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Multifuncional translucent ferroelectric $Ba_{1-x}Ca_xTiO_3$ ceramics produced by laser sintering

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ABSTRACT

Multifunctional transparent ferroelectric ceramics can be used in a wide range of applications, such as optical modulation and image memory devices, optical shutters, switchers, etc. Frequently, electro-optical ceramics are lead-based and have the disadvantages of being harmful to the environment. For this reason, continuous effort has been done in the research for lead-free optical transparent ferroelectric ceramics. In this work, we have successfully sintered bulk lead-free translucent and nanostructured $Ba_{1-x}Ca_xTiO_3$ (X = 0–0.30) ceramics by the laser sintering technique. In this technique, a CO_2 laser is used as the main heating source for sintering. The laser-sintered ceramics presented high relative density, suitable ferro- and dielectric properties, transmittance up to 42% at 950 nm for $Ba_{0.70}Ca_{0.30}TiO_3$ sample and average grain size changing from 420 nm to 600 nm when the Ca concentration increases.

1. Introduction

Barium calcium titanate ($Ba_{1-X}Ca_XTiO$–BCT) is a perovskite-structured ferroelectric system, with tetragonal 4 mm point group. In particular, the $Ba_{0.77}Ca_{0.23}TiO_3$ (BCT23) composition is the only congruently melting compound in this system [1]. Single crystals from this compound present Curie temperature (denoting the temperature of paraelectric-to-ferroelectric phase transition upon cooling $-T_C$) at 98 °C, and in contrast to undoped $BaTiO_3$ (BT), do not show any further structural transition down to −120 °C [1]. BCT has been reported as a promising multi-layer ceramic capacitor (MLCC) [2], whose main advantages are the good dielectric performance on cheap electrode (such as nickel), and the increasing temperature range of the tetragonal phase [3]. The calcium addition also inhibits the formation of the unwanted hexagonal $BaTiO_3$ phase [1]. BCT ceramics show a modest increase in T_C for low Ca concentration and decrease up to the solid solution limit of X = 0.30 [4]. Due to all these and other attractive properties, considerable efforts have been devoted to optimize preparation, (micro)structural and dielectric properties of ferroelectric BCT ceramics.

Transparent/translucent ferroelectric ceramics have received a great deal of attention because of both their unique combination of optical and ferroelectric properties [5,6] and their low production cost compared with conventional single crystal ferroelectric materials. Electro-optical ceramics can be used as optical modulation devices, optical shutters, switchers and image memory devices [6]. Frequently, transparent ferroelectric ceramics are lead-based and have the disadvantages of being harmful to the environment and can gradually degrade their optical efficacy due to lead volatilization [6]. Due to these undesirable characteristics, a continuous search for lead-free green ferroelectric ceramics with good optical transparence has been done. Moreover, several special sintering techniques including hot pressing [7], high-energy ball-milling [8] and spark plasma sintering (SPS) [9] have been used to fabricate transparent/translucent (Pb,La)(Zr,Ti)O_3 (PLZT) ceramics. Recently, lead-free bulk-dense nanostructured $BaTiO_3$ translucent ceramics were sintered by SPS [6] and laser sintering technique [10]. The ceramics showed excellent optical and electrical properties.

In the last few years, laser technology has been employed in an increasing variety of processes. For instance, laser heating can be controlled for use in cutting, soldering, ablation and coating [11,12]. The potential use of lasers for deposition, sintering and texturing of thin films [13] and for crystallization of glasses [14] has also been widely investigated. CO_2 laser has also been successfully employed in the laser sintering of bulk-ceramics. This technique allows a rapid processing without crucibles, thus reducing the risk of contamination and very high heating and cooling rates (about 2000 °C/min) [15]. It additionally enables the sintering of materials that exhibit high melting point such as Y_2O_3 [16]. The laser sintering technique has been also successfully used to

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Table 1
Composition, theoretic density (ρ_0), relative density (ρ_{rel}) and average grain size (AGS) of the laser-sintered ceramics. (*[23], #[24], ♦[25]).

Composition	Name	ρ_0 (g/cm^3)	ρ_{rel} (%)	AGS (nm)
$BaTiO_3$	BT	6.02♦	98 ± 1	400
$Ba_{0.95}Ca_{0.05}TiO_3$	BCT05	5.90*	98 ± 1	520
$Ba_{0.90}Ca_{0.10}TiO_3$	BCT10	5.83*	98 ± 1	560
$Ba_{0.85}Ca_{0.15}TiO_3$	BCT15	5.67*	98 ± 1	620
$Ba_{0.77}Ca_{0.23}TiO_3$	BCT23	5.55#	98 ± 1	580
$Ba_{0.70}Ca_{0.30}TiO_3$	BCT30	5.39*	99 ± 1	620

produce $Bi_4Ge_3O_{12}$ ceramics with good transparency and scintillation properties [17,18] and translucent persistent luminescent $SrAl_2O_4:Eu^{2+},Dy^{3+}$ ceramics in an air atmosphere [19]. Moreover, in previous papers by the authors, laser-sintered ceramics with different physical properties [10,16] when compared with conventional ones have been obtained. Laser-sintered $Bi_4Ti_3O_{12}$ ceramics presented changes in the electric conductivity of the bulk, increased the relative permittivity of the grain boundary and the remnant polarization [20]. Ji et al. [21] showed that after the laser irradiation an enhancement of 2 times was achieved in the dielectric permittivity of the Ta_2O_5 ceramics. The authors attributed this behavior due to the stabilization of a high-temperature phase at room temperature. Additionally, in a previous paper, we have achieved translucent and nanostructured $BaTiO_3$ ceramics with average grain size of 400 nm by laser sintering technique [10], however no electric or dielectric property of this material was presented. Therefore, in this work, we will present the laser sintering and di-electric properties of the $Ba_{1-x}Ca_xTiO_3$ (x = 0–0.30) translucent ceramics.

2. Experimental procedure

Barium calcium titanate nanopowders ($Ba_{1-x}Ca_xTiO_3$ – X = 0, 0.05, 0.10, 0.15, 0.23 and 0.30) were synthesized by the modified polymeric precursor method, using as precursor materials, titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$–Alfa Aesar, 97%), barium acetate ($C_4H_6BaO_4$–Synth, 99%) and calcium carbonate ($CaCO_3$–Alfa Aesar, 99.95%). To best stabilization of the precursor solution, its pH was adjusted at 8.5 by adding ammonium hydroxide. Table 1 summarize some characteristics of the synthesized powders. The details of the synthesis process are described in reference [22]. For sintering, the powders calcined at 600 °C for 5 h were mixed with a binder solution of polyvinyl alcohol (concentration of 0.1 g/ml) and uniaxially compacted at 120 MPa into disks of 4 mm diameter per 1.5 mm thickness.

Sintering was performed using a CO_2 laser (GEM–100 L – Coherent) in continuous-wave mode as the main heating source, i.e., the laser sintering technique. In this technique, the samples were put on a base composed of the same material to be sintered and the laser beam (diameter of 4.5 ± 0.2 mm) was directed and held at the center of the sample throughout the sintering process [10,15,19]. The base composition and the laser beam diameter are essential to reduce the heat exchange between the pallet and environment thus minimizing the temperature gradients. After a preheating stage at 300 °C, the laser power was raised at a linear rate of 0.01 W/mm^{2}s (~450 ± 50 °C/min) up to 0.28 W/mm^2 (~500 ± 50 °C) and held at this value for 15 s. This initial power-ramping stage was used to decrease the thermal gradient in the sample, inhibiting the formation of cracks. Afterwards, the power density was raised again, at a linear rate of 0.04 W/mm^{2}s (2300 ± 180 °C/min), up to (4.5 ± 0.1) W/mm^2 (1250 ± 15 °C) for 30 s (this was the best condition). After the irradiation of the first sample side, the process was repeated on the opposite side. Using these procedures the total BCT laser sintering time was 8 min, which is significantly faster than the conventional sintering in an electric furnace, which takes several hours. In these experiments, the temperature was measured using a type *S* thermocouple (cross-section = 0.25 mm) positioned at the center of the sample surface [15,19]. Density of the laser-sintered ceramics was determined by using the Archimedes principle.

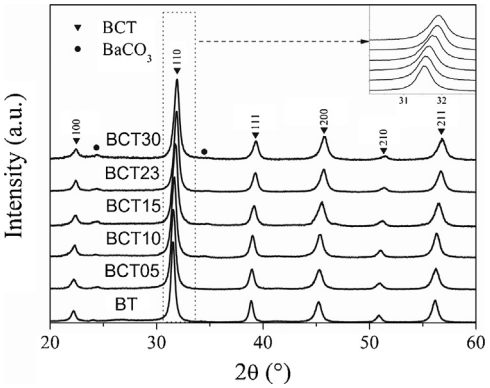

Fig. 1. XRD patterns of the BCT powders calcined at 600 °C for 5 h. The peaks were indexed according to ICSD number 03-1890 (BT) and 41-0373 ($BaCO_3$).

The structural investigation was made by powder X-ray diffraction analysis in a XRD – Rigaku Rotaflex RU-200B, using Cu Kα radiation. The measurements were carried out at room temperature in continuous mode, in the 2θ range between 20° to 60°, in steps of 0.02°. The microstructures of the ceramics were analyzed through scanning electron microscopy (SEM). The images were collected at as-sintered sample surface, and the average grain size (AGS) was evaluated by applying the standard intercept length method [26]. Transmittance measurements were performed with a CARY 17 spectrophotometer covering the spectral range from 400 to 1000 nm. Finally, electric contacts were fabricated on both major surfaces of polished ceramic samples by applying Pt paste, followed by firing at 700 °C for 30 min. Subsequently, permittivity data of these samples were recorded at 1 kHz using a Solartron 1260 Impedance Analyzer controlled by a personal computer. The measurements were carried out during cooling from 200 to 25 °C, with a cooling rate of 0.5 °C/min and an applied potential of 1000 mV. Ferroelectricity was investigated using a modified Sawyer-Tower circuit attached to a Tektronix 2232 digital oscilloscope and taken at room temperature.

3. Results and discussion

Fig. 1 presents the X-ray diffraction patterns of the BCT powders calcined at 600 °C for 5 h. As can be seen all samples presented the majority BCT and a small amount of the $BaCO_3$ phase, indexed according to Inorganic Crystal Structure Database (ICSD) numbers 03-1890 and 41-0373, respectively. According to discussed in previous work [22,27], this small amount of $BaCO_3$ did not influence the phase formation in the sintered samples. In detail in Fig. 1 is shown the main peak displacement (110) as a function of the calcium concentration. This shift to higher angles is a good indication of Ca diffusion in the BT host network. The Ca^{2+} (1.34 Å) substitution on Ba^{2+} (1.61 Å) site promotes the cell contraction and indicates development of strain in the materials, and peak broadening due to creation of stacking fault [28].

The nanometric particle size was confirmed by FEG-SEM images as shown in Fig. 2. The average particle size was determined between 30 and 40 nm for all samples. It can also be observed that the agglomeration degree of the particles is relatively low. This fact allowed preparing highly-homogeneous green compacts that resulted in slightly-higher starting (green) densities. As consequence, a much more effective process of densification with

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