Li-containing (1-x)$BaTiO_3$–x$Li_{0.5}Bi_{0.5}TiO_3$ solid solutions with colossal dielectric permittivity

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INTRODUCTION

Ferroelectric barium titanate (BT) is widely used in the manufacture of multilayer ceramic capacitors (MLCC) and electro-optics devices. In order to blur its phase transition temperature to achieve a small change in the dielectric constant, relaxor materials are added. When $M_{0.5}Bi_{0.5}TiO_3$ (M = Li, Na, K) are added to solid solutions, due to the high temperature of synthesis and sintering of barium titanate, large losses of volatile components such as bismuth and alkali metal are observed. To reduce the temperature of synthesis and sintering of barium titanate, an adequate synthesis procedure needs to be employed.

Various wet chemical methods have been used to produce $BaTiO_3$ fine powders. There are no detailed data in the literature on the effect of lithium bismuth titanate synthesized by wet chemical methods on the dielectric properties of barium titanate in a wide concentration range of (1-x)$BaTiO_3$–x$Li_{0.5}Bi_{0.5}TiO_3$.

Thus, the aim of this work was to investigate the effect of lithium and bismuth on the electrophysical properties of solid solutions which is of great helpfulness to understand this (1-x)$BaTiO_3$–x$Li_{0.5}Bi_{0.5}TiO_3$ system since no literature is available for its special structure. Also, to reduce the loss of volatile components during solid-state synthesis, a preliminary synthesis of barium titanate was carried out by the hydrothermal method.

EXPERIMENTAL METHODS

In the first step, nanocrystalline $BaTiO_3$ powders were prepared by a hydrothermal reaction of $TiCl_4$ and a $BaCl_2$ solution. In the second step, extra-pure Li_2CO_3, Bi_2O_3, and TiO_2 were added to $BaTiO_3$ to prepare (1-*x*)$BaTiO_3$–*x*$Li_{0.5}Bi_{0.5}TiO_3$ solid solutions. The resultant mixtures were fired for 4 h at 800 °C. The morphology of particles was studied by transmission electron microscope JEOL JEM-1400.

After firing, the powders prepared by both methods were pressed at 150 MPa in the presence of polyvinyl alcohol into pellets (10 mm in diameter and 2 mm in thickness), which were sintered in the air at a temperature range 1100–1240 °C. The heating/cooling rate was 300 °C/h in all of our preparations.

The lithium contents of the ceramic samples were determined by flame photometry on a Pye Unicom SP9 spectrophotometer using an air-acetylene flame. Bismuth was determined by trilon titration with xylenol orange as an indicator. The phase composition of the samples was determined by X-ray diffraction on a DRON 4-07 powder diffractometer (Cu *Kα* radiation, 40 kV, 20 mA). Structural parameters were evaluated by the Rietveld full profile analysis method.

Electrical contacts with the surface of the samples were made by firing an argentum paste. The dielectric parameters were measured as a function of temperature in the range of 20 to 500 °C. In impedance measurements, we used a Solartron Analytical 1260 impedance/gain phase analyzer in the range of 1 Hz to 1 MHz.

RESULTS AND DISCUSSION

It was shown that the use of pre-synthesized barium titanate reduces the sintering temperature by more than 100 ºC compared to the pure solid-state reaction technique (Fig. 1) and as a result, significantly reduces the loss of volatile components during heat treatment. The particles appear to have a fairly narrow size from 40 to 80 nm with a preferred size of about 54 nm (Fig. 2).

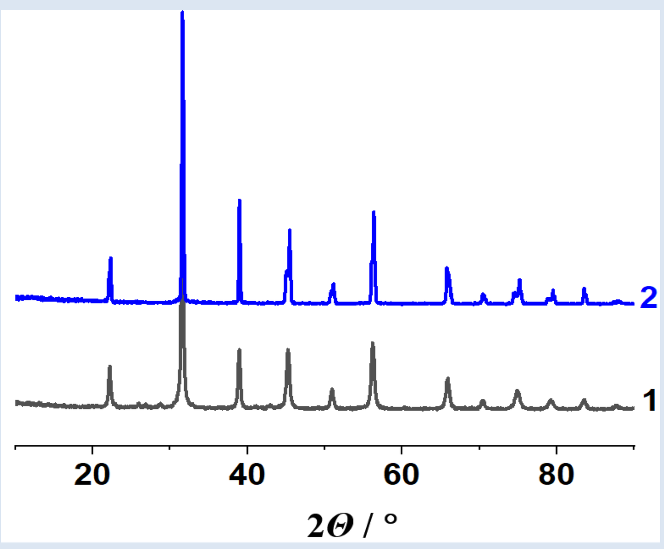

Fig. 1. XRD patterns for $BaTiO_3$ samples after hydrothermal synthesis without (1) and after calcination at 300 ºC for 4 h (2).

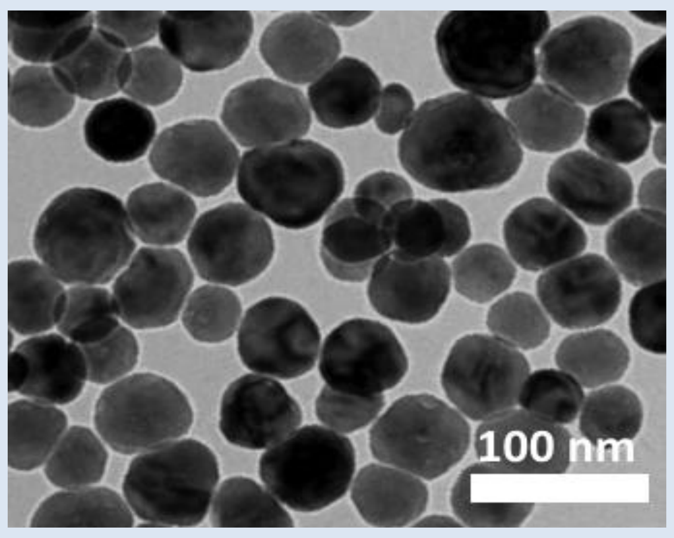

Fig. 2. TEM image of the $BaTiO_3$ nanoparticles calcined at 300 ºC for 4 hours.

Rietveld analysis shown that the structure of (1-*x*)$BaTiO_3$–*x*$Li_{0.5}Bi_{0.5}TiO_3$solid solutions for $0 \le x < 0.5$ is tetragonal, whereas at higher concentrations of lithium-bismuth titanate ($0.5 \le x$) it becomes cubic (Fig. 3). The decrease in the sintering temperature can be associated with lower melting points of lithium carbonate and bismuth oxide compared to barium titanate, As well as with the formation of a liquid phase at the grain boundaries (Fig. 4).

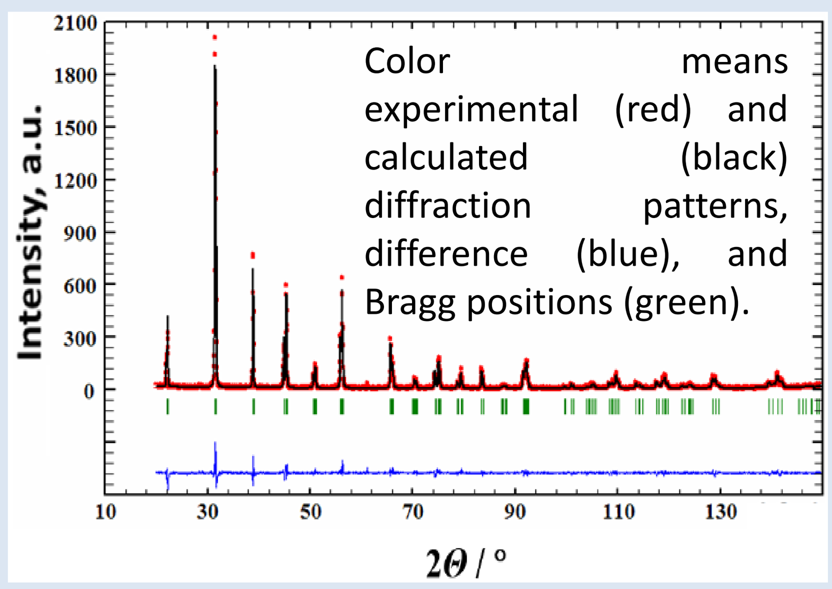

Fig. 3. Rietveld refinement of (1-x)$BaTiO_3$–x$Li_{0.5}Bi_{0.5}TiO_3$ (x = 0.1) sintered at 1200 ºC for 2 hours.

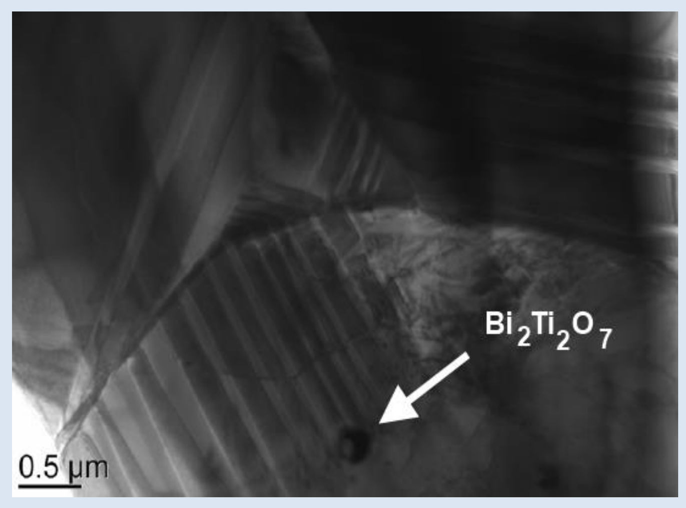

Fig. 2. TEM image of the nanoparticles calcined at 300 ºC for 4 hours.

Fig. 5 shows the microstructure of ceramics based on solid solution of the system (1-*x*)$BaTiO_3$–*x*$Li_{0.5}Bi_{0.5}TiO_3$. With an increase in *x* value the grain size of lithium-containing ceramics decreases, which may be due to the segregation of bismuth and lithium ions at grain boundaries during sintering ceramics, which reduces the rate of transfer and formation of small grain.

The temperature of the dielectric peak maximum (*T*max = 120 °C) almost unchanged at various Li doping contents in (1-*x*)$BaTiO_3$–*x*$Li_{0.5}Bi_{0.5}TiO_3$ solid solution (Fig. 6a), whereas dielectric constant decreases from $4{\cdot}10^4$ (*x* = 0.05) to $5{\cdot}10^3$ (*x* = 0.3).

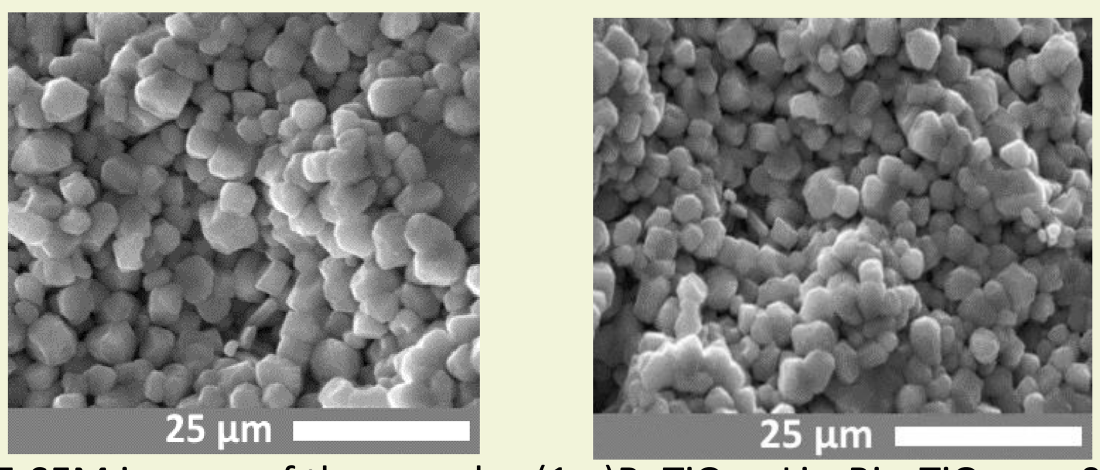

Fig. 5. FE-SEM images of the samples (1-*x*)$BaTiO_3$–*x*$Li_{0.5}Bi_{0.5}TiO_3$, *x* = 0.1 (a), *x* = 0.25 (b) sintered at 1200 and 1150 °C, respectively.

Increasing the content of *x* in solid solutions leads to a blurring of the phase transition, this behavior can be associated with the presence of internal stresses or with uneven distribution in the lattice of different ions, which leads to different local Curie temperatures in different microvolumes of the crystal. The substitution of Ba for Li and Bi increases the temperature stability: "high-temperature window" in the change in dielectric constant with temperature, $(\varepsilon-\varepsilon_{Tc})/\varepsilon_{Tc}$) becomes wider (Fig. 6b). In particular, (1-*x*)$BaTiO_3$–*x*$Li_{0.5}Bi_{0.5}TiO_3$ materials are characterized by $\varepsilon = 3.7{\cdot}10^4 \pm 20\%$ at the temperature range 105–130 °C at (*x* = 0.05) and $\varepsilon = 5.3{\cdot}10^3 \pm 20\%$ at the temperature range 90–160 °C at (*x* = 0.3).

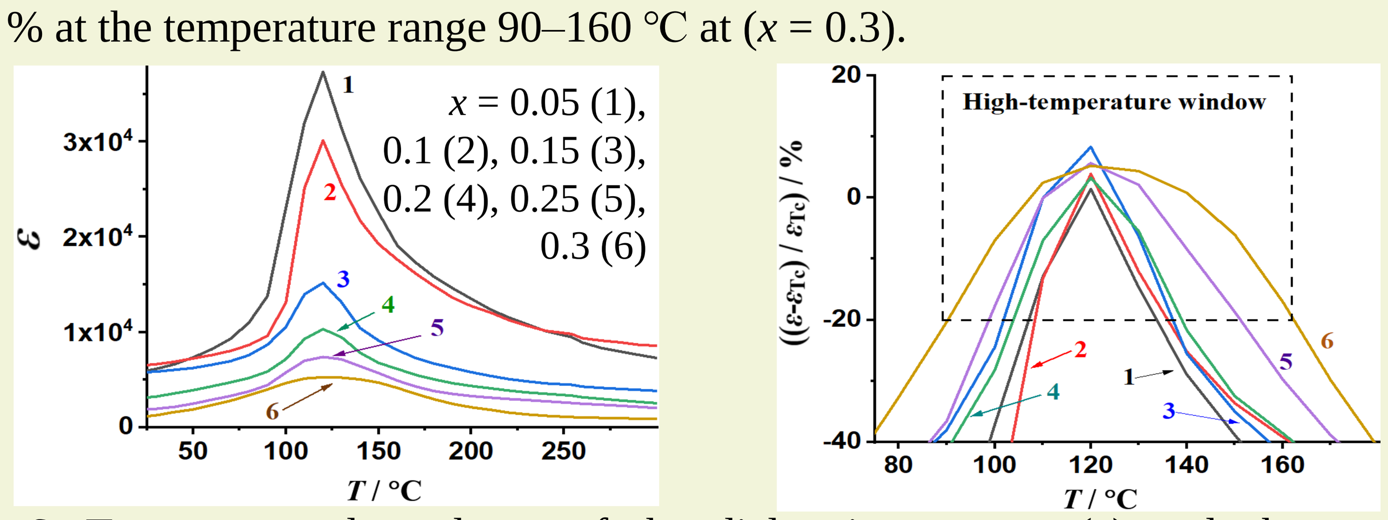

Fig. 6. Temperature dependence of the dielectric constant (a) and change in dielectric constant $(\varepsilon-\varepsilon_{Tc}) / \varepsilon_{Tc}$ at 1kHz in (1-*x*)$BaTiO_3$–*x*$Li_{0.5}Bi_{0.5}TiO_3$.

CONCLUSION

A relatively simple low-temperature synthesis route by a two-step methodology for the preparation of (1-x)$BaTiO_3$–x$Li_{0.5}Bi_{0.5}TiO_3$ solid solutions was described. The proposed first step hydrothermal method allows the preparation high activity powder of barium titanate with a nanoparticle size ~ 54 nm. Prepared samples have good crystallinity and homogeneity. On the second step, solid solutions (1-x)$BaTiO_3$–x$Li_{0.5}Bi_{0.5}TiO_3$ with different content x were fabricated by the solid-state reaction method.

The effects of x values on the sintering temperature, microstructure, and dielectric properties were studied. XRD results of all the samples exhibited atypical perovskite structure for all samples (1-x)$BaTiO_3$–x$Li_{0.5}Bi_{0.5}TiO_3$ at $0 \le x < 0.5$. All samples are characterized by colossal dielectric constant $\varepsilon \ge 10^3$. It was found that Li and Bi substitution of Ba leads to an expansion of the temperature region stability ΔT with ε change less than 20% from ΔT = 25 to 70 °C. These results showed that (1-x)$BaTiO_3$–x$Li_{0.5}Bi_{0.5}TiO_3$ ceramics are a promising candidate dielectric material for high-temperature capacitor applications.

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