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ScienceDirect

Ceramics International 42 (2016) 3751–3756

CERAMICS INTERNATIONAL

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Preparation and characterization of $K_{0.5}Bi_{0.5}TiO_3$ particles synthesized by a stirring hydrothermal method

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Received 30 July 2015; received in revised form 29 October 2015; accepted 30 October 2015
Available online 14 November 2015

Abstract

Nanoparticles of potassium bismuth titanate $K_{0.5}Bi_{0.5}TiO_3$ (KBT) with an average particle size of 38 nm were prepared using a stirring hydrothermal method. The pure KBT was obtained in 8 h reaction time instead of 24–48 h for conventional hydrothermal method. X-ray diffraction, Raman spectroscopy and TG analysis were used to check the proportion of hydroxyl group existing into the crude and the calcined KBT. A Hydroxyl group was found to affect the crystallite structure parameters and cell volume. When temperature increases from 25 to 1050 °C, the tetragonal structure presents a *c/a* ratio which decreases from 1.048 to 1.012. TG analysis and Raman vibration at high frequencies show that *c/a* is affected by hydroxyl group content below 750 °C and by potassium and bismuth vacancies above this temperature. The ceramic KBT showing a 300 nm size presents an improved $\varepsilon_r = 780$ and a dielectric loss tan $\delta = 0.062$ at room temperature. Electric conductivity σ_{ac} was also lowered to 10^{-6} $(\Omega\,m)^{-1}$ with an activation energy change at 673 K from 0.35 to 0.605 eV.

Keywords: C. Dielectric properties; $K_{0.5}Bi_{0.5}TiO_3$; Hydrothermal synthesis; Nanoparticule

1. Introduction

In the last years, KBT attracted much attention due to its dielectric and piezoelectric properties. Nanoparticles and nanowires were obtained by soft chemical processes. This perovskite crystallizes in tetragonal symmetry at room temperature ($a = 3.913$ Å and $c = 3.990$ Å) [1] which has a high Curie temperature about 380 °C. Pure ceramic of KBT is difficult to prepare specially the densification step [2]. The conventional method, i.e synthesis by solid–solid reaction [3], gives agglomerate and inhomogeneous micrometric particle sizes. The sintering of such particles needs high temperatures which may induce a modification in chemical stoichiometry due to the loss of volatile oxides (K_2O and Bi_2O_3) [4]. On the contrary, nanometric particles enhance densification kinetics and lead to higher densities at lower temperatures, stoichiometry is also kept unchanged. To obtain nano-particles, many synthetic methods must be used. Thus sol gel method [5], sol–gel-hydrothermal [6], conventional hydrothermal [7,8] and molten salt synthesis [9] were reported to give small grain size and high ceramic densities. In this work, we chose to perform synthesis by stirring hydrothermal method. The latter is known to be simple, rapid and reliable. In addition, it allows controlled morphology and grain sizes.

Thus, Jiang et al. [7] obtained KBT by conventional hydrothermal method at 200 °C after 48 h which a grain size about 250 nm. Density of ceramic was 98% after sintering at 1060 °C. Lim et al. [8] reported pure KBT at 240 °C in 24 h with grain size 90 nm, 96% of relative density was obtained by sintering at 1050 °C. The works stated above used a static hydrothermal method. Our aim is to use the stirred

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http://dx.doi.org/10.1016/j.ceramint.2015.10.158
0272-8842/

hydrothermal process in order to enhance kinetic and to reduce reaction time.

One of the characteristics of the hydrothermal products is the presence of a high content of hydroxyl groups since the reaction media are composed of higher alkaline solutions. In the present paper, stirred hydrothermal KBT has been calcined at different temperatures. Behavior of hydroxyl groups has been followed, as well as variation of volume cell and tetragonality. Dielectric properties of the ceramic have been measured.

2. Experimental

2.1. Powder synthesis and ceramic preparation

KBT samples were synthesized by the stirring hydrothermal process at 220 °C using bismuth nitrate and titanium oxide in a10 M KOH solution. The mixture was then poured into a stainless steel autoclave with mechanical stirring. Reactions times were 2, 4, 6 and 8 h. The autoclave was left to cool to room temperature and samples were collected, washed several times with distilled water, and finally dried at 80 °C for 48 h. The sample corresponding to 8 h was pressed into pellets of 13 nm diameter under uniaxial stress of 3 MPa. Conventional sintering was performed at 1050 °C for 2 h with a heating rate of 3 °C/min. Relative density was measured by the Archimedes method. Platinum electrodes were put on the two sides of the sintered ceramics.

2.2. Processing and analysis of powders

DRX (Bruker D8 Advance), Raman spectroscopy (Renishaw inVia) were used to control hydroxyl groups for calcined samples at 150, 500, 750, 900 and 1050 °C during 2 h. Processing temperatures for the KBT were selected from the examination of the weight losses observed on the TG curve (Q500 TGA-Hp). Raman measurements were performed directly for each treated powder using frequencies ranged from 50 to 4000 cm^{-1}. DRX patterns were registered at room temperature with rotating anode using CuKα radiation ($\lambda = 1.5405$ Å), a step of 0.017 and a counting time of 10 s.

2.3. Ceramic characterization and dielectric measurements

The KBT powder and ceramic were characterized by using X-ray diffraction, Raman spectroscopy used at room temperature to define bond vibrations. Microstructure was observed using scanning electron microscopy SEM (JOEL 7600F). An impedance meter (HP4284A) was used to dielectric measurements of KBT ceramics with frequency ranging from 10^2 Hz to 10^6 Hz at temperatures varying between 300 and 750 K.

3. Results

Fig. 1 shows the XRD patterns of powders synthesized at 220 °C in 10 M KOH for reaction times ranging from 2 to 8 h. All the characteristic peaks of tetragonal KBT phase appeared after 6 h reaction time with very weak Bi-rich phase impurity. When time of reaction was increased to 8 h, a pure material of tetragonal KBT crystallized without any impurity. By solid state and sol gel method, a secondary phase was reported in the final powder [4,10].

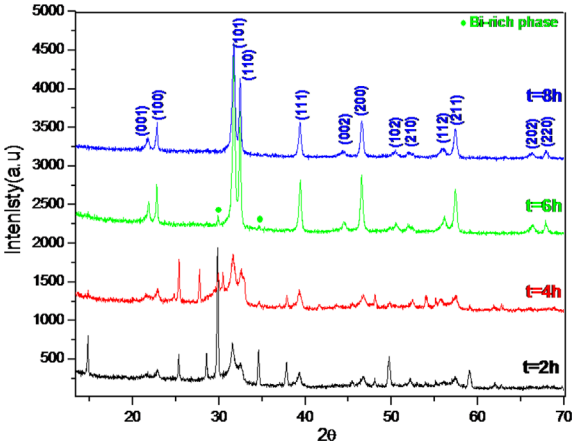

Fig. 1. XRD patterns of KBT powders synthesized by stirring hydrothermal method at 220 °C for various reaction times of 2, 4, 6 and 8 h under 10 M KOH concentration.

A long reaction time estimated between 24 and 48 h was necessary for crystallization of KBT by conventional hydrothermal method [7,8]. The stirring hydrothermal process reduced the crystallization of KBT to only 8 h. Therefore, stirring during the chemical reaction helps to promote contact between the reactants, and to increase the diffusion and the kinetic of chemical reaction. Subsequently, pure crystalline KBT was formed in short time (8 h) at low reaction temperature (220 °C) without any calcination step. In the studied powders, large unit cell parameters were obtained ($a = 3.902$ Å, $c = 4.091$ Å and $c/a = 1.048$). These values were compared with the reference structure from JCPDS-36-0339 data of $c/a = 1.024$ ($a = 3.918$ Å, $c = 4.013$ Å) from polycrystalline sample.

Due to the use of concentrated KOH solution it is natural that some hydroxyl groups could remain inside the synthesized compounds. Many perovskites synthesized by hydrothermal processes reported these hydroxyl impurities like $KNbO_3$, $KTaO_3$ [11], $SrTiO_3$ [12], $BaTiO_3$ [13]. Hydroxyl groups were controlled under a calcination of the KBT at different temperatures.

Fig. 2 shows the DRX diffraction patterns of the hydrothermal KBT treated at various temperatures. In all the samples, KBT is pure and there is no secondary phase. A change in diffraction pattern is observed when temperature is increased. The two peaks of (002) and (200) plans at 2θ about 44.36° and 46.54° respectively come closer indicating lattices parameters variation. Samples structure was refined using Rietveld method. Several refinements were used; refinement with constraint, refinement without including the constraints and refinement without correction z. In these samples, it is clear that the symmetry remains tetragonal and the phase transition to cubic symmetry does not occur. Fig. 3a shows the variation of c/a and volume of lattice cell with temperature of