length dimension of about 6.6 mm. The results are shown in Fig. 5. Both ceramic and crystal fibers of CaTiO₃ expanded as the temperature increased and changed linearly and reversibly to 850°C, which occurred reversibly. No significant changes, which could be attributed to a phase transition, are observed in the measured temperature range. CaTiO₃, as a typical A²⁺B⁴⁺O₃ Pcmn-perovskite at ambient conditions, has for a long time been suspected of undergoing phase transitions upon heating: viz orthorhombic-tetragonal-cubic [17]. Most of the experimental evidence for the existence of phase transitions in CaTiO₃ have been reported in the temperature range between 1300 K and 1600 K [6,7,17]. The thermal expansion coefficients of a CaTiO₃ ceramic and crystal fiber (along growth direction) were measured to be $12.2 \times 10^{-6}/^{\circ}\text{C}$ and $11.1 \times 10^{-6}/^{\circ}\text{C}$, respectively on the temperature range 30 to 700°C.

Single crystals of CaTiO₃ were oriented, cut and polished to parallel smooth surfaces with their

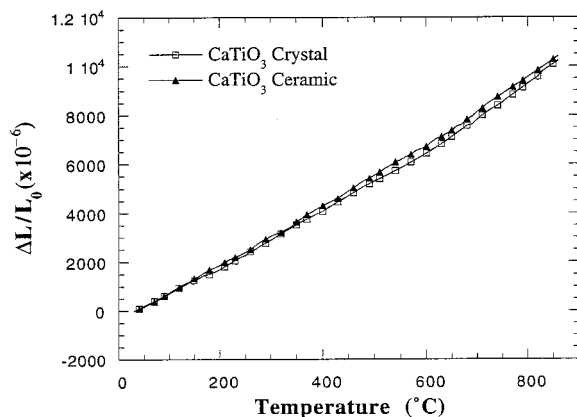


Fig. 5. Thermal expansion of CaTiO₃ ceramic and crystal fiber parallel to the growth direction.

normals along the [010]_o direction. Both top and bottom surfaces were polished to optical quality with 0.5 μm diamond powder. The domain structure was observed using a Zeiss Axioshop optical polarizing microscopy with transmission beam model. During the observation, the polarizer and analyzer were perpendicular to each other. Figure 6 is a typical optical micrograph of the twin structure of the orthorhombic phase in a CaTiO₃ single crystal at room temperature. Two sets of twins, with domain walls approximately perpendicular to each other, can be observed as reported earlier by Bowman [18] and Kay & Bailey [2]. These are the most common forms of twinning in CaTiO₃. Other two types of complex twinning reported in the natural CaTiO₃ crystals [18] have never been observed in our synthetic crystal fibers.

4. Conclusions

Single crystal fibers of CaTiO₃ can be grown successfully with the LHPG technique. The crystal, characterized by X-ray diffraction analysis, have the distorted orthorhombic perovskite structure.

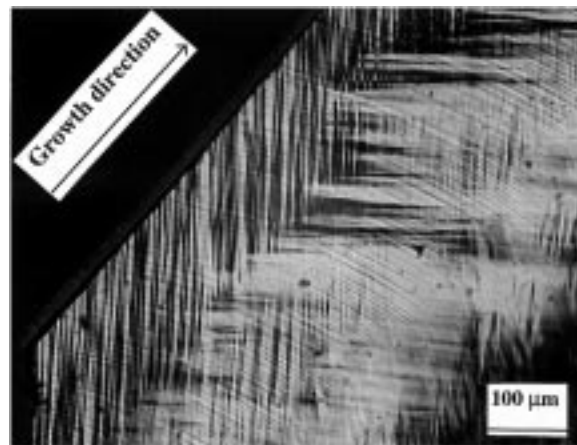


Fig. 6. Domain structure of CaTiO₃ crystal fiber observed on (010)_o plane.

Dielectric constant, dielectric loss and temperature coefficient of resonant frequency along the [101]_o and [010]_o direction of the crystal were measured and a large anisotropy in dielectric constant in CaTiO₃ single crystal was observed. No phase transition was noticed in CaTiO₃ based upon dielectric measurements at low temperature (−250 to 100°C) and thermal expansion measurements at high temperature (30 to 850°C). The grown CaTiO₃ crystal fibers have a simple twinned structure.

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