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Preparation and characterization of Ce-doped $BaTiO_3$ thin films by pulsed laser deposition

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Thin films of $BaTiO_3$ doped with 5.5 mol%CeO_2 have been deposited on Pt/Si substrate by pulsed laser deposition. These films crystallize on the tetragonal $BaTiO_3$ structure without any preferential orientation. Ce-doped $BaTiO_3$ films deposited by PLD at 675°C in 30 Pa ambient oxygen exhibits a smooth surface: mean surface roughness (Rms) of 48 nm, mean size of grain of ∼40 Å, average size of aggregates of ∼315 nm. Thin films as prepared presented good dielectric characteristics: dielectric constant and dielectrics loss (tan δ) at a frequency of 1 KHz were 220 and 0.2, respectively. The temperature dependence of dielectric constant exhibited a diffuse ferroelectric to paraelectric phase transition at about 0–10°C. The ferroelectric nature of Ce-doped $BaTiO_3$ film was confirmed by the hysteresis of the C-V curves. *© 2004 Kluwer Academic Publishers*

1. Introduction

The ferroelectrics thin-films have applications in integrated devices where they reduce the size and weight [1]. Characteristics of thin film devices are: low operating voltages, high switching speeds and possible integration with the existing semiconductor technology. Ferroelectric $BaTiO_3$ thin films have applications such as high dielectric capacitors, non-volatile memories with low switching voltage [2, 3], infrared sensors, and electro-optic devices [4]. Cerium-doped $BaTiO_3$ bulk ceramics were studied due to their high endurance under dc field stress, grain growth inhibition, and the effective Curie temperature shift [5]. Among the dopants used to modify the dielectric and semiconducting properties of $BaTiO_3$ ceramics, cerium has a special interest, because it could be incorporated in the perovskite ABO_3 lattice as Ce^{4+} at the B sites or as Ce^{3+} at the A sites [6]. Kolar *et al.* [5] reported incorporation of Ce^{4+} in $BaTiO_3$ and solubility of 5–20 mol%$Ba(Ce^{4+})O_3$ in $BaTiO_3$. Itakura *et al.* [7] founded that CeO_2 acts as donor dopant in $BaTiO_3$ when Ce^{3+} substitutes Ba^{2+}. Hennings *et al.* [8] reported that cerium could also be incorporated into the $BaTiO_3$ lattice as Ce^{3+} at Ba sites, when CeO_2 is added to $BaTiO_3$ together with an excess of TiO_2. Up to Ce concentrations of 8 mol%, a linear decrease of the Curie point (T_c) of 21°C per mol%Ce was found in bulk ceramics fired at 1350°C in air with equimolar additives of TiO_2 and CeO_2 [9]. Pulsed laser deposition (PLD) method was employed due to its advantage of maintaining the stoichiometry of multicomponent material [10–13]. In this paper, the preparation and characterisation of thin films of $BaTiO_3$ doped with 5.5 mol%CeO_2 are reported.

2. Experimental details

Ceramic target was prepared from $BaTiO_3$, CeO_2, and TiO_2 powder (purity >99%). We added CeO_2 and TiO_2 in molar ratio 1:1 to $BaTiO_3$. The concentration of the dopant CeO_2 was 5.5 mol%. The powders were mixed, pressed at 200 MPa into discs 1.3 cm in diameter and 2 mm thick, and sintered at 1300°C for 2 h in air. Ce-doped $BaTiO_3$ films were deposited by KrF excimer

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laser ablation (wavelength 248 nm and repetition rate 2 Hz). Laser energy density was set at 4 J$\cdot$ cm^{-2} at the target. The substrate was held at temperature of 675°C and O_2 pressure was kept at 30 Pa during the film deposition. The pulses with energy of 90 mJ were focused onto the target surface at 45°. To avoid drilling, the target was rotated during the multipulse laser irradiation. For each deposition, a series of 10^4 laser pulses was applied. After deposition, the chamber was filled with oxygen at 10^3 Pa and the sample was slowly cooled to room temperature. The substrate Pt/Si(100) was aligned parallel to the target at a separation distance of 3 cm. Platinum layer ($\sim$100 nm) was deposited by electron beam evaporation at 500°C on Si wafer. Before the Pt film deposition, the wafer was cleaned and etched in an HF buffer solution to strip off the SiO_2 layer. The deposition rate of dielectric film was 2.5 nm/min and the thickness of deposited film was 900 nm. To test the dielectric properties of Ce-modified $BaTiO_3$ film, a structure MIM was formed by deposition of a top gold electrodes of 1mm diameter and 50 nm thickness by sputtering at room temperature.

The crystalline structure of the Ce-doped $BaTiO_3$ thin films were analyzed by X-ray diffraction (XRD), with Cu K_α radiation ($\lambda = 0.154$ nm), using a Siemens D 5000 X-ray diffractometer. The local order of (TiO_6) octahedra was studied by Raman spectroscopy using a Dilor XY spectrometer. The samples were excited with the 482 nm line of an Ar ion laser of 50 mW power. The acquisition consisted of three accumulations of 180 s. The film surface morphology was observed by scanning electron microscopy (SEM) using a Philips XL 30 scanning electron microscope and by atomic force microscopy (AFM) with an Autoprobe CP, (Park Scientific Instruments) microscope. The capacitance-voltage (C-V) properties were characterized using a Hewlett Packard 4284 A LCR-meter from 100 Hz to 1 MHz frequency range. The dielectric constant and dissipation factor were measured as a function of frequency at 20°C. The constant dielectric was plotted as a function of temperature at two frequencies (100 Hz and 1 KHz).

3. Results and discussion

Fig. 1 shows the XRD pattern of the Ce-doped $BaTiO_3$ film deposited at 675°C. The film obtained was crystallized consisting of a single-phase tetragonal $BaTiO_3$, without any preferred orientation. The parameters of the crystal unit cell calculated from XRD patterns were: $a = b = 4.032(1)$ Å, $c = 4.064(2)$ Å, and the volume of the unit cell was $V = 66.1(1)$ Å^3.

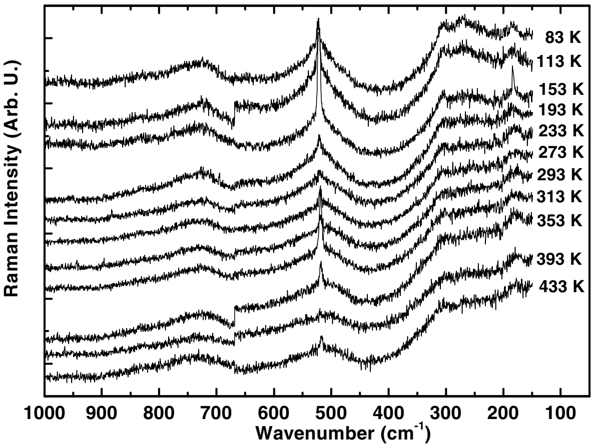


Figure 2 Raman spectra vs. temperature of $BaTiO_3$ doped with 5.5 mol%Ce film.

Fig. 2 shows the Raman spectra of Ce-doped $BaTiO_3$ thin film recorded at temperatures ranged between -190 to $+160$°C. The spectra show no essentially changes in the crystalline structure of the film suggesting that cerium stabilizes the structure. The peaks placed observed in these spectra are at 720, 520–530, 310, 264, and 187 cm^{-1}. The peaks at 720 and 310 cm^{-1} suggests a tetragonal $BaTiO_3$ structure. Also, the peaks at 520–530 cm^{-1} and at 264 cm^{-1} correspond to both tetragonal and cubic $BaTiO_3$ phases. The band at $\sim$187 cm^{-1} is attributed to $BaTiO_3$ orthorhombic. Unfortunately, the peak at 526 cm^{-1} coincides with the strong Si band of the substrate [14]. The feature of the Ce-doped $BaTiO_3$ Raman spectra characterizes a structure composed from small crystallites and also, suggests a structure with internal stress caused by deposition conditions.

The SEM analysis of Ce-doped $BaTiO_3$ surface film (Fig. 3) shows a uniform film. Droplets of various sizes (from 420 to 530 nm) are visible on the film surface.

Fig. 4 presents an AFM image of Ce-doped $BaTiO_3$ film deposited at 675°C by PLD method. This shows a

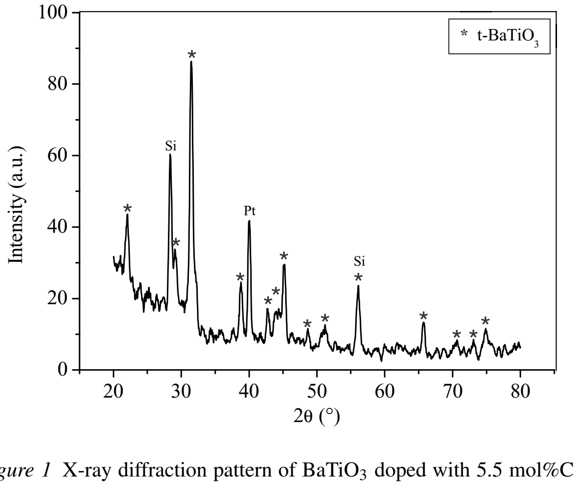


Figure 1 X-ray diffraction pattern of $BaTiO_3$ doped with 5.5 mol%Ce thin film.

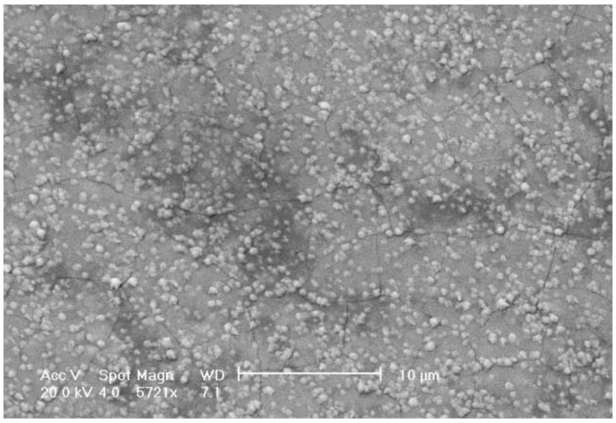
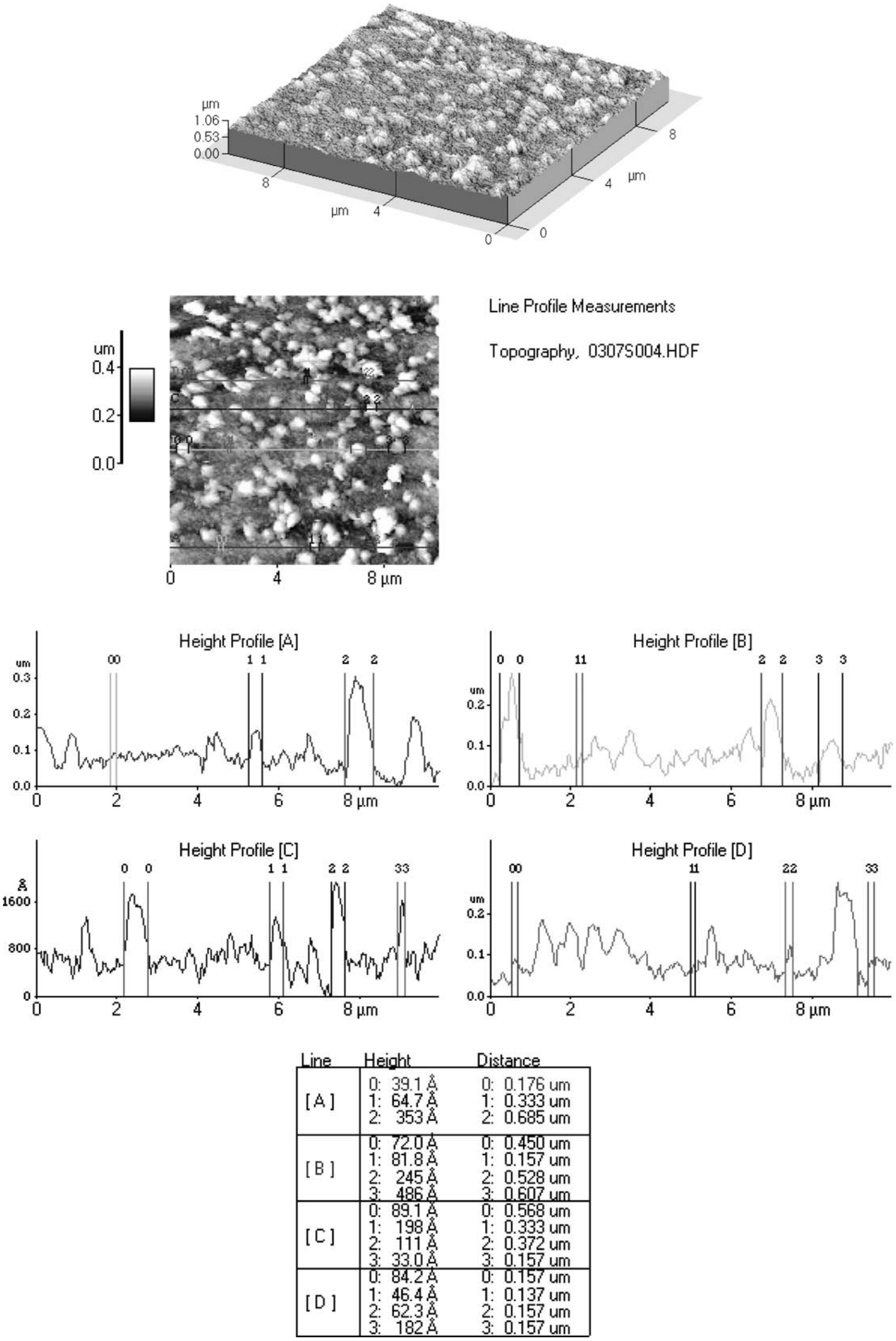


Figure 3 SEM image of $BaTiO_3$ doped with 5.5 mol%Ce thin film.



Line	Height	Distance
[A]	0: 39.1 Å 1: 64.7 Å 2: 353 Å	0: 0.176 um 1: 0.333 um 2: 0.685 um
[B]	0: 72.0 Å 1: 81.8 Å 2: 245 Å 3: 486 Å	0: 0.450 um 1: 0.157 um 2: 0.528 um 3: 0.607 um
[C]	0: 89.1 Å 1: 198 Å 2: 111 Å 3: 33.0 Å	0: 0.568 um 1: 0.333 um 2: 0.372 um 3: 0.157 um
[D]	0: 84.2 Å 1: 46.4 Å 2: 62.3 Å 3: 182 Å	0: 0.157 um 1: 0.137 um 2: 0.157 um 3: 0.157 um

Figure 4 AFM image of $BaTiO_3$ doped with 5.5 mol%Ce film.

surface morphology characterized by an average roughness of 73 Å, a mean surface roughness (Rms) of 48 nm and a mean peak height of 143.8 Å. Large grains (∼568 nm) were accumulated on the surface consisting of smaller grains (∼40 Å). Average size of grains was 315 nm. The Rms value of the surface film indicates a smooth film. The growth mechanism should be in a diffusion-limited mode in which a slow growth rate and a smooth surface would be expected to occur.

The investigation of the bias voltage dependence of the capacitance is one of the most useful methods to characterize ferroelectric films. Fig. 5 shows the capacitance-voltage (C-V) characteristics of Ce-doped $BaTiO_3$ thin films in the frequency range from 10 KHz to 1 MHz. The capacitance changed from 710 to 610 pF with the applied voltage in the −6 to +6 V range at a frequency of 10 KHz. The C-V plots showed hysteresis effect caused by switching of the ferroelectric

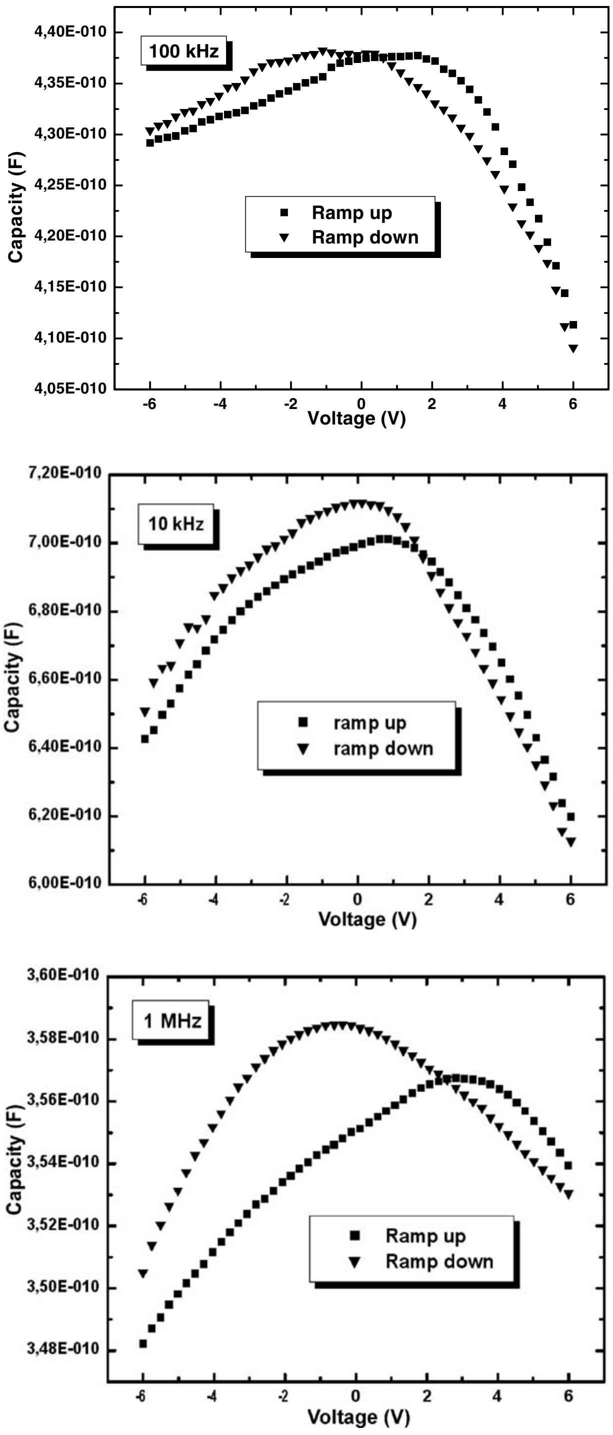


Figure 5 C-V curves of $Ba_{1-x}Ce_xTiO_3$, $x = 0.055$ film films at the frequencies of 100 Hz, 10 KHz and 1 MHz.

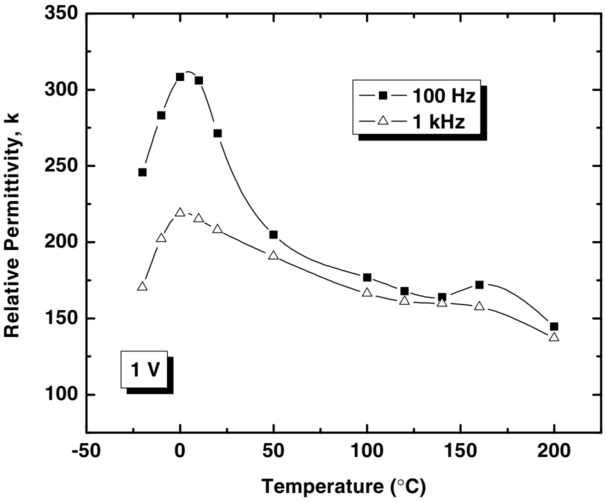


Figure 6 Variation of relative permittivity of $Ba_{1-x}Ce_xTiO_3$, $x = 0.055$ film with temperature at frequencies of 100 Hz and 1 KHz.

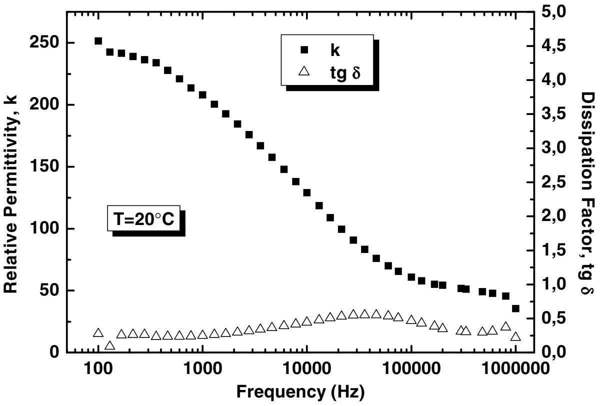


Figure 7 Dielectric constant and dissipation factor of $Ba_{1-x}Ce_xTiO_3$, $x = 0.055$ thin films as a function of frequency.

domains. The films' butterfly-shaped C-V curves indicate that the films have a ferroelectric nature. The relative permittivities of $Ba_{1-x}Ce_xTiO_3$, $x = 0.055$ film at frequencies of 100 Hz and 1 KHz were 310 and 220, respectively (Fig. 6). Films deposited at 675°C present a diffuse ferroelectric–paraelectric phase transition with a broad permittivity maximum specific to fine-grained thin films with significant internal stress. The Curie temperature is ranged between 0–10°C and a dielectric constant value of 220 in this temperature domain and at 1 KHz frequency was recorded. Fig. 7 shows the frequency dependence of the dielectric constant and dissipation factor of $Ba_{1-x}Ce_xTiO_3$, $x = 0.055$ thin films. The dissipation factor for $BaTiO_3$ doped with 5.5 at %Ce thin film showed no noticeable dispersions at frequencies from 100 Hz to 1 MHz, indicating the good quality of thin film prepared by pulsed laser deposition technique. There is a tendency for dielectric constant to decrease when the frequency increase. This phenomenon is attributed to the presence of the barrier layers between the insulating film and the electrodes. The permittivity and T_c values are influenced by the valence state of the dopant (the Ce^{3+}/Ce^{4+} ratio), lattice site occupation and solubility of Ce in $BaTiO_3$. Thus, when Ce is incorporated at Ti sites one obtain a $Ba(Ti_{1-y}Ce_y)O_3$ solid solution and, there is no significant change in conductivity behaviour and in Curie temperature value compared with the undoped $BaTiO_3$. The Curie temperature is systematically lowered when Ce^{3+} acts in the $BaTiO_3$ lattice as a donor at the Ba sites. The excess charge in Ce^{3+}-doped $BaTiO_3$ is compensated by the formation of ionised vacancies at Ti sites $(V'''')_{Ti}$ [5, 15]. In this case, a $Ba_{1-x}Ce_x^{3+}Ti_{1-x/4}(V'''')_{x/4}O_3$solid solution is formed. In fact, in CeO_2-doped $BaTiO_3$, coexist Ce^{3+} and also Ce^{4+} and their ratio influences the dielectric behaviour of doped $BaTiO_3$. Therefore, the chemical formula for $BaTiO_3$doped with z mol%CeO_2 can be considered as $Ba_{1-x}Ce_x^{3+}Ti_{1-y}^{4+}Ce_y^{4+}O_3$, where $x + y = z$.

4. Conclusions

Thin films of $BaTiO_3$ doped with 5.5 mol%Ce were prepared by pulsed laser deposition at 675°C and 30 Pa O_2. XRD analysis and Raman spectroscopy emphasized a predominant $BaTiO_3$ tetragonal structure with some orthorhombic local ordering of TiO_6 octahedra. The value of the mean surface roughness shows a smooth film. The variation of relative permittivity and of dielectric loss of Ce-doped $BaTiO_3$ film vs. temperature and frequency, as well as the C-V characteristics pointed out a ferroelectric behaviour of the film.

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