



Mechanochemical preparation of BaTiO₃–Ni nanocomposites with high dielectric constant

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ABSTRACT

A mechanochemical procedure is proposed for an easy preparation of a BaTiO₃–Ni composite in a single step. BaTiO₃ and Ni powders available in the market are mixed by dry ball milling producing a decrease of particle size and an evenly distribution of both phases. In the sintered pellets the nickel particles are homogeneously distributed into the BaTiO₃ matrix and isolated from others Ni particles. The dielectric constant of the composite is considerably higher than that of the barium titanate. Moreover, the temperature of the ferroelectric ↔ paraelectric transition of the BaTiO₃–Ni composite here prepared is much lower than the one of the pure BaTiO₃ single phase.

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1. Introduction

Ferroelectric ceramics are widely used in a broad range of applications, especially in the design of electronic devices such as capacitors, dielectrics or electroactive materials [1–3]. Barium titanate (BaTiO₃) is one of the most used ferroelectric ceramic in electronics due to its high dielectric constant, which makes it a very attractive material to use in capacitors such as boundary layer capacitors (BLC) and multilayer ceramic capacitors (MLCC) [3–5]. Because of its extensive use, it has been widely studied and several methods have been proposed to enhance its dielectric constant. Thus, it has been observed that the homogeneous dispersion of an electrically conductive filler, such as small metal particles, into an insulating matrix leads to an increase in the dielectric constant of the composite [3,6]. This raise reaches its maximum in the neighbourhood of the percolation threshold, where the dielectric constant experiments an abrupt increase [7–9]. As the metal content grows over the percolation threshold, an insulator–conductor transition is recorded and both conductivity and permittivity increase [10,11]. This phenomenon may be explained by the isolation of the metal particles by thin dielectric layers near the percolation threshold. Hence the composite turns into a capacitor with good charge storage properties. This behaviour is well known and it has been explained by the percolation theory [12]. Moreover, it has been observed that the incorporation of metal particles improve the sintering process, because metal particles undergo plastic deformation and thereby relax the internal stresses induced during the sintering [3,13–17].

These kind of insulator/conductor composites have been intensely investigated in the last years [3,18–21] and present a great scientific and engineering interest. Recently, Pecharroman et al. [22] have designed a BaTiO₃–Ni composite with an extremely high dielectric constant. In a similar way, Chen et al. [3] reported the enhancement of the dielectric properties of X7R barium titanate ceramic by addition of nickel nanoparticles, while Qiao and Bi observed an improvement in the dielectric behaviour of BaTiO₃–Ni composite ferroic film. Lin et al. [23] registered an analogue behaviour when incorporating silver particles to an NBT ceramic matrix, Panteny et al. in barium titanate–silver composite [11] and George et al. in barium samarium titanate–silver composite [10].

The most common method of preparing these metal–ceramic composites is colloidal processing, which implies using nanoparticles of both constituents and high volumes of water [7,22]. Other methods involves using co-sputtering methods [24] or wet grinding [10]. In this work we propose the preparation BaTiO₃–Ni nanocomposites by dry grinding starting from conventional powders. Additionally, the dielectric behaviour of BaTiO₃–Ni nanocomposite prepared are investigated.

2. Experimental

The composites were prepared from commercial Ni (Sigma–Aldrich 266,981–500G, 3 μm, 99.7% in purity) and BaTiO₃ (Aldrich 12047–27–7, 2 μm, 99.9% in purity) samples. Powder mixtures containing 28 vol.% nickel and 72 vol.% BaTiO₃ were placed in a agate jar (300 cc volumen) with 12 agate balls 20 mm in diameter and milled using a centrifuge mill (model Pulverisette 6, Fritsch) at 730 r.p.m. Different milling times were used for comparison. The surface areas of all powders were determined with a surface area

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analyzer (model FlowSorb III 2310, Micrometrics Instruments), using N_2 as an adsorbate at the liquid nitrogen temperature. Size measurements were also made by light scattering procedure by means of a particle size analyzer (model Mastersizer, Malvern).

Ball milled powders were pressed into discs of 13 mm in diameter and 1 mm in thickness by uniaxial pressing at 860 MPa. Then, the discs were sinterized at 1300 °C under N_2 atmosphere for 2 h using a Carbolite 1500 °C horizontal tube furnace. The densities of all discs were determined both before and after sintering using the Archimedes method.

Dilatometric curves for pure $BaTiO_3$ and for $BaTiO_3$ -Ni composite under nitrogen atmosphere were obtained with a home-made dilatometer that measures the thickness change with temperature during the sintering process.

The microstructures of both powders and sintered discs were studied by scanning electron microscopy (SEM) in a Jeol instrument equipped with energy dispersive X-ray spectrometer (EDX).

X-ray powder diffraction patterns were obtained with a Siemens D501 instrument using $CuK\alpha$ radiation and a graphite monochromator. The full-width of the half-maximum (FWHM) of (1 1 1) diffraction peak was used for calculating the coherently diffracting domain for both Nickel and $BaTiO_3$ particles, according to the Scherrer equation.

The sintered discs were placed between two platinum electrodes for measuring their dielectric constant and the dielectric loss by means of a LCR meter (IET, model IMF 600A). The two parallel surfaces of the sintered discs were covered with gold by means of a sputtering device for improving the electrical contact with the platinum electrodes. The temperature dependences of the dielectric constant and dielectric loss were measured at temperatures ranging from 25 to 200 °C at 1 kHz.

3. Results and discussion

Fig. 1 shows the XRD patterns corresponding to a starting barium titanate and nickel mixture before milling (Fig. 1a) and to a $BaTiO_3$ -Ni powder milled for one (Fig. 1b), four (Fig. 1c) and 8 h (Fig. 1d). Both phases, Ni and $BaTiO_3$, remain crystalline after grinding treatment, but diffraction peaks become broader with the treatment due to a decrease in crystallite size. Thus, the crystallite size decreases for the starting powders from 117.0 and 136.3 nm for the $BaTiO_3$ and Ni, respectively, to about 45.5 and 63.8 nm for the $BaTiO_3$ and Ni, respectively, after grinding for one hour (Table 1). As grinding time proceeds, crystalline sizes decrease, yielding a minimum value of 28.4 and 30.3 nm for the $BaTiO_3$ and Ni, respectively, after eight hours treatment. The BET specific surface values obtained for the different milled samples are presented in Fig. 2. The specific surface value quickly rises with the grinding time, from about $1.2 \text{ m}^2 \text{ g}^{-1}$ for the unmilled sample to a maximum value of $11.6 \text{ m}^2 \text{ g}^{-1}$ for the sample ground for 4 h. After 4 h of milling, the specific surface starts to decrease until reaching a steady state value of $7.4 \text{ m}^2 \text{ g}^{-1}$ from 8 h of treatment. Thus, these results indicate that although the crystallite size decreases with the grinding time in entire studied range, surface area reaches a maximum at a 4-h of milling time, and starts decreasing thereafter, probably due to aggregation produced by the grinding procedure.

Fig. 3 shows the scanning electron micrographs of starting nickel and barium titanate powders (Fig. 1a and b, respectively) and $BaTiO_3$ -Ni powder milled for 4 h (Fig. 1c). Original powders consist of irregular and micron-sized particles highly aggregated. It can be appreciated that composite particles are also highly aggregated, although the subunits are smaller than in the starting powders. The micrograph of milled sample also reveals that nickel and $BaTiO_3$ particles present a very homogeneous distribution, which is

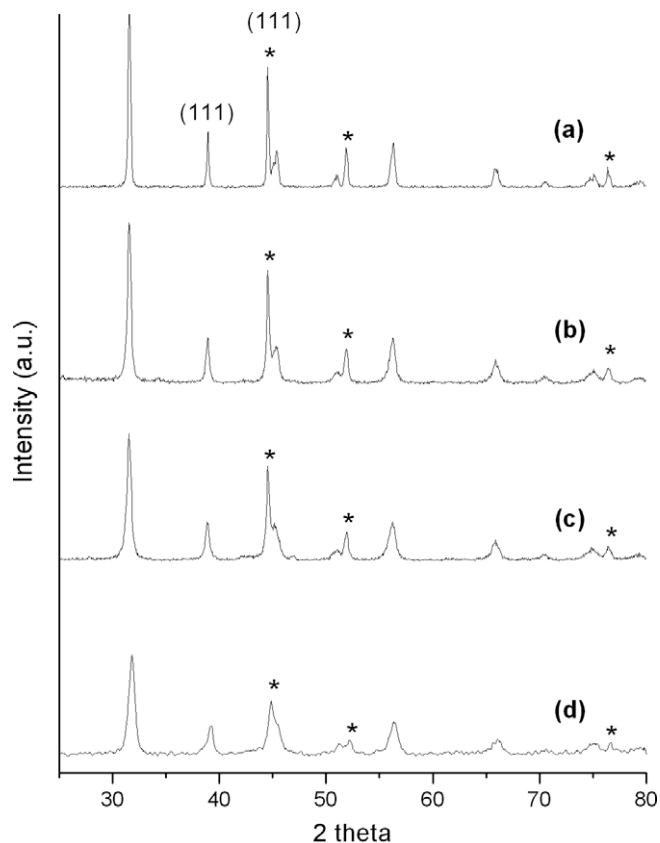


Fig. 1. X-ray diffraction patterns of barium titanate and nickel mixture before milling (a) and after grinding for 1 h (b), 4 h (c), and 8 h (d). Peaks corresponding to Ni phase are marked with an asterisk, all other peaks correspond to $BaTiO_3$ phase.

Table 1

Coherently Diffracting Domains values corresponding to starting nickel and barium titanate powders, and to the nanocomposite after different milling times.

Sample	Milling time (h)	d_{111} (nm) $BaTiO_3$	d_{111} (nm) Ni
Starting $BaTiO_3$	0	117.0	–
Starting Nickel	0	–	136.3
$BaTiO_3$ -Ni mixture	1	45.5	63.8
	2	38.8	58.7
	4	37.5	49.4
	8	28.4	30.3

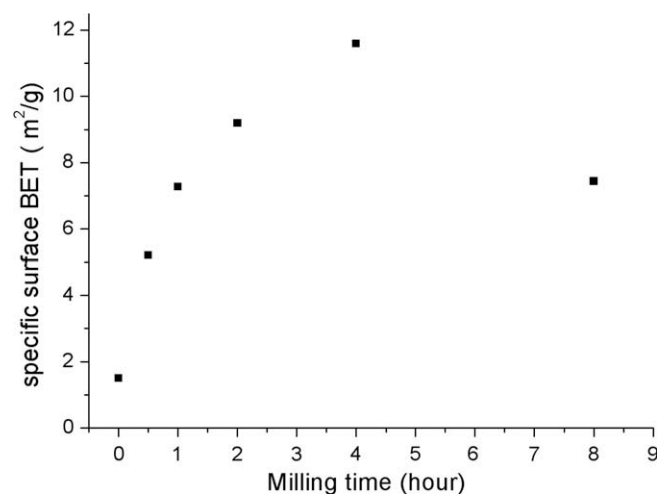


Fig. 2. BET specific surface values for the $BaTiO_3$ -Ni composite powder after different milling times.

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