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ScienceDirect
Journal of the European Ceramic Society 26 (2006) 3241–3246
www.elsevier.com/locate/jeurceramsoc

Sol–gel synthesis and characterization of Ce doped-$BaTiO_3$

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Received 27 April 2005; received in revised form 20 August 2005; accepted 3 September 2005
Available online 11 November 2005

Abstract

Barium titanate ($BaTiO_3$) have been doped "in situ" with 5.5 mol% cerium by a sol–gel method using barium acetate, titanium (IV) isopropoxide, and cerium (III) acetylacetonate as starting materials. The dried gel showed a microstructure consisting of nano-sized grains (∼140 nm) with great tendency to agglomeration. Several thermal analysis techniques were used to study the decomposition process of the gel. The presence of hydroxyls up to 720 °C suggests a strong bonding Ti—OH that is responsible for the existence of aggregates even at high temperatures. The as-prepared gel powder was found to be amorphous, and then decomposes through oxides and barium carbonate around 500 °C and crystallizes on the perovskite structure of tetragonal $BaTiO_3$ at 1100 °C for 3h in air. A small influence of the frequency on the dielectric properties of the $Ba_{0.945}Ce_{0.055}TiO_3$ ceramics was observed in 100 Hz to 1 MHz domain. At the Curie temperature point (22 °C) the dielectric constant was 10130 at 100 Hz while the dielectric loss (tan δ) was 0.018.

Keywords: $BaTiO_3$; Sol–gel processes; Dielectric properties; Sol–gel methods

1. Introduction

Ferroelectric bulk ceramics have found wide applications as electronic, acousto-optic and piezoelectric devices.[1,2] Dielectric ceramics of barium titanate doped with cerium present practical interest because cerium decreases significantly the Curie temperature of $BaTiO_3$. Up to 8 mol% Ce concentration, a linear decrease of the Curie point (T_c) of 21 °C per mol% Ce was observed in bulk ceramics fired at 1350 °C in air with equimolar additives of TiO_2 and CeO_2.[3] Thus, we predict that the cerium concentration of 5.5 mol% can decreases the Curie temperature of $BaTiO_3$ to near ambient temperature where this dielectric material will be use as capacitors. According to Hwang et al.,[4] the Curie temperature was systematically lowered when Ce^{3+} was incorporated into Ba^{2+} sites, whereas the substitution of Ce^{4+} for Ti^{4+} sites does not change this parameter. The valence states of cerium ions depend on the starting formula and sintering atmosphere. It is difficult to maintain cerium ions as Ce^{3+} in proportion of 100%, in sintered stoichiometric $BaTiO_3$ ceramics due to their tendency to oxidize. In contrast to most of the rare-earth elements which are stable in air at an oxidation state of 3^+, cerium is more stable in oxidation state 4^+. When it forms stable compounds, for example: Ce^{3+}-$BaTiO_3$ solid solutions, cerium can react at high temperatures in air even in oxidation state 3^+. On the other hand, CeO_2 is partially reduced and cerium enters into the $BaTiO_3$ lattice as a donor at the Ba sites, when $BaTiO_3$ is sintered in air together with CeO_2 and an excess amount of TiO_2.[5]

Various methods such as conventional solid state reaction, coprecipitation, hydrothermal technique and sol–gel have been utilized for the fabrication of ferroelectric $BaTiO_3$ bulk powder and ceramics.[6] The sol–gel process is an excellent technique for formulating new compositions due to the possibility to control the stoichiometry and homogeneity of the resulting material.[7–10] Among the various techniques, sol–gel offers the advantages of obtaining fine particle size and processing at lower temperatures. Thus, at the sintering temperature, a smaller amount of Ce^{3+} will be oxidized at Ce^{4+} and it is expected that the temperature of Curie point of $BaTiO_3$ will decrease.

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doi:10.1016/j.jeurceramsoc.2005.09.039

In the present work, a sol–gel method for the synthesis of Ce^{3+}-doped $BaTiO_3$ powder, using an original combination of Ce(III) precursor and organic raw materials is described. The structure and dielectric properties of derived cerium doped-$BaTiO_3$ ceramics were investigated.

2. Experimental procedure

Barium acetate, 99%, $(CH_3CO_2)_2$ Ba (Aldrich), titanium (IV) isopropoxide, 97% solution in 2-propa nol (Aldrich), and cerium (III) 2,4-pentanedionate hydrate $[(CH_3COCH{=}C(O\text{-})CH_3]_3$ Ce·xH$_2$O, F.w. = 437.45 (Aldrich), where used as starting materials to prepare barium cerium titanate ($Ba_{0.945}Ce_{0.055}TiO_3$) powder. Barium acetate was firstly dissociated in water to obtain a concentrated solution (1 M). Acetic acid glacial was added to the barium acetate solution, in molar ratio 2:1. Titanium (IV) isopropoxide and cerium (III) acetylacetonate hydrate were mixed in molar ratio 1:0.055 under constant stirring and reflux conditions (75 °C). Propanol-2 and acetyl acetone were added to the mixture of titanium and cerium alkoxydes in ratio of 20/1. We used a ratio [isopropanol]/[acetylacetone] = 3:2. Acetylacetone (acac) is added as a chelating agent in the aim to decrease the reactivity of titanium alkoxide and to stabilize the sol.[11–15]

Acetic acid decreases the kinetics of hydrolysis and polycondensation of $Ti(OPr^i)_4$.[11,16–19] Acetic acid initiates hydrolysis via an esterification reaction as fellows[11]:

$$C_3H_7{-}OH + CH_3{-}COOH \leftrightarrow H_2O + C_3H_7COO\,CH_3$$

Moreover, it has been shown that the acetic acid induces a modification of the molecular structure of the alkoxide precursor.[20] Titanium alkoxides reacts directly with glacial acetic acid or acetylacetone at a molecular level:

$$M(OR)_4 + H\text{-}(OAc) \rightarrow M(OR)_3(OAc) + R{-}OH$$

$$M(OR)_4 + acac\text{-}H \rightarrow M(OR)_3(acac) + R{-}OH$$

where M: metal cation, OAc:acetate, OR-alkoxy, acac-H:acetylacetone and OH-hydroxy groups. The molecularly modified precursor's hydrolysis and polycondensation reactions are slowed down considerably since on exposure to water although the alkoxy groups hydrolyze rapidly, the modifying groups are quite stable towards such reactions and remain unhydrolyzed even on addition of large excess of water.

$$M(OR)_3(OAc) + H{-}OH \rightarrow M(OR)_2(OH)(OAc)$$

$$M(OR)_3(acac) + H{-}OH \rightarrow M(OR)_2(OH)(acac)$$

Then, the aqueous solution of barium acetate, previously prepared, was added drop wise, while stirring, to the organic mixture containing titanium and cerium precursors to produce a Ba–Ce–Ti complex solution with the molar ratio 0.945:0.055:1. The as obtained sol, was maintained at reflux with magnetic agitation, for 6 h, to achieve the gelification process. The solvents were evaporated from the gel by drying at 100 °C. Heating the gel at 1100 °C, a (Ba, Ce)TiO_3 solid solution was obtained. The ceramic samples were prepared by uniaxial (at 200 MPa) and cold isostatic (at 3500 atm) pressing methods. The pellets with 1.2 cm diameter and 0.2 cm thick as obtained were then sinterized at various temperatures from 1100 to 1250 °C, for 2 h in air. Samples with apparent densities of 94.8% from theoretical density were obtained by sintering the pellets at 1250 °C, for 2 h in air.

Apparent densities of the sintered pellets were measured by Arhimede method using a density balance. The thermal behaviour of the gel was investigated by thermal analyses, IR spectroscopy, scanning electronic microscopy (SEM) and X-ray diffraction (XRD). The thermal gravimetry (TGA) and sample controlled thermal (SCTA) Analyses were recorded by using a TA Instrument, model Q500 and an apparatus home built,[13] respectively. The totality of evolved gases is continuously analysed by a RIBER mass spectrometer coupled to the apparatus for sample controlled thermal analysis. FT-IR spectra were recorded on these samples using an EQUINOX 55 FTIR spectrometer. The microstructure of the powders and ceramic (Ba, Ce)TiO_3 was investigated using a Philips XL 30 scanning electron microscope. The structure of the gel powder was characterized by X-ray diffraction using a Siemens D 5000 X-ray diffractometer. For powder diffraction we used Cu Kα_1 radiation, a LiF crystal monochromator and Bragg-Brentano diffraction geometry. The data were collected at 25 °C with a step-scan interval of 0.020° and a step time of 10 s. For refinement we used a program package DIFFRAC^{plus} from Bruker. The dielectric properties of the bulk ceramics were measured with a Hewlett-Packard impedance meter Model 4194. The electrical measurements were carried out in the metal-ferroelectric-metal (MFM) configuration, where the electrodes M consist of a silver paste heated at 650 °C, 15 min.

3. Results and discussion

3.1. Thermal analyses

The thermal stability of the precursor-gel of (Ba, Ce)TiO_3 was analysed using thermogravimetry (TG) at 10 °C/min in a flowing nitrogen (60 ml/min flow rate) environment (Fig. 1) and sample controlled thermal analysis (SCTA) coupled with mass

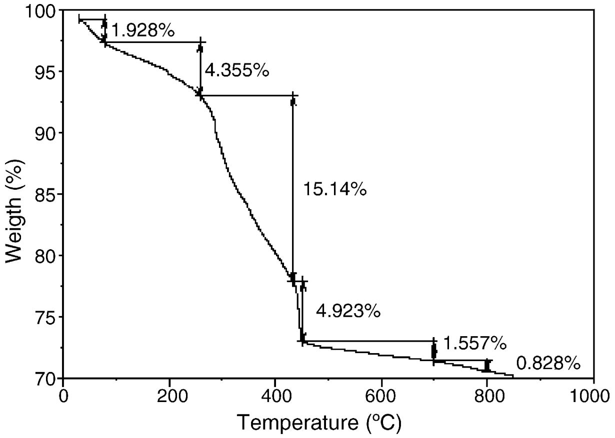


Fig. 1. TG curve at 10 °C/min in N_2 of Ce-doped-$BaTiO_3$ precursor gel.

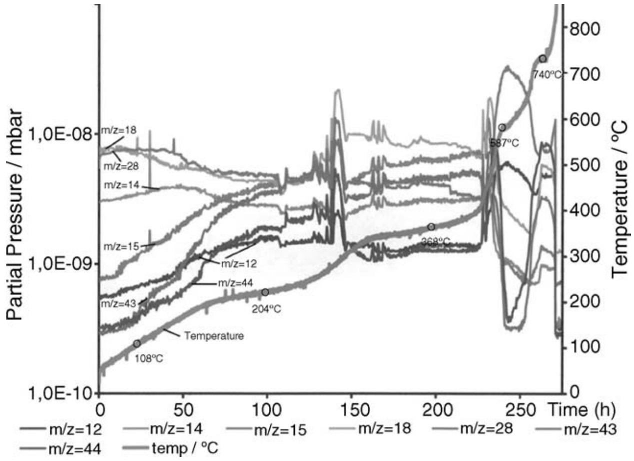


Fig. 2. SCTA curve and masspectra of (Ba,Ce)TiO_3 precursor gel.

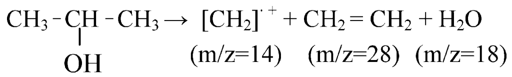
spectrometry for analysis of the evolved gases (Fig. 2). The TG analyse in air is performed too but there are no differences. In SCTA, the rate of production of the gaseous phase can be permanently controlled at a low enough rate such that, both temperature and pressure gradients can be lowered so as to avoid any overlaps of the successive steps of reaction. This thermal analysis was carried out at a residual pressure of $\sim 5 \times 10^{-3}$ mbar.[21] At times, the volume of the evolved gases is equal to the volume of extracted gases from SECTA apparatus. In this way, the residual presure is maintained at $\sim 5 \times 10^{-3}$ mbar value.

For sample controlled thermal analysis, approximately 30 mg dried gel of (Ba, Ce)TiO_3 was thermally decomposed in the temperature range of 25–825 °C during 275 h with a weight loss of 28.73% in good agreement with that observed by TGA. According to TG and SCTA curves of Ce doped-$BaTiO_3$ gel in the temperature range of 25–825 °C, we can divide these thermograms into six domains, more clearly separated by SCTA. The spectra of the volatile decomposition products (Fig. 2) are complex as they correspond to a mixture of species. The first major step occurs between 100 and 200 °C. The main species evolved during this range are $m/z = 14$, 18 and 28 which are likely to CH_2, H_2O and $CH_2{=}CH_2$ species resulted by the degradation of a part of the isopropoxide and acetate groups bonded to Ti and Ba respectively. The second step, in the range 200–250 °C, shows major changes in the composition of the evolved decomposition products caused by the decomposition of acetylacetonate groups. Thus, the new peaks appeared for $m/z = 14, 15, 28$ and 43 suggest the loss of CH_2, CH_3, CO and $CH_3{-}C{=}0$ from acetylacetonate groups of Ce(acac)$_3$. The next step observed in the SCTA curve occurs between 250 and 432 °C and corresponds also to the losses of $m/z = 14$, 15, 28 and 43, respectively. Compared to prior step of the thermolyse, in this step, the intensity ratio of $m/z = 18{:}28$ peaks increases suggesting a decrease of acetylacetonate groups in the gel. The peaks at 12(C) and 28(CO) that appear in the domain 470–620 °C, could be due to the formation of $BaCO_3$ by decomposition of $Ba(CH_3COO)_2$.[14]

Reaction of barium acetate decomposition is:

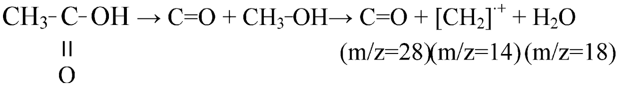
$$Ba(CH_3COO)_2 \rightarrow BaCO_3 + CO + 2C + 3H_2$$

Isopropanol and isopropoxid groups decompose by broking of C–C bond near oxygen atom[22]:



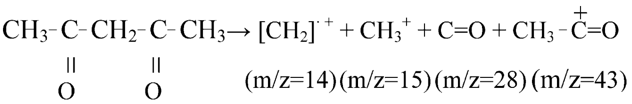
$$\underset{\text{OH}}{\overset{}{CH_3-\underset{|}{C}H-CH_3}} \rightarrow \underset{(m/z=14)}{[CH_2]^{\cdot +}} + \underset{(m/z=28)}{CH_2=CH_2} + \underset{(m/z=18)}{H_2O}$$

Acetic acid and acetate groups and decompose by broking the bonds near C=O and set free M–OH[22]:



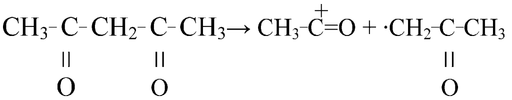
$$CH_3-\underset{\underset{O}{\|}}{C}-OH \rightarrow C{=}O + CH_3\text{-}OH \rightarrow \underset{(m/z=28)}{C{=}O} + \underset{(m/z=14)}{[CH_2]^{\cdot +}} + \underset{(m/z=18)}{H_2O}$$

The decomposition flow of acetylacetone occurs in three steps[22]:



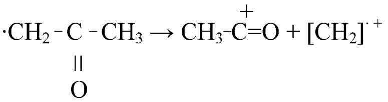
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 \rightarrow \underset{(m/z=14)}{[CH_2]^{\cdot +}} + \underset{(m/z=15)}{CH_3^{+}} + \underset{(m/z=28)}{C{=}O} + \underset{(m/z=43)}{CH_3-\overset{+}{C}{=}O}$$

Step 1:



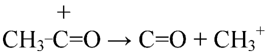
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 \rightarrow CH_3-\overset{+}{C}{=}O + \cdot CH_2-\underset{\underset{O}{\|}}{C}-CH_3$$

Step 2:



$$\cdot CH_2-\underset{\underset{O}{\|}}{C}-CH_3 \rightarrow CH_3-\overset{+}{C}{=}O + [CH_2]^{\cdot +}$$

Step 3:



$$CH_3-\overset{+}{C}{=}O \rightarrow C{=}O + CH_3^{+}$$

In the temperature range of 720 and 760 °C, the peaks observed were at $m/z = 12$(C), 16(O), 18(H_2O), 28(CO) and 44(CO_2), respectively, which could be associated with the decomposition of $BaCO_3$ and the formation of $BaTiO_3$ phase. The presence at high temperature of the peak at $m/z = 18$ representing water, suggests the possible loss of water by the condensation of the groups –Ti–(OH) present in the gel.

3.2. Infrared spectroscopy

The Fourier transform infrared spectroscopy FT-IR spectra of the (Ba, Ce)TiO_3 gel were recorded after the gel had been dried at temperature of 100 °C and then fired up to 350 °C, in air. As shown in Fig. 3, the dried gel presented IR absorption bands at: 3600–3200, 1573, 1550, 1423, 1338, 1049, 1020, 931, 651, 616 and 466 cm^{-1}.

The large band centred at 3400 cm^{-1} corresponds to the symmetric and asymmetric stretching vibrations of weakly bound water interacting with its environment via hydrogen bonding and to stretching vibrations of hydrogen-bonded OH groups.[23,24] The strong bands at 1400–1600 cm^{-1} are characteristic to organic groups (acetylacetonate and acetate). Thus, the bands at 1573 and 1550 cm^{-1} are due to acac groups bonded to cerium and titanium.[9] The acetate complex present a strong asymmetrical stretching band ν(C=O) near 1573 cm^{-1} which masks the

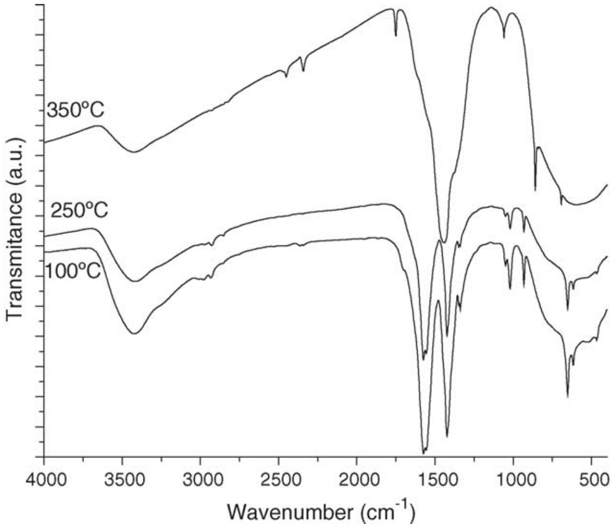


Fig. 3. FTIR spectra of Ce doped-$BaTiO_3$ gel heated at 100–350 °C.

band corresponding to acac groups and, a weaker, symmetrical stretching band ν(C–O) at ∼1423 cm^{-1}.[25] The low-frequency region of the spectrum (1049–1020 cm^{-1} and 651–616 cm^{-1}) shows a mixture of bands due to the carboxylate group and titanium isopropoxide.[9,25,17] The bands at 1338–931 cm^{-1} are attributed to O–H bonded to titanium while the band at 466 cm^{-1} is due to metal-oxygen bonds.[26,25] The IR spectrum of the gel fired at 350 °C show a set of bands at 1445, 858 and 693 cm^{-1} that, according to the literature, correspond to $BaCO_3$ obtained by thermal decomposition of barium acetate at ≥350 °C.[27] The presence of a broad band of TiO_2 at 607 cm^{-1} is also noted.[28]

3.3. SEM analysis

SEM micrographs of the dried gel (100 °C) and heated powders (1100 °C) derived from the precursor gel of $(Ba,Ce)TiO_3$ are shown in Fig. 4. Both powders present nano-sized grains. The oven-dried powders exhibits agglomerates consisting of very fine (∼140 nm) primary particles (Fig. 4(a)).

The fired powders of $(Ba, Ce)TiO_3$ solid solution show homogeneous particles size of about 400 nm with tendency to agglomeration, as can be seen in Fig. 4(b).

Ceramic pellets sintered at 1250 °C, for 2 h in air shown uniform grains size morphology of 0.5–1 µm as can be seen in Fig. 5.

3.4. XRD analysis

The precursor gel of Ce doped-$BaTiO_3$ was heated at various temperatures and then analysed by XRD. The gel dried at 100 °C was found to be amorphous. A lot of intermediate phases were observed at different temperatures up to 1100 °C. Thus, X-ray patterns of heated gel at 750 °C exhibit peaks corresponding to the $BaCO_3$, cubic $BaTiO_3$ and tetragonal $BaTiO_3$ structures. A mixture of tetragonal $BaTiO_3$ and $BaCO_3$ phases was identified in the powder fired at 900 °C. The gel powder heated at 1100 °C, 3h in air has been presented as a single phase with the perovskite structure of tetragonal $BaTiO_3$ (Fig. 6).[29]

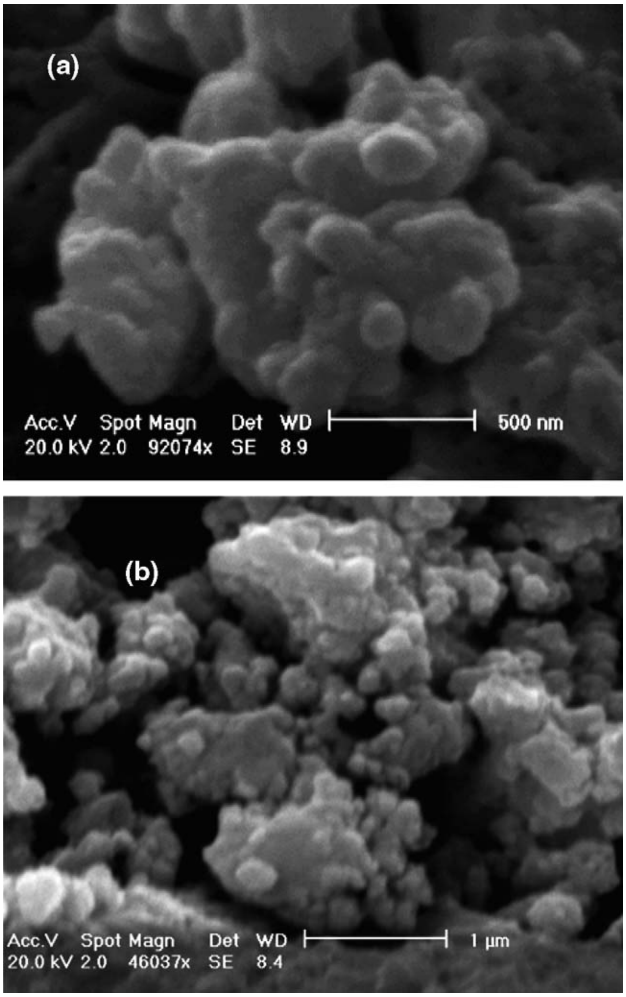


Fig. 4. SEM micrographs of the gel heated at 100 °C and 1100 °C.

Lattice parameters of as-obtained phase ($Ba_{0.945}Ce_{0.055}TiO_3$ solid solution) were $a = 0.40043$ nm and $c = 0.40229$ nm. The decrease of the tetragonality (c/a) of $BaTiO_3$ from 1.011 to 1.0046 is due to the incorporation of Ce ions in $BaTiO_3$.

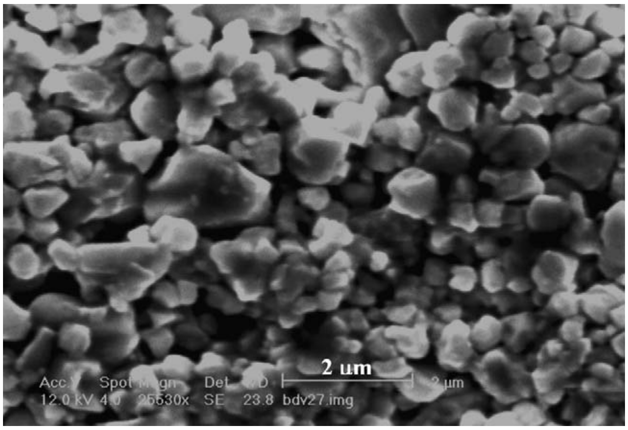


Fig. 5. SEM micrographs of the ceramic sintered at 1250 °C, for 2 h in air.

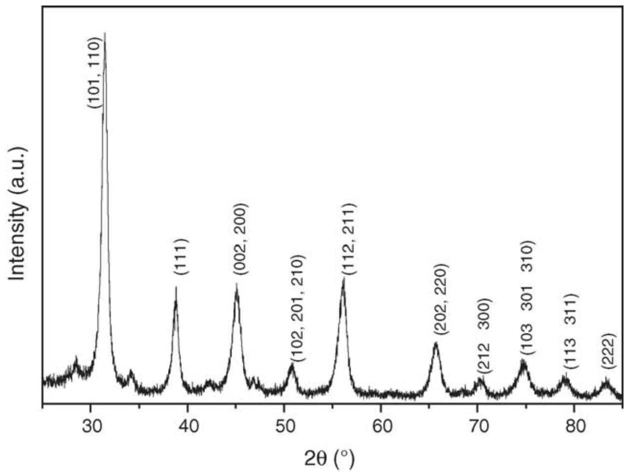


Fig. 6. X -ray diffraction pattern of (Ba,Ce)TiO_3 gel powder fired at 1100 °C.

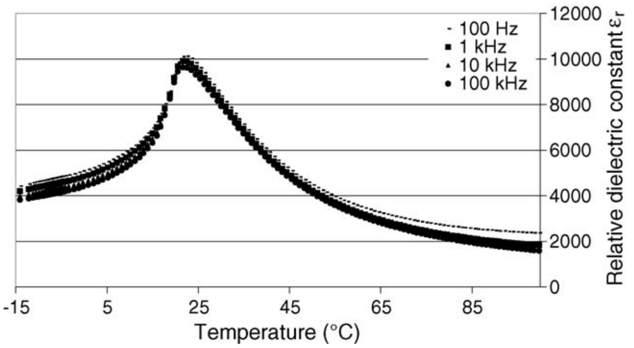


Fig. 7. Variation of dielectric constant (ε) of Ce doped-$BaTiO_3$ ceramic with temperature and frequency.

3.5. Dielectric properties

The dielectric constant (ε_r) and dielectric loss ($\tan\delta$) of $BaTiO_3$ ceramics doped with 5.5 mol% Ce were measured at various frequencies from 100 Hz to 1 MHz. The highest dielectric constant of $Ba_{1-x}Ce_xTiO_3$, $x = 0.055$ was 10130 at 100 Hz and decreased up to 9630 at 1 MHz, at the Curie point temperature (Fig. 7). The dielectric loss was 1.8% la 100 Hz and increased at 1 MHz up to 2.9% (Fig. 8).

These values of Ce doped $BaTiO_3$ ceramic prepared by sol–gel method indicate that this material can be used for capacitors with high permittivity. The Curie temperature (T_c) was $T_c = 22$ °C. The decrease of Curie point of $BaTiO_3$ is in good agreement with reference data[3] and indicates a partial substitution of Ba ions with Ce^{3+} in the perovskite lattice.

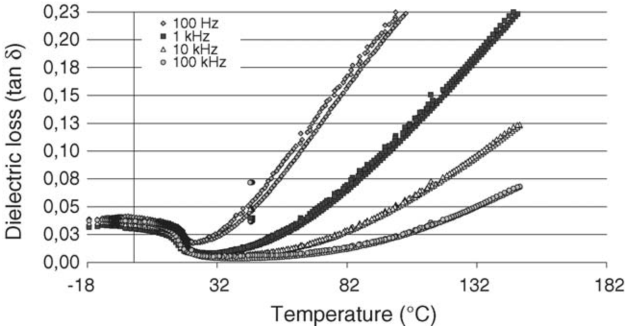


Fig. 8. Variation of loss tangent (δ) of Ce doped-$BaTiO_3$ ceramic with temperature and frequency.

4. Conclusion

Ferroelectric Ce-doped $BaTiO_3$ powder have been prepared by a sol–gel technique from precursors type acetate and alkoxide modified molecular with acetic acid and acetyl acetone.

The FTIR and thermal analyses showed a gel structure comprising organic groups partially hydrolyzed which are completely evolved at temperature of around 450 °C. The gel shows a structure polymeric and grains of about 140 nm.

Unfortunately, the precursors decompose through oxides and barium carbonate around 500 °C. The reaction leading to the pure material occurs then only around 850 °C upon a long time, and sintering effect is weak. Fired gel-precursor at temperatures of 1100 °C, 3 h in air, shown grains size of about 400 nm and revealed the existence of monophasic perovskite with the structure of ferroelectric $BaTiO_3$.

A small influence of the frequency on the dielectric properties of the $Ba_{0.945}Ce_{0.055}TiO_3$ ceramics was observed in 100 Hz to 1 MHz domain. At the Curie temperature point (22 °C) the dielectric constant was 10130 at 100 Hz and 9630 at 1 MHz while the dielectric loss ($\tan\delta$) was 0.018 at 100 Hz and 0.029 at 1 MHz.

Acknowledgement

We thank NATO office from Paris for financial support.

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