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LHPG GROWN CRYSTAL FIBERS OF $MgTiO_3$–$CaTiO_3$ EUTECTIC SYSTEM

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Abstract—Fiber crystals of $MgTiO_3$–$CaTiO_3$ eutectic system are grown using the laser heated pedestal growth (LHPG) technique. The as grown crystal fibers of composition $(Mg_{0.95}Ca_{0.05})TiO_3$ contain $MgTiO_3$ and $CaTiO_3$ crystals, and are analyzed by X-ray powder diffraction, SEM and EPMA. Crystal fibers grown between 1650 and 1680°C represent 2:3 and 1:3 composite configuration, while those grown between 1700 and 1720°C show 1:3 connectivity. $CaTiO_3$ crystal grows along the fiber growth direction and $MgTiO_3$ phase forms the body matrix of the fiber. The dielectric constants, loss factors of $(Mg_{0.95}Ca_{0.05})TiO_3$ and $CaTiO_3$ ceramics are measured and their relationship to crystal growth conditions and microstructure are discussed. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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1. INTRODUCTION

The development of microwave communication systems requires materials which can be used at microwave frequencies as resonators in filters or oscillators in radar detectors, cellular telephones and global positioning satellite devices [1, 2]. In order to satisfy this particular demand, these materials should present a reasonably high dielectric constant value ($\kappa > 20$) to allow size reduction of the component, a low dielectric loss ($\tan\delta$) in a microwave frequency range, and the materials should be stable with respect to temperature ($TC_f \approx 0$) [3, 4]. There are several dielectric ceramic materials that fulfil the above requirements and have been investigated for microwave resonators [2, 5, 6]. Among them, magnesium titanate ($MgTiO_3$)-based ceramic compositions are important [7–9].

$MgTiO_3$ has the ilmenite type structure, belonging to the trigonal space group $R\bar{3}$. At microwave frequency range, $MgTiO_3$ ceramics show a very low $\tan\delta$ value (4.5×10^{-5}) and negative TC_f (~45 ppm/°C) [8, 10]. With doping perovskite $CaTiO_3$ which has large positive TC_f (800 ppm/°C), $(Mg_{0.95}Ca_{0.05})TiO_3$ ceramic was found to yield $TC_f \sim 0$, $\kappa = 21$ and $\tan\delta = 1.25 \times 10^{-4}$ at 7 GHz [8, 11] due to the temperature compensating effect of mixed compositions. It is envisaged that in $(Mg_{0.95}Ca_{0.05})TiO_3$ crystal, because of its good quality and anisotropy of physical properties, the loss factor can be lower and dielectric constants may be larger in some crystal directions than those in ceramics (characteristics which are very useful in microwave devices). Tanaka *et al.* have reported the crystal growth of compositions in the $MgTiO_3$–$CaTiO_3$ system by the floating zone method, and found that the change of dielectric properties of $MgTiO_3$ by adding $CaTiO_3$ results from the independent distribution of $CaTiO_3$ in $MgTiO_3$ [12]. However, to the authors' knowledge, there have been no reports so far on other crystal growth methods of this eutectic system, especially methods for growing long and fiber geometry crystals of this family and their electrical properties.

In this paper, the crystal growth of $(Mg_{0.95}Ca_{0.05})TiO_3$ eutectic system using the laser heated pedestal growth (LHPG) technique and their properties are described. The microstructure of the crystal fibers and the distribution of constituents are presented on the basis of analysis by X-ray diffraction, SEM and EPMA. The dielectric constants, loss factors of $(Mg_{0.95}Ca_{0.05})TiO_3$ crystal fibers and TC_f of $MgTiO_3$, $(Mg_{0.95}Ca_{0.05})TiO_3$ and $CaTiO_3$ ceramics are characterized and their relationship to crystal growth conditions and microstructure are discussed.

2. EXPERIMENTAL PROCEDURE

Ceramic samples were prepared by conventional solid state reaction method. X-ray diffraction technique was used extensively to characterize the crystallographic phase and to adjust the processing conditions. Some of the processing parameters used are summarized in Table 1. The sintered pellets were sliced into wafers approximately 1 mm in thickness, ground to 0.5–0.8 mm thick, and then cut into square rod forms.

The laser heated pedestal growth technique is a powerful tool for rapid growth of small diameter single crystals (particularly high melting temperature oxides and incongruent melting compositions) for both property study and fiber devices [13, 14]. The LHPG equipment used in

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Table 1. Ceramic processing conditions

Composition	Starting chemicals (purity)	Calcination	Sintering
$MgTiO_3$	MgO (3 N) TiO_2 (3 N)	1100°C/3 h	1300°C/4 h
$CaTiO_3$	$CaCO_3$ (3 N) TiO_2 (3N)	1100°C/3 h	1350°C/4 h
$(Mg_{0.95}Ca_{0.05})TiO_3$	MgO (3 N) $CaCO_3$ (3 N) TiO_2 (3 N)	1100°C/3 h	1300°C/4 h

this work consisted of a power source (water-cooled, tunable flowing gas CO_2 180 W laser), an optical layout, and a growth chamber. 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 with an estimated accuracy of $\pm$ 30°C. Additional details can be found elsewhere [15, 16].

Dielectric constants and loss factors of ceramic samples were measured from 100 Hz to 100 kHz using an automated dielectric setup equipped with a HP4274 LCR meter. The measurement temperature ranges from −200 to 200°C. Dielectric properties of crystal fibers were measured using a General Radio 1621 Capacitance Measurement System. The accuracy of the measurements was in the range of $\pm$ (10–50) ppm for capacitance measurements and $\pm$ (0.1 + 1) step in the least significant decade for conductance measurements. The stray capacitance, lead and contact resistance were corrected during measurement by taking an open circuit measurement.

Thermal expansion measurements were conducted from room temperature to 700°C using a vertical push-rod dilatometer equipped with a high sensitivity linear variable differential transformer. Expansion measurements were regulated at 1.5 or 2.0°C/min using a microprocessor based temperature controller.

3. RESULTS AND DISCUSSION

It was rather difficult to optimize the best conditions to grow $(Mg_{0.95}Ca_{0.05})TiO_3$ single crystal fibers since the $MgTiO_3$–$CaTiO_3$ system is a eutectic composite containing crystals of two compounds, $MgTiO_3$ and $CaTiO_3$. During the growth, the growth conditions strongly affect the formation, stability and quality of the composite. The primary difficulty was realized due to the occurrence of intermediate phases of $MgTi_2O_5$ and Mg_2TiO_4 during the growth which were difficult to eliminate completely from the reaction products and molten zone [17]. Therefore, careful alignment of the sample and precise control of the shape and temperature of the molten zone were found to be critical for successful growth.

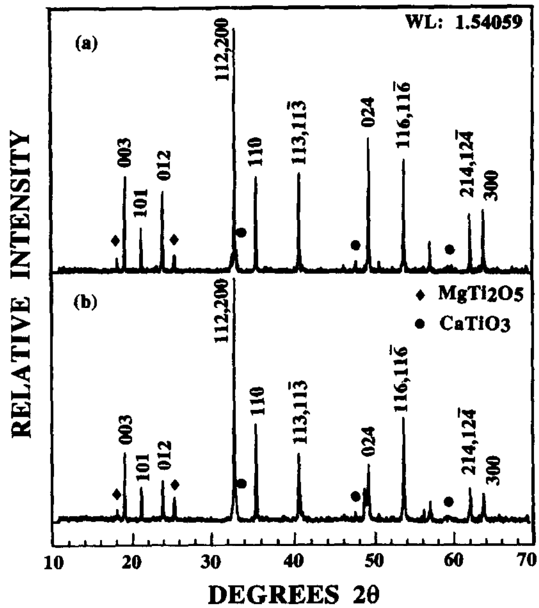

Fig. 1. X-ray diffraction patterns of $(Mg_{0.95}Ca_{0.05})TiO_3$ single crystal fiber (crushed powder): (a) grown between 1650 and 1680°C; (b) grown between 1700 and 1720°C.

Crystals of $(Mg_{0.95}Ca_{0.05})TiO_3$ were finally grown successfully using the LHPG technique. Both the feeding rods (~0.30 mm^2 cross-section) and the pulling seeds (~0.25 mm^2 cross-section) were ceramics prepared as described in Section 2. Under the growth conditions summarized in Table 2, two kinds of $(Mg_{0.95}Ca_{0.05})TiO_3$ single crystal fibers of ~500 μm diameter and up to 25 mm length were obtained. All growth runs were performed in air.

X-ray powder diffraction patterns as shown in Fig. 1 revealed that there are three crystallographic phases in $(Mg_{0.95}Ca_{0.05})TiO_3$. Besides the main $MgTiO_3$ phase and $CaTiO_3$ phase (5%), a small amount of $MgTi_2O_5$ phase could also be observed. For fibers grown between 1650 and 1680°C, the percentage of $MgTi_2O_5$ phase was about 8%, larger than that (~5%) in fibers grown between 1700 and 1720°C. These results suggested that in $MgTiO_3$–$CaTiO_3$ crystals, $CaTiO_3$ did not enter the lattice of $MgTiO_3$, and was present as a discrete phase; the amount of intermediate phase $MgTi_2O_5$ could be decreased at higher growth temperature. The overall symmetry and lattice parameters of the crystal fibers

Table 2. LHPG parameters used for growth of $(Mg_{0.95}Ca_{0.05})TiO_3$ crystal fibers

$(Mg_{0.95}Ca_{0.05})TiO_3$ sample no.	Color	Temperature of molten zone (°C)	Shape of molten zone	Pulling speed (mm/h)	Feeding speed (mm/h)
1	Brown	1650–1680	Positive	22	20
2	Colorless	1700–1720	Positive	25	20

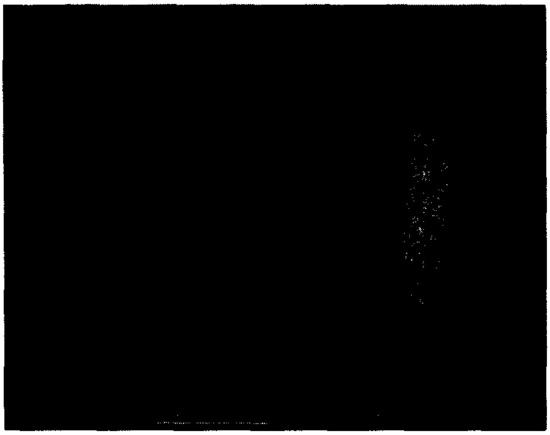

Fig. 2. SEM micrograph of $(Mg_{0.95}Ca_{0.05})TiO_3$ crystal fiber grown between 1650 and 1680°C on polished surface parallel to the crystal growth direction.

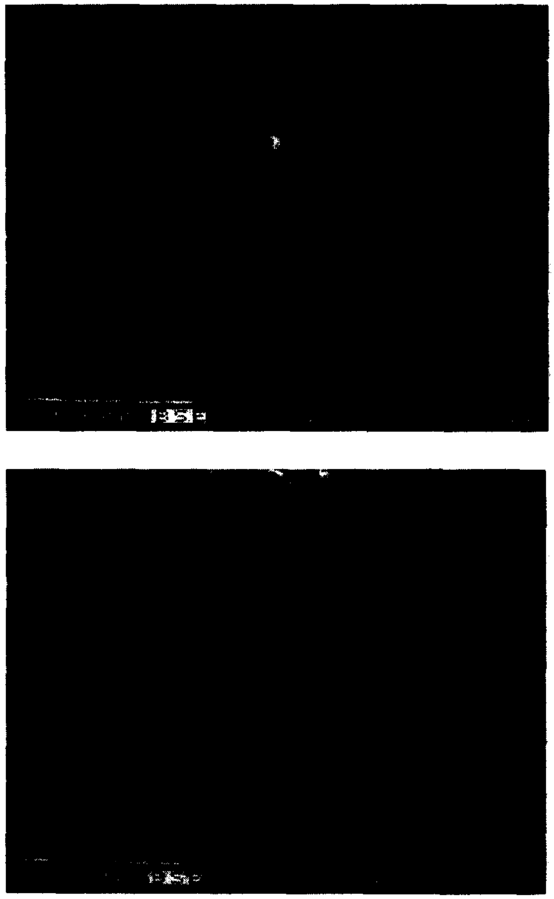

Fig. 3. EPMA back-scattering image of $(Mg_{0.95}Ca_{0.05})TiO_3$ crystal fibers grown between 1650 and 1680°C on polished surface: (a) perpendicular to the crystal growth direction; (b) parallel to the crystal growth direction.

grown in different temperature ranges were practically the same. The crystal fiber growth direction was found to be along $[10\bar{1}0]$ determined by Laue back-reflection photograph.

LHPG grown crystal fiber $(Mg_{0.95}Ca_{0.05})TiO_3$ samples were examined and analyzed for microstructure and chemical compositions by using electron probe microscopic analysis (EPMA) (CAMECA, SX-50 with spatial resolution 2 μm for surface area and 0.2 μm for depth) and scanning electron microscopy (SEM) (ISI SX-40). The relative analytical accuracy of EPMA was 2%.

Fig. 2 shows SEM photography of a $(Mg_{0.95}Ca_{0.05})$-TiO_3 crystal fiber grown between 1650 and 1680°C. Along the fiber growth direction, the light color phase is embraced by the matrix (dark color) phase. With quantitative analysis of EPMA [Fig. 3(a) and (b)], the light color phase was found to be $CaTiO_3$, and the major matrix phase was confirmed to be $MgTiO_3$. The fiber is formed by eutectic $CaTiO_3$ and $MgTiO_3$ crystals with $MgTiO_3$ as the matrix and $CaTiO_3$ forms lamellar or needle-like crystals parallel to the fiber growth direction. Titanium distribution is overall uniform across the fiber section.

In $(Mg_{0.95}Ca_{0.05})TiO_3$ crystal fibers grown between 1700 and 1720°C, as shown in Fig. 4(a) and (b), $CaTiO_3$ phase (light color) is embraced by $MgTiO_3$ (matrix) phase with 1:3 connectivity and grown along the fiber pulling direction. The size of $CaTiO_3$ fine needles is much smaller than that of plates or ribbons grown at lower temperature. The distribution of $CaTiO_3$ is more uniform in fibers grown at the higher molten zone temperature.

Dielectric properties of $MgTiO_3$, $CaTiO_3$ and $(Mg_{0.95}Ca_{0.05})TiO_3$ ceramic samples at radio frequency were examined as a function of temperature. Fig. 5 shows the temperature dependence of dielectric constant at 100 kHz and Table 3 presents the temperature coefficient of resonant frequency (−50–50°C) of the above ceramics. The temperature coefficient of resonant frequency (TC_f) is given by [18]

$$TC_f = -TC_\kappa/2 - \alpha$$

where TC_κ is the temperature coefficient of the dielectric constant and α is the coefficient of linear thermal expansion.

From Fig. 5 and Table 3, one can see, in the present system, that addition of a small amount of $CaTiO_3$ does improve the TC_f of $MgTiO_3$. This improvement does not result from the formation of solid solutions, but is ascribed to the fact that the TC_fs for both materials have mutually opposite signs, the TC_f for the mixed system becoming complementarily smaller. More studies on the temperature dependence of dielectric properties at microwave frequencies are in progress.

Table 4 summarizes the dielectric properties of two kinds of $(Mg_{0.95}Ca_{0.05})TiO_3$ crystal fibers with respect to the frequency and crystal orientation. The dielectric constant parallel to the fiber growth direction is larger than that perpendicular to the fiber growth direction and that of ceramics, which is ascribed to the anisotropy of physical properties of $MgTiO_3$ and $CaTiO_3$ crystals.

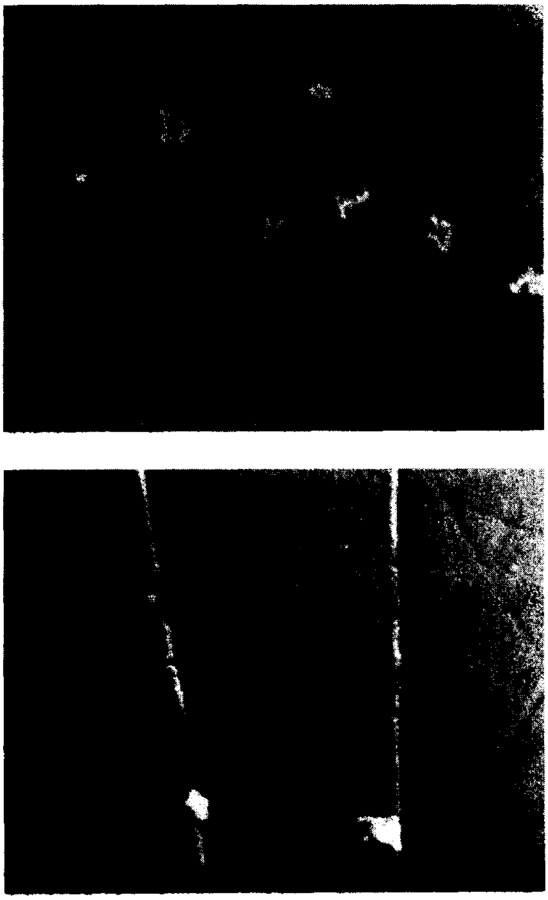

Fig. 4. SEM micrographs of $(Mg_{0.95}Ca_{0.05})TiO_3$ crystal fibers grown between 1650 and 1680°C on polished surface: (a) perpendicular to the crystal growth direction; (b) parallel to the crystal growth direction.

With the selected seed orientation, one can design new crystals having large dielectric constant along the crystal growth direction.

The dielectric loss (tan δ) in the crystal fiber grown between 1700 and 1720°C was smaller than that in the crystal fiber grown between 1650 and 1680°C. With the growth at the higher molten zone temperature, the amount of intermediate phase $MgTi_2O_5$ was found to be smaller, and the distribution of $CaTiO_3$ fine needles was much more uniform, which led to better crystal quality and lower dielectric loss. Therefore, it appears that 1700 to 1720°C is a better temperature range of molten zone to grow $(Mg_{0.95}Ca_{0.05})TiO_3$ crystal fibers.

4. SUMMARY

Through controlled crystallization, crystals of eutectic compositions can be grown by using the LHPG technique. In $MgTiO_3$–$CaTiO_3$ crystal, $CaTiO_3$ does not enter the lattice of $MgTiO_3$, but presents a lamellar or needle form. With growth temperature between 1650 and 1680°C, the $(Mg_{0.95}Ca_{0.05})TiO_3$ crystal has 2:3 and 1:3 connectivity; and with growth temperature between 1700 and 1720°C, the $(Mg_{0.95}Ca_{0.05})TiO_3$ crystal has a 1:3 composite configuration with better crystal quality and dielectric properties. The presence of $MgTi_2O_5$ phase in $MgTiO_3$–$CaTiO_3$ strongly affects the growth stability and crystal quality. By optimizing growth conditions (temperature, growth rate, etc.), its content can be partly reduced. The TC_f of $(Mg_{0.95}Ca_{0.05})TiO_3$ is confirmed to be improved based upon the temperature compensating effects of two individual compositions which have mutually opposite sign of TC_f. Large anisotropy in dielectric properties of $(Mg_{0.95}Ca_{0.05})TiO_3$

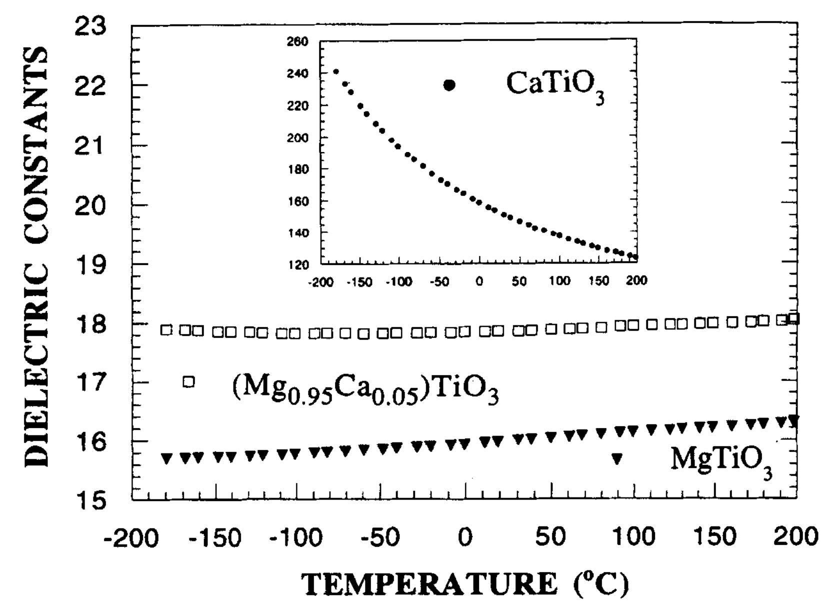

Fig. 5. Temperature dependence of the dielectric constants at 100 kHz in $MgTiO_3$, $CaTiO_3$ and $(Mg_{0.95}Ca_{0.05})TiO_3$ ceramics.

Table 3. Temperature coefficient of dielectric constant and resonant frequency

Ceramic sample	κ (25°C)	TC_κ (ppm/°C) (−50 ~ 50°C)	α (ppm/°C) (20–500°C)	TC_f (ppm/°C) (−50 ~ 50°C)
$MgTiO_3$	16	120	10	−70
$CaTiO_3$	~140	−1763	13	870
$Mg_{0.95}Ca_{0.05}TiO_3$	18	32	10	−26

Table 4. Dielectric properties of $(Mg_{0.95}Ca_{0.05})TiO_3$ crystal fibers at room temperature

Crystal fiber		κ		
		10.1 kHz	995 Hz	100 Hz
Grown between 1650 and 1680°C	∥ growth direction	19.2	19.7	20.4
	⊥ growth direction	14.9	15.0	15.2
Grown between 1700 and 1720°C	∥ growth direction	22.9	23.2	23.4
	⊥ growth direction	15.3	15.7	15.9

crystal fibers was measured, which is of special significance in one-dimensional microwave dielectric devices. The laser heated pedestal growth technique has been demonstrated to be useful in the crystal growth of a eutectic system. It is therefore possible to engineer and design new materials and tailor continuously the materials properties for specific device applications in other areas of ferroelectric, dielectric, and optics utilizing the LHPG technique.

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