Examination of the influence of cobalt substitution on the properties of barium titanate ceramics

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Abstract
Cobalt (Co) doped Barium titanate (BaTiO3) powders, with Co concentration (0.5 and 10 mol%), are synthesized by the sol-gel technique and characterized by Thermogravimetric analysis (TGA), and Differential thermal analysis (DTA), X-Ray diffraction (XRD), Fourier Transform Infrared (FT-IR) and scanning electron microscopy (SEM). X-ray diffraction (XRD) patterns of the obtained powders, calcined at a relatively low temperature (1000 °C/3 h), found their crystallization in the pure perovskite structure without the appearance of secondary phases. XRD results reveal that the Co decreases the lattice parameters, the volume of the unit cell and the crystallite size of BaTiO3. The investigations carried out by FT-IR spectroscopy allow the investigation of the substitution procedure behavior associated to the Co incorporation into BaTiO3 lattice. The evolution of the physical parameters as functions of the dopant content have been examined based on XRD and FT-IR results. Furthermore, the morphology and the shape variation of particle size were studied through SEM.

Keywords: barium titanate, co-doping, ferroelectrics, synthesis, XRD, SEM

Kulcszszavak: bárium-titanát, co-doping, ferroelektromos, szintézis, XRD, SEM

1. Introduction

Recently, the research progression in the area of technical ceramics [1]–[7] has drawn great attention [4], [8]–[17]. Perovskite ferroelectric materials (ABO3) have had great interest due to the presence of a ferroelectric phase, their relatively simple structure which can allow theoretical interpretations and finally the feasibility of modifying their physical properties by numerous ionic substitutions. In addition, these materials exhibit high-physical performance, dielectric, electro-optical, and electronic properties [18]–[23], which make the materials widely used in various applications in different areas.

Barium titanate (BaTiO3) is one of the most important perovskite materials. It is a ferroelectric material, with piezoelectric properties and photorefractive effect. As a solid, it has five phases ranging from low to high temperature: rhombohedral, orthorhombic, tetragonal, cubic and hexagonal crystal structure. Indeed, all of the crystal structures show the ferroelectric effect except cubic structure. It has the appearance of a transparent powder or white crystals. It is soluble in concentrated sulfuric acid perhaps not in water.

Interesting and exotic properties are theoretically expected in doped BaTiO3 like ferromagnetism at room temperature enhanced dielectric properties etc. [24]. Moreover the synthesis technique also influences the level of doping and physical properties. Based on this fact, several studies are made adopting various synthesis methods such as solid state ceramic technique, laser ablation, sol-gel and chemical routes etc. [25]–[27]. In response to these reports, various types of doping have been attempted for BaTiO3, including Fe, Mn, Co etc. [24]–[28].

In the present paper, Co-doped BaTiO3 (BTCox) ceramics, with x = (0, 5 and 10%) were prepared using the sol-gel technique, the choice of this method of processing was based on its various advantages, low processing temperature, high purity, homogeneity and an excellent control of the stoichiometry of the products [29]. We have investigated the phase and structural properties of the prepared samples...
using X-ray diffraction (XRD), Fourier Transform Infrared (FT-IR) spectrometer and Scanning Electronic Microscopy (SEM). Experimental results are analyzed and then discussed as function of the doping concentration and compare the obtained values to those of the literature.

2. Experimental methods

2.1 Materials and synthesis method

Crystalline powders BTCox were synthesized and obtained using sol-gel method [30] through the destabilization of colloidal solution (DCS). This process provides numerous advantages such as an excellent control of the stoichiometry and a good homogeneity of the powders in spite of crystallization at relatively low temperature [8], [10], [29].

The powders were prepared using barium acetate trihydrate (Ba(CH₃COO)₂·3H₂O) (99.9% purity), titanium isoproploxide Ti[OCH(CH₃)₂]₄ (97% purity) and Cobalt acetate Co(CH₃CO₂)₂·4 H₂O(99.9% purity) as precursors, lactic acid (CH₃CH(OH)COOH) as peptizing agent and distilled water as solvent. The different steps relating to the preparation of BTCox powders are shown schematically in the flowchart in Fig. 1. A white sol with adequate proportions was obtained, which was dried in an oven at 80 °C for 72 h to obtain a dry gel. The raw powders, after grinding, were calcined in air in a programmable oven at the temperature of 1000 °C for 3 h.

The samples in pellet shapes were obtained by pressure with an uniaxial pressure equal to 10 tonnes/cm². Then, the pellets were sintered 1200 °C for 6 h reached with a heating rate 5 °C/min.

2.2 Characterization

Thermal study using Thermogravimetric analysis (TGA), and Differential thermal analysis (DTA) were performed on the sample BTCo15. The crystallinity and phases of the ceramic powders were examined using X-ray diffraction. The powder X-ray pattern was recorded for all samples with various cobalt concentrations by using an X-ray diffractometer equipped with [XPERT-PRO diffractometer with Cu-Kα radiation (λ = 1.5405980 Å)]. XRD spectrum was recorded in the 2θ range of 20 to 80°. The morphology of the ceramic powders was characterized by Scanning electron microscopy (SEM). Moreover, the functional groups in powders were detected by using of a Bruker-Tensor 27 spectrophotometer FT-IR spectroscopy in the wave number range 450- 4000 cm⁻¹.

3. Results and discussion

3.1 Thermal analysis

Fig. 2 shows the thermal analysis (TGA and DTA) of the sample 15% doped BaTiO₃ performed in air up to 1200 °C with a temperature rate 5° C / min. The TGA curve reveals three steps of decomposition (corresponding to an overall mass loss of approximately 28mg). The first step (33–320 °C), represents a weight loss which attributed to the elimination of water and excess lactic acid. This mass loss is accompanied by an endothermic peak in the DTA curve. The second stage (320–631 °C), represents a progressive mass loss, accompanied by several peaks endothermic and the other exothermic peaks in the DTA curve which can be attributed to the decomposition of the organic matter and the elimination of CO₂. In this temperature range, rearrangements of chemical bonds in the gel occur and the gel is converted to polymers [31]. The last stage of mass loss located in the range of (631–1000 °C) was detected, accompanied by an endothermic peak in the DTA curve, which is attributed to the decomposition of organic polymers and the formation of inorganic substances (the starting formation of BTCo0.15). No reaction or mass loss was noticed above 1000 °C, showing complete crystallization of the ceramic powders. This relatively low temperature compared to other reported from other works using different synthetic techniques [32] is due to the sol gel preparation method [8], [30].

3.2 Structural study

XRD patterns of the as-prepared powders were investigated, and they are reported as function of the Cobalt concentrations in Fig. 3. It shows that the BTCo crystallize in the perovskite phase without any secondary phase. The peaks are indexed as
the respective planes on the basis of JCPDS cards. Phan et al. [33] prepared BTCO using the classical solid state reaction method, after annealing at 1300 °C—4h, but with the presence of the secondary phases. The diffractograms reveal well-resolved peaks, which are a clear indication of the good particle’s crystallinity. These peaks are assigned in pure sample, i.e., x=0% to the perovskite structure with the tetragonal phase, which exists throughout the whole concentration ranges. This is supported by the presence of well resolved (002)–(200) doublet peaks around 2θ of 44–46° on the diffractogram.

The lattice parameters (a and c) were determined from XRD data analysis considering tetragonal phase with an accuracy of ±0.002 Å using the following relations:

\[
\frac{1}{d^2} = \frac{n^2 + k^2}{a^2} + \frac{l^2}{c^2}
\]

Where a is the lattice constant, d is interplanar spacing and (hkl) are Miller indices.

The fitted and calculated parameters are given in Table 1. The values of lattice constants (a and c) are given in Table 1 and were found that the lattice constant a increase while c decreases with Co concentration. Lattice parameters of pure the BaTiO₃ sample are in good agreement with reported values a = b = 3.988 Å and c = 4.026 Å (α = β = γ =90°) [33]. Moreover, the decrease in lattice parameters can be attributed to Co⁺ ions (0.58 Å) replacing the Ti⁴⁺ (0.605 Å), having higher ionic radii.

![XRD patterns of Co-doped BaTiO₃ powder samples calcined at 1000 °C for 3h](image)

Fig. 3 XRD patterns of Co-doped BaTiO₃ powder samples calcined at 1000 °C for 3h

The crystallite size and micro-strain was calculated using Williamson–Hall (W–H) plot which explains x-ray diffraction peak broadening [36].

\[
\beta = \beta_{\text{size}} + \beta_{\text{strain}}
\]

\[
\beta = \frac{0.944}{D \cos \theta} + 4\varepsilon \tan \theta
\]

Where, β is the full width of half maximum, ε is the strain, and D is the crystallite size. Figures 4(a), (b) and (c) show the linear plots, the intercepts and the slopes pointing out the crystallite size, as well as the strain of the prepared plotted samples as plotted by Williamson–Hall method. The crystallite size and the strain of single-phase samples are shown in Table 1. The nature of the strain formed was determined by the nature of the slope, that is, with a positive slope indicating a tensile strain and the negative slope indicating a compressive strain [37].

The results revealed that all the samples had a positive slope and were subjected to tensile strain. The strain values of BTCO.05 compound was found to be higher than the value of the other samples (Pure BaTiO₃ and BTCO.1). The higher value of lattice strain induced in the BTCO.05 sample is considered due to the creation of oxygen vacancies [38]. Table 1 illustrates the obtained crystallite size and the deviation of strain values BTCO (x=0, 5 and 10%) samples. In addition, the crystallite size was found in the range of 42.27–59 nm (from W–H plot).

3.3 Morphological investigation

Fig. 5 shows the evolution of the morphology and grain size of the BaTi₁₀₋₉CoₓO₄ (x=0, 0.05 and 0.1) powders as a function of the cobalt concentrations. Fig. 5a shows that the microstructure is completely anarchic, this is due to the shape of the precursors which have not yet reacted with each other, while the SEM image of the BTCO.05 powder (Fig. 5b) we notice the start of the incorporation of the precursors together, which is in good agreement with the results of the previous characterizations. Concerning Fig. 5c, we obtained a fine microstructure of average size less than 1 µm, homogeneous and of regular and well-defined shape, which indicates that the powder crystallizes in the perovskite phase without the presence of impurities.
Fig. 4 Williamson–Hall plot of pure and Co doped BaTiO₃ samples

4. ábra A tiszta és a Co adalékolt BaTiO₃ minták Williamson–Hall diagramja

Fig. 5 Morphology images of pure and Co-doped BaTiO₃ samples. a) BaTiO₃, b) BaTi₀.₉₅Co₀.₀₅O₃, c) BaTi₀.₉Co₀.₁O₃

5. ábra A tiszta és a Co adalékolt BaTiO₃ minták mikroszerkezete. a) BaTiO₃, b) BaTi₀.₉₅Co₀.₀₅O₃, c) BaTi₀.₉Co₀.₁O₃
3.4 FT-IR study

IR spectra of the as prepared (BTCox) powders, heat treated at 1000 °C for 3 h, were recorded in a wavelength range of 400 cm⁻¹ to 4000 cm⁻¹. Indeed, the above XRD results is supported by FTIR spectra, as shown in Fig. 6. The peak of absorption at 990 cm⁻¹ attributed to the vibration of the Ti-OR bond [39] dimens slightly in intensity and is transformed into a single band indicating the disappearance of the alkoxide groups. The characteristic absorption at the range of 1455 cm⁻¹ to 1457 cm⁻¹ are assigned to the stretching vibrations of carboxylate as there is a small amount of BaCO₃ [40]. In addition, Indeed, we can always observe the appearance of a single absorption bands at around 493, 480 and 490 cm⁻¹ respectively, which can be assigned to the stretching and bending vibrations of the Ti-O bond in [TiO₆]²⁻ octahedron. The obtained results are therefore in good agreement with those of X-ray diffraction.

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