SOL-GEL SYNTHESIS AND CHARACTERIZATION OF BaTiO$_3$ POWDER

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Barium acetylacetonate and titanium (IV) isopropoxide, dissolved in adequate solvents, were used to produce stoichiometric BaTiO$_3$. The purity of the gel powder was >99.98 %. The particle size range was 80 nm for the dried gel powder and 1-1.5 μm for the powder calcined at 950 °C. X-ray analyses indicates that the material calcined at 950 °C in air or, at 825 °C under vacuum, exhibits a tetragonal, poorly crystallized, BaTiO$_3$ structure. The powder pressed and sintered at 1275 °C show high dielectric constants, i.e. 1300 at 25 °C and, 3020 at the Curie temperature (104 °C). The melting point for BaTiO$_3$ prepared by sol-gel technique is 1290 °C.

1. Introduction

The methods for preparation of the BaTiO$_3$ thin films have been reviewed in [1]. The sol-gel method seems to be a convenient method for the preparation of both thin films and powder material.

The sol-gel method has been chosen for the preparation of BaTiO$_3$ due to the advantages of this technique namely: fine particle size, simple compositional control and low processing temperature. The aim of this work is to prepare a dielectric ceramic for a properly using as a monolith capacitor. Different authors have used sol-gel methods for the synthesis of oxide based-materials [2-6]. They presented the synthesis conditions as a function of the used precursor and of form of the final product (powder, film, monolith and fibre). The structural and physical properties of the gel are strongly dependent on: selection of starting material, rate of hydrolysis and condensation, chemical modifications of the sol-gel system and other processing parameters [3]. Mazdiyasni *et al.* [4,5] used barium isopropoxide derived from high-purity Ba metal, whereas Flaschen [6] chose Ba(OH)$_2$ as a starting material. Ritter *et al.* [7] studied the alkoxide-based synthesis of phases in the system BaO-TiO$_2$. Phule *et al.* [8] presented a comparison of different starting materials used in BaTiO$_3$ synthesis. The main objective of the present work was to prepare BaTiO$_3$ powder by sol-gel route using Ba and Ti precursors with long alkyl chains, and other awards to prepare a dielectric ceramic for capacitors. We selected Ba acetylacetonate and Ti(IV) isopropoxide chelated *in situ* with acetylacetone for a more precise control of the rate of hydrolysis and condensation observing that the hydrolysis rate decreases with the alkyl chain length.

2. Experimental procedure

Titanium isopropoxide and barium acetylacetonate were used as precursors to prepare the BaTiO$_3$ powder by sol-gel method. Titanium isopropoxide was chosen because it is known that the transition metal alkoxides are highly reactive due to the presence of strongly electronegative OR groups that stabilize the metal in the highest oxidation state and make the nucleophilic attack to the metal possible [9,10]. Such alcoxides are used as precursors in sol-gel processing considering that

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they are strongly electrophilic and thus less stable toward hydrolysis, condensation, and other nucleophilic reactions. Furthermore, the group R from Ti(OR)$_4$ influences the morphology (particle size and surface area) and the crystallization behaviour of resulting gel [11]. Chemical modification of the transitional metal alcoxide with chelating ligands, is used to control the condensation route and the evolution of the polymer [9,12]. We used acetylacetone (abbreviated as acac) to chelate titanium isopropoxide (molar ratio Ti(OPr^i)$_4$:acac=1:2) to obtain a highly condensed product and to promote the gelification process. The excess water added to Ti(OPr^i)$_2$.acac$_2$ causes the preferential hydrolysis of OPr^i ligands [13] and conducces to a unidimensional polymer [14]. Barium acetylacetonate hydrate, which is a more stable precursor towards ambient moisture than barium alcoxides, was added in adequate ratio to a solution of the titanium precursor in isopropanol. The mixture was refluxed in dried air (using CaCl$_2$) for 2 h, while stirring. The mixed solutions were refluxed at a temperature of around 80 °C before an excess of water and glacial acetic acid was slowly added, for 2 hours and the pH maintained at 2.5-3.5. The mixture was stirred for 8 hours before collecting the gel. The gel was separated by removing the solvents at 80°C without filtration, then the gel was dried at 100 °C, for 3h. The gel powders were calcined and analysed at various temperatures up to 1000 °C. The impurities were analysed by emission spectrographic analysis. The gel was characterized by thermogravimetric analysis (TG), differential thermogravimetric analysis (DTG) and differential scanning calorimetry (DSC) (TGA Model V5 1A 2000, DuPont, Wilmington, DE). Sample controlled thermal analysis (SCTA) was also used for a better separation of thermal decomposition steps of the gel. The structure of the gel was analysed by infrared spectroscopy method using a Fourier transform infrared spectrometer FTIR (Model 8201 PC, Schimadzu Corp.). The morphology of the samples was investigated using a Philips XL 30 scanning electron microscope. The crystalline structure of the gel powder was characterized by X-ray diffraction using a Siemens D 5000 X-ray diffractometer. Raman spectrum was recorded at room-temperature using a spectrometer R−2001^{TM}. The 785 nm line of a laser operating at 500 mw was used for excitation. The unpolarized radiation was collected with an instrumental resolution of ~30 cm^{-1}. The melting point of BaTiO$_3$ was measured by a Heating Microscope: ES Expert System Solutions (Model Misura 3). The dielectric properties of the bulk ceramics were measured using a Hewlett-Packard impedance meter (Model 4194).

3. Results and discussion

Table 1 presents a comparison between the chemical compositions of the precursors and of the synthesized product (BaTiO$_3$) determined by atomic absorption. This analysis shows a high purity of the BaTiO$_3$ powder (>99.98 %) due to high purity of the precursors and absence of contamination during the sol-gel synthesis.

Table 1. Emission spectrographic analysis of the as- prepared BaTiO$_3$.

Elements	Cd (%)	Co (%)	Mg (%)	Mn (%)	Sn (%)	Fe (%)	Cr (%)	Ni (%)	Al (%)	Si (%)
Ba(acac)$_2$.2H$_2$O	nd	nd	1×10^{-3}	nd	nd	1×10^{-3}	3×10^{-3}	nd	2×10^{-3}	3×10^{-2}
Ti(OPr^i)$_4$	nd	nd	1×10^{-3}	nd	nd	nd $<1\times10^{-3}$	nd $<1\times10^{-3}$	nd	nd	1×10^{-3}
BaTiO$_3$	nd	nd	1×10^{-3}	nd	nd	1×10^{-3}	3×10^{-3}	nd	3×10^{-3}	1×10^{-2}

nd = not detected less than 1×10^{-3} (%)

Some thermal analyses (TG, DTG, DSC and SCTA) of the BaTiO$_3$ precursor dried gel at 100 °C are presented in Fig. 1a,b and Fig. 2. The TG and DTG of the gel were carried out at a heating rate of 20 °C/min up to 900 °C, in air (Fig. 1a). DSC was used to emphasize the solvent evaporation steps in the temperature interval 25-400 °C (Fig. 1b). Furthermore, SCTA under reduced pressure (5×10^{-3} mbar) (Fig. 2) was used for a finer separation of the thermal decomposition stages of the gel. The principle of SCTA used here is the control of the temperature in order to maintain constant reaction rate [15]. The experimental set-up controls the rate of gas production constant with time thus, ensuring a constant rate of weight loss. In the temperature domain 25 °C to 228 °C, the

DTA curve shows two endothermic peaks at 130.9 °C and 165.4 °C (Fig. 1a) corresponding to the volatilisation of absorbed water on the grain surface, isopropanol and acetic acid (heat of 228.1 J/g) and, to the evaporation of acetyl acetone (71.16 J/g) respectively, (Fig. 1b). The second major weight loss (Fig.1a) that occurs in the temperature range 325 to 350 °C is due to the pyrolysis of the organic groups (exothermic peak). A further exothermic peak at 620 °C probably due to the crystallization of the perovskite phase appears in Fig. 1a and Fig. 2. The last exothermic peak observed in the temperature domain 732-760 °C is associated with the decomposition of small amounts of barium carbonate formed by decomposition of acetyl groups.
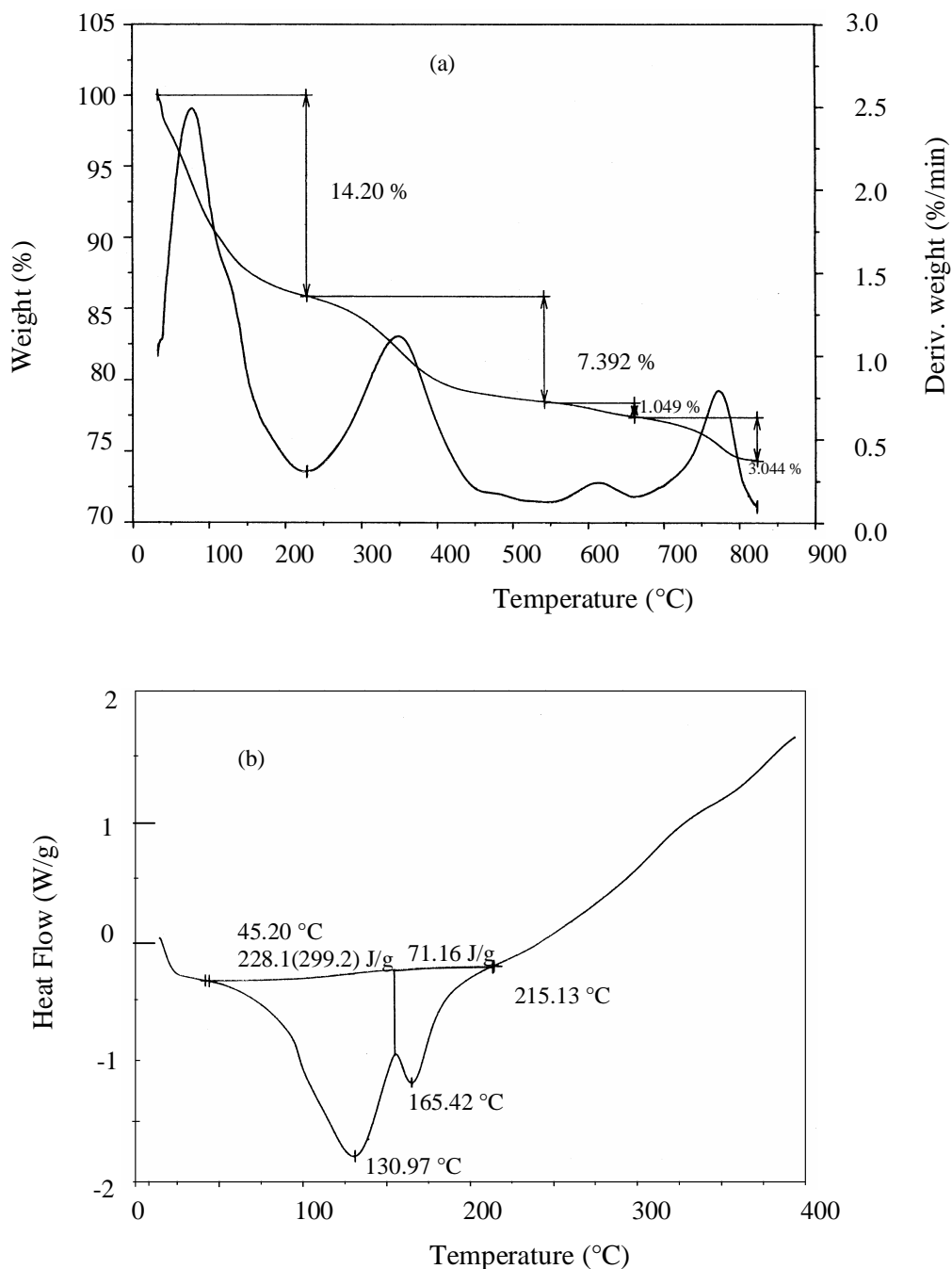
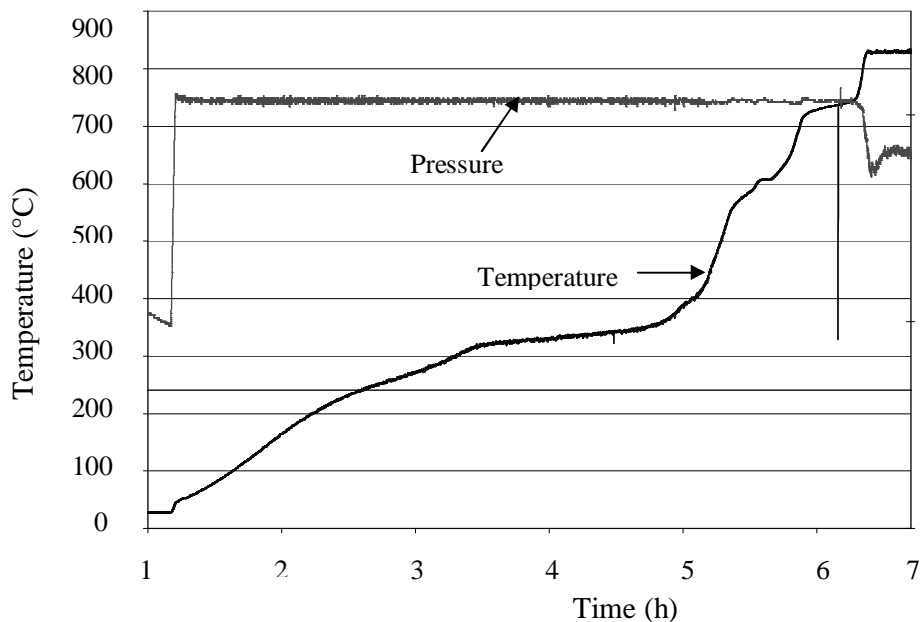Fig. 1(a,b). TG, DTG and DSC curves of the gel of BaTiO₃

Fig. 2. SCTA curves of the gel of BaTiO$_3$.

For IR spectroscopic measurements, the sample was pressed into thin wafer and placed on a KBr plate. Fig. 3 shows the FT-IR spectra of barium acetylacetonate-(1), titanium isopropoxide-(2), and gel powder dried at 100 °C-(3).
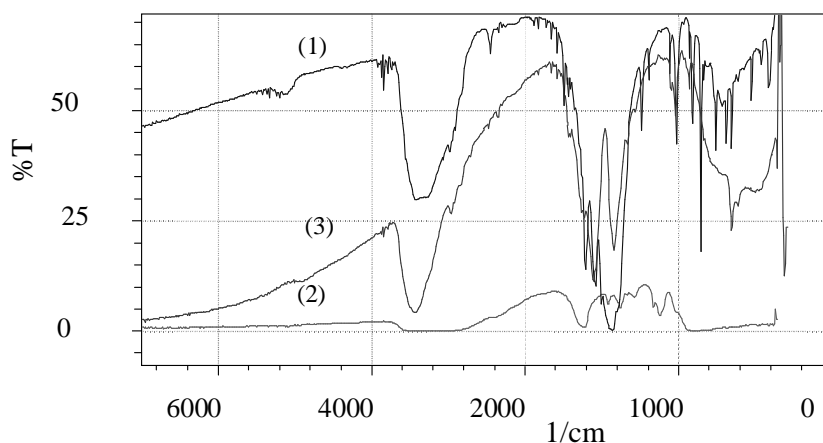

Fig. 3. FTIR spectra of Ba(acac)$_2 \cdot$2H$_2$O-(1), Ti(OC$_3$H$_7$)$_4$ (2) and dried gel at 100°C-(3).

As shown in Fig. 2(3), the dried gel presented a large band centred at 3450 cm^{-1} corresponding to lattice water absorbed (antisymmetric and symmetric OH stretching). The two very small bands present at 2335 and 2350 cm^{-1} in the spectrum of dried gel are due to adsorbed CO$_2$. The strong bands at 1590 and 1430 cm^{-1} are due to the organic groups. Thus, the bands at 1590 cm^{-1} (and also, 1530 cm^{-1}) are due to acac groups bonded to titanium [16] but these bands are almost masked by the acetato complex bands: ν(C = O) at ~1578 cm^{-1} and ν(C-O) at ~1414 cm^{-1}); in Fig. 2,(3) at 1430 cm^{-1}. In the spectra of our gel are present IR absorption bands due to titanium isopropoxide at 620 cm^{-1} assigned to ν (Ti-O-Pr^i) and to CO stretching metal (Ti, Y) alkoxides at 1000 cm^{-1} [16]. The peaks at 875 and 533 cm^{-1} are attributed to stretching metal-oxygen.

Electron micrograph (Fig. 4a) of the dried gel at 100 °C shows a structure consisting of agglomerates of 350 nm in size constituted of small particles of about 80 nm. On firing the gel at 950 °C, a microstructure with the grain size of 1-1.5 μm (Fig. 4b) is observed.
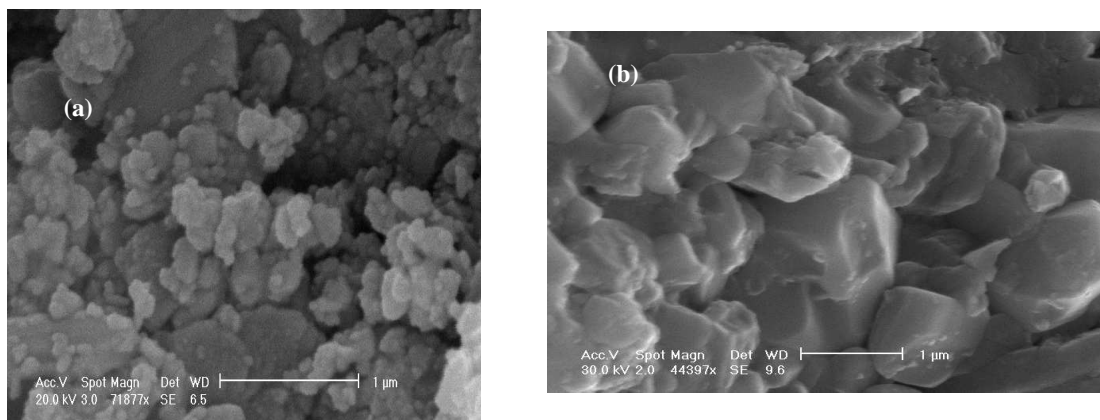

Fig.4 (a,b). SEM micrographs of the gel dried at 100 °C (a) and heated at 950°C (b).

Fig. 5 shows the XRD patterns of the dried gel (at 100 °C) and of the powder heated at 825 °C. The dried gel was found to be partially crystallized as TiO_2 anatase (Pattern: 21-1272). Examination of the X-ray patterns of the gel powders heated to temperatures of 400-950 °C in air or under vacuum (after SCTA) suggests the formation of intermediate phases such as TiO_2, $BaCO_3$ and cubic $BaTiO_3$.
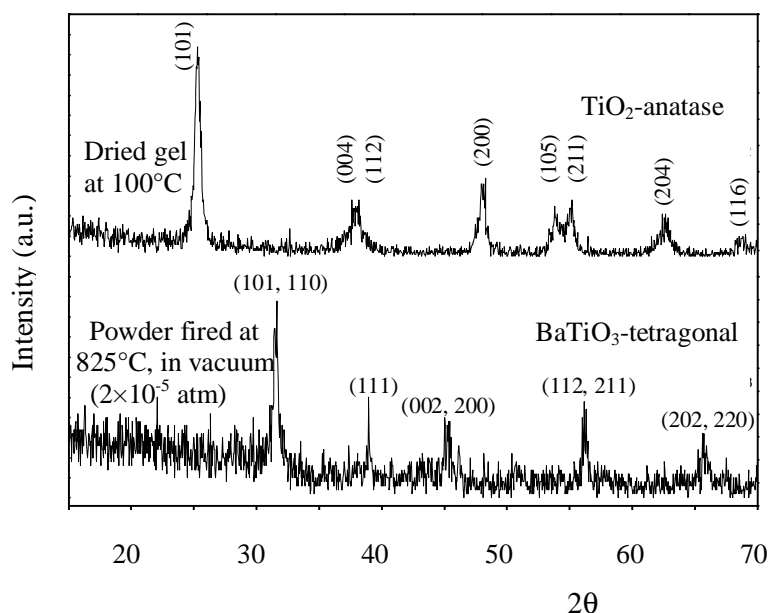

Fig. 5. X-ray diffraction pattern of sol-gel processed BaTiO₃ powder.

The tetragonal $BaTiO_3$ single phase (Pattern: 5-626) was identified by XRD in the poorly crystallized powders fired at 825 °C in vacuum (2×10^{-5} atm pressure) and also, in the gel calcined to 950 °C for 6 h. It's also possible to exist as traces, the cubic $BaTiO_3$ phase that continues to transform in tetragonal phase. The carbonated phase ($BaCO_3$) was present in the gel sintered in air up to 900 °C. For powder diffraction we used CuKα1 radiation, (wavelength 1.5406), 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 10s. For refinement we used a program package DIFFRAC[plus] from Bruker.

The Raman spectrum of $BaTiO_3$ powder calcined at 950 ℃ was registred (Fig.6). This spectrum presents peaks at 292, 517, and 719 cm^{-1} and suggests a tetragonal $BaTiO_3$. For single-crystal $BaTiO_3$, Perry *et al.* [17] have been observed peaks of tetragonal $BaTiO_3$ at 269, 306, 516, and 720 cm^{-1}.
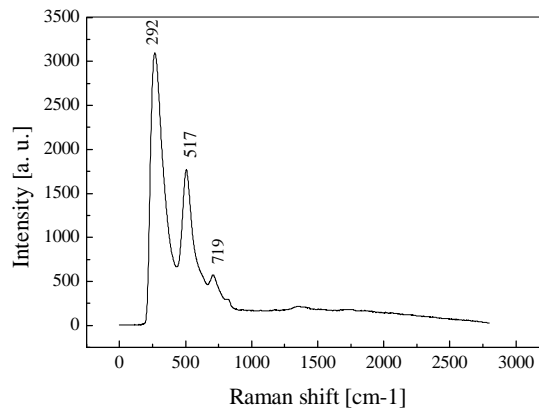

Fig. 6. Raman spectrum from $BaTiO_3$ powder calcined at 950 ℃.

The $BaTiO_3$ powder was pressed at 100 MPa into discs of 12 mm in diameter and 1.5-2 mm thickness. The pellets were sintered at 1275 °C, for 3h in air. Other pellets of $BaTiO_3$ sintered at 1300 °C, for 3h in air were melted. In this case, the melting point for $BaTiO_3$ obtained by sol-gel method it was measured. As can be seen in Fig. 7, the pellets start the melting at about 1290 °C and at 1345 °C the entire material is melted. The decrease of $BaTiO_3$ melting point from 1650 °C to 1290 °C could be related to the nanosized grains of the powder prepared by sol-gel method.
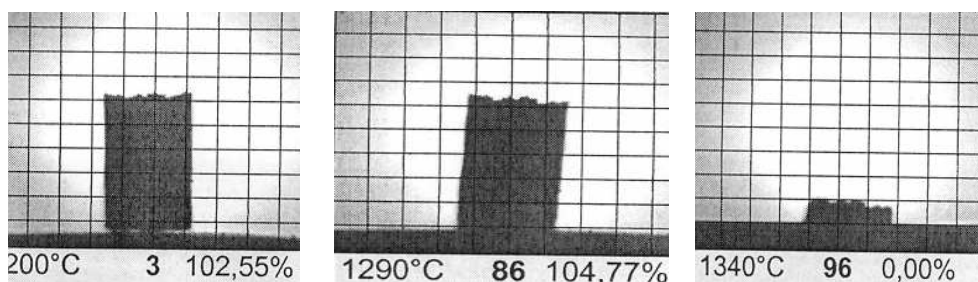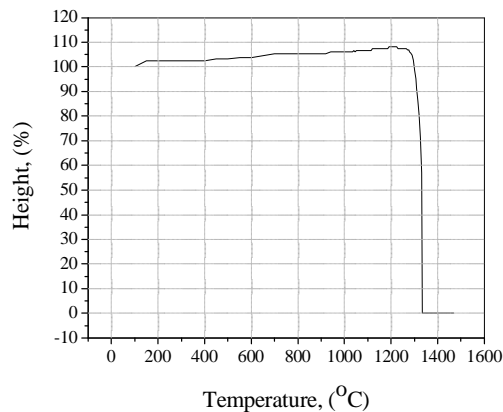

Fig. 7. Thermal behaviour on the melting route for $BaTiO_3$ pellets obtained from gel- powder.

The electrical measurements were carried out in the metal-ferroelectric-metal (MFM) configuration. Silver paint is printing on the ceramic samples and then heated at 650 °C for 1 h. Fig. 8 shows good values of the dielectric constant at room temperature (1275 °C) and at Curie temperature of 104 °C (3020). High room-temperature values obtained for the dielectric constant together with the decreasing of Curie temperature are due to the fine grain size of the material.
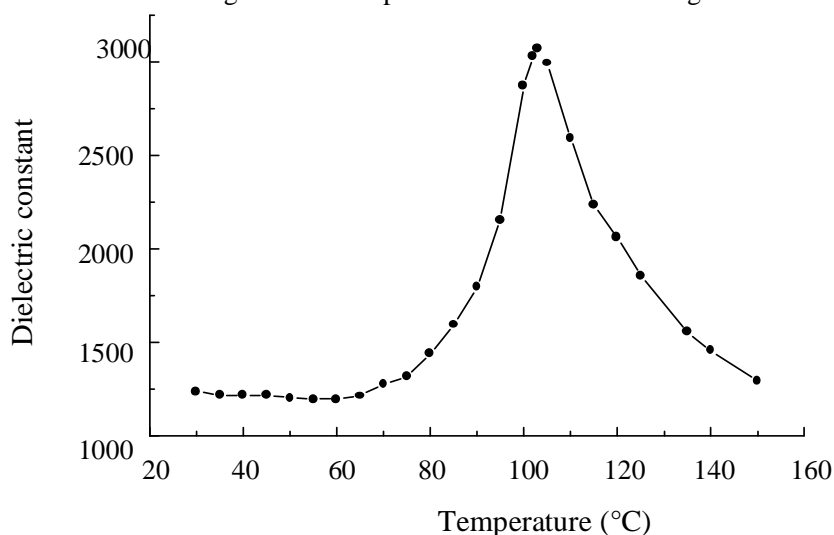

Fig. 8. Variation of dielectric constant with temperature for BaTiO$_3$ ceramic.

These values of dielectric constant and Curie temperature can be improved by improving the densification process of BaTiO$_3$ ceramic as prepared.

4. Conclusions

A sol-gel process was used to synthesize high-purity barium titanate powder using barium acetylacetonate, titanium (IV) isopropoxide, acetylacetone as a hydrolysis rate-retarding agent, and an acetic acid aqueous solution for hydrolysis of the precursors. The gel obtained was converted to crystalline tetragonal barium titanate powder by air calcination at 950 °C. The melting point for BaTiO$_3$ prepared by sol-gel method was about 1290 °C. The ceramic prepared from this powder exhibit convenient dielectric properties (dielectric constant of 3020 at Curie temperature Tc=104 °C). The decrease of Curie temperature at 104 °C and the value of dielectric constant (3020) are due to the small density of the pellets (aprox. 87 % from the theoretical density of BaTiO$_3$).

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