

Structural characterization of barium titanate–cobalt ferrite composite powders

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Abstract

Barium titanate–cobalt ferrite composite powders prepared by sol–gel method and by mixing of precursors were characterized by Raman spectroscopy, scanning electron microscopy and Rietveld refinement of XRD data. Ba vacancies and BaTiO₃–CoFe₂O₄ interfacial stress were associated to lowering of tetragonal distortion in the ferroelectric structure. Raman spectroscopy suggested the encapsulation of ferrite inside clusters of particles in the sol–gel composite.

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1. Introduction

Magnetoelectric (ME) materials are promising candidates for technological applications since the multiferroic coupling allows the interconnection between magnetic and electric fields. New memory devices electrically written and magnetically read have been proposed based on ME materials [1].

ME structures can be prepared as single-phase materials or composites combining magnetostrictive and piezoelectric components. In the past few years, ME composites have been subject of many investigations [2–5] since they can yield a giant ME response at room temperature while the single-phase materials exhibit weak magneto–electric coupling at low temperature. The ME coupling in the composite materials depends strongly on their microstructure. Many inherent preparation problems as atomic diffusion and undesirable chemical reactions between phases [6] can affect the interface,

modifying its chemical and structural properties and thus lowering the coupling.

BaTiO₃–CoFe₂O₄ composites are interesting magnetoelectric materials due to the individual properties of their components. CoFe₂O₄ has a spinel structure with large coercivity and magnetostriction [7]. BaTiO₃ exhibits polymorphs depending on the temperature. The tetragonal polymorph (t-BaTiO₃) is the most interesting due to its ferroelectric and piezoelectric properties. The cubic polymorph (c-BaTiO₃) is paraelectric. Although the tetragonal-to-cubic transition occurs at the Curie temperature ($T_c \approx 130$ °C in single-crystal), it is well known that c-BaTiO₃ can be found at room temperature in very fine particles, below the critical size of 10–35 nm [8–12]. Studies on BaTiO₃ ferroelectric behavior relate the cubic structure of ultrafine particles to the lack of long-range cooperative interactions, the presence of internal strains, depolarization fields and structural defects [13,14].

X-ray diffraction (XRD) is a limited method to distinguish between c- and t-BaTiO₃ in ultrafine particles due to the extensive broadening of Bragg reflexions. Raman vibrational spectroscopy can provide information on local lattice disorder, defects and has proved to be more sensitive to detect small distortions of the tetragonal unit cell than XRD.

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This work aimed at evaluating the structural properties of BaTiO_3 and CoFe_2O_4 in single-phase and in composite powders prepared by sol–gel process focusing mainly on the tetragonal distortion of BaTiO_3 .

2. Synthesis

The syntheses of BaTiO_3 , CoFe_2O_4 and BaTiO_3 – CoFe_2O_4 composite powders were described elsewhere [15]. Briefly, BaTiO_3 powder was prepared by sol–gel method and calcined at 900 °C (sample B9) and 1100 °C (sample B11). CoFe_2O_4 powder was prepared by coprecipitation followed by freeze-drying and calcination at 900 °C (sample F9) and 1100 °C (sample F11). The composites BaTiO_3 – CoFe_2O_4 14:11 wt% were prepared by: (a) mixing and calcination of precursor powders of BaTiO_3 and CoFe_2O_4 at 900 °C (sample M9) and 1100 °C (sample M11); (b) dispersing the CoFe_2O_4 precursor powder into BaTiO_3 wet gel, drying of the resulting brown gel and calcination of the dried gel at 900 °C (sample C9) and 1100 °C (sample C11).

3. Characterization

Raman spectra were collected using a T64000 Horiba–Jobin Yvon triple–monochromator spectrometer equipped with a confocal microscope and a liquid N_2 cooled charge coupled device (CCD). The scattering was excited using an argon ion laser at 514.5 nm. The spot size of the laser was $1 \mu\text{m}^2$ using a 100× objective and the laser power was kept at 1.0 mW in order to avoid sample heating.

XRD data were recorded using a Siemens D5000 diffractometer with $\text{Cu K}\alpha$ radiation and graphite monochromator, 2θ step of 0.05° . The samples were measured under spinning at 60 rpm to prevent preferred orientation. The major crystalline phases were assigned to spinel CoFe_2O_4 (JCPDS-22-1086, 1997), c- BaTiO_3 (JCPDS-01-0104, 1997) or t- BaTiO_3 (JCPDS-05-0626); $\text{BaFe}_{12}\text{O}_{19}$ (JCPDS-34-0129, 1997) was identified as minor crystalline phase.

Rietveld refinement with FullProf program was performed to evaluate particle size, lattice parameters and microstrain. Due to the low solubility of Ba in comparison with Ti, the stoichiometric Ba/Ti ratio was also evaluated. The Thompson–Cox–Hastings pseudo-Voigt function with axial divergence asymmetry was chosen as profile function. The statistics R_{exp} , R_{wp} and GOF were used to evaluate fitness [16].

Scanning electron microscopy (SEM) was carried out using a secondary electron detector (FEI, Quanta 200 FEG). The particulate material was previously dispersed in isopropanol and deposited on a Si plate.

4. Results and discussion

4.1. Raman spectroscopy

The Raman spectra of samples B9, B11, shown in Fig. 1a, were characteristic of t- BaTiO_3 as evidenced by the vibrational modes at around 257, 306, 520, 720 cm^{-1} (Table 1). Both

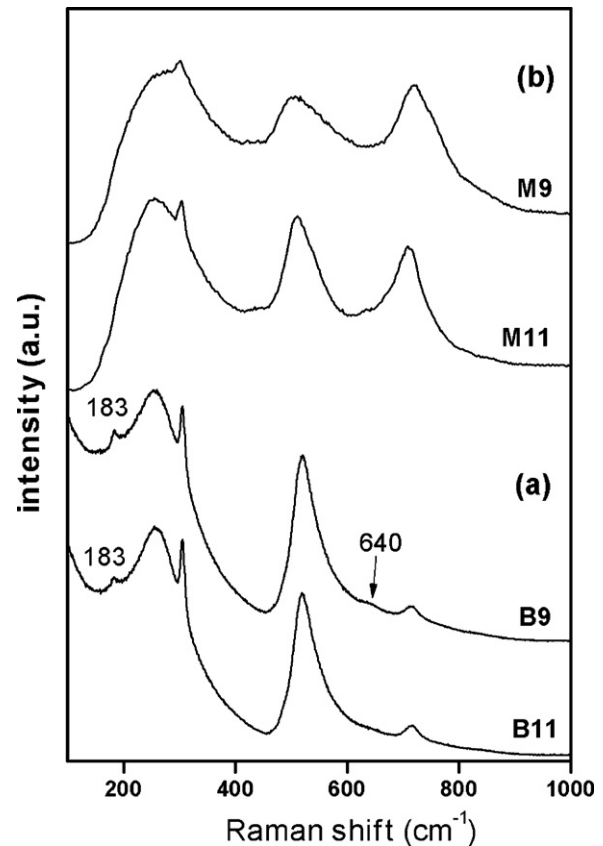


Fig. 1. Raman spectra of samples (a) B9, B11 and (b) M9, M11 (white region).

spectra exhibited a small peak at 183 cm^{-1} that could be ascribed to lattice defects or small amounts of orthorhombic phase [17,18]. Sample B9 showed an interesting feature at 640 cm^{-1} which might be assigned to hexagonal BaTiO_3 [19,20]. As this feature decreased with increasing thermal treatment temperature, it was considered to be a satellite peak due to planar defects in the tetragonal structure [21].

In the mixture samples M9, M11, the laser beam could clearly discriminate between white and dark regions assigned to t- BaTiO_3 and CoFe_2O_4 particles, respectively. Typical Raman spectra of white regions, shown in Fig. 1b, presented t- BaTiO_3 characteristic modes. The bands were broader than those found in samples B9, B11, suggesting decreased structural coherence [11]. The higher intensity of the band at $\approx 720 \text{cm}^{-1}$ relative to the band at $\approx 510 \text{cm}^{-1}$ was also found by Busca et al. [22] and assigned to particles with sub-stoichiometric Ba/Ti ratio due to Ba segregation as BaCO_3 . BaTiO_3 vibrational modes were downshifted in comparison with the corresponding modes in samples B9, B11, as shown in Table 1.

Table 1

Raman vibrational modes in BaTiO_3 samples and white region of the composite samples (M).

Sample	Raman shift (cm^{-1})				
B9, B11	256, 259	305, 306	521, 519	718, 722	
M9, M11	274, 255	301, 304	506, 510	722, 711	
BaTiO_3^a	242, 266	303, 311	514, 530	713, 720	

^a Polycrystalline as reported in Refs. [9,11,12,17,18,21,32–34].

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