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Structural, thermal, dielectric and ferroelectric properties of $K_{0.5}Bi_{0.5}TiO_3$ ceramics

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ABSTRACT

Dense $K_{0.5}Bi_{0.5}TiO_3$ (KBT) lead-free ceramics were prepared by conventional solid reaction route. Their temperature behavior (up to 600 °C) was investigated by X-ray diffraction, DSC, dielectric spectroscopy and electric field-polarization technique. The first temperature dependent Raman scattering studies were also performed. X-ray and Raman scattering results show that samples exhibit a single perovskite structure with cubic symmetry at temperatures higher than approximately 400 °C and with coexistence of the cubic and tetragonal phases below this temperature. Two structural phase transitions between tetragonal phases in temperature range 200–225 °C and between tetragonal and cubic ones near 400 °C are observed. The content of the tetragonal phase increases with decreasing temperature and at room temperature it reaches more than 70%. Temperature- dependent P-E loops and pyroelectric data revealed a polar behavior in KBT up to about 400 °C, which means that the intermediate phase (~270–380 °C) is rather ferroelectric than antiferroelectric.

1. Introduction

Lead-based piezoelectric ceramics such as lead zirconate titanate (PZT) are widely used in many electronic devices (actuators, sensors, transducers etc.) due to their superior ferroelectric, piezoelectric and pyroelectric properties [1]. However, the environmental issues call for the use of nonhazardous substances for device fabrication. Therefore, a great effort has been paid to the development of lead-free piezoelectric ceramics with properties comparable to PZT. Experimental studies and first-principles calculations [2] showed that some excellent applicable properties appear for compounds with the coexisting and competing different structural, magnetic and polar phases, which are energetically close to each other. Then even a small external signal may cause state switching. For example, the colossal magnetoelectric effect, magnetoresistance effect and giant piezoelectricity were found in some multiferroics [3], nanometer-scale structured transition metal oxides [4] and in ferroelectrics from the morphotropic phase boundary [5], respectively. For the above reasons, research activities have mainly been focused on $Na_{0.5}Bi_{0.5}TiO_3$ (NBT), $K_{0.5}Na_{0.5}NbO_3$ (KNN) and the materials based on them.

It is important for ferroelectric materials to have a high Curie temperature T_c in order to be applicable in wide temperature range such as T_c = 490 °C ($PbTiO_3$) or $T_c \approx$ 675 °C (lead-free bismuth titanate $Bi_4Ti_3O_{12}$) [6]. Potassium bismuth titanate $K_{0.5}Bi_{0.5}TiO_3$ (KBT) with $T_c \approx$ 370 °C belongs to such materials [7,8]. KBT undergoes a sequence of two phase transition: from the high temperature cubic phase to the pseudo-cubic one at about 410 °C, and then to a tetragonal phase at $T_1 \approx$ 300 °C [9] (at about 270 °C according to [10]). The tetragonal phase is known to exhibit ferroelectricity. The broad maximum of electric permittivity occurs at $T_m \approx$ 380 °C. The kind type of electric ordering in the intermediate phase (T_1–T_m) is a subject of controversy. Antiferroelectric [9] or ferroelectric [11–13] characters of this phase have been suggested. A number of reports on KBT is very limited, because of the technological difficulties in synthesizing of this compound. The high volatility of the potassium and bismuth components at high sintering temperature is assumed to be the main reason of the poor sinterability and secondary-phase formation during synthesis of KBT [7,14]. Additionally, available structural studies require verification and there is no temperature-dependent Raman study of KBT.

Basing on the above description, it may be stated that the preparation of good quality, dense and stoichiometric KBT ceramics, and investigations of their structural, dielectric, thermal and vibrational properties in wide temperature range seem to be very fruitful. These studies may deliver deep insight into phase transitions and nature of electric order of the intermediate phase of KBT. Obtained results were discussed combined with temperature-dependent Raman studies data.

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2. Experimental procedures

$K_{0.5}Bi_{0.5}TiO_3$ ceramic samples were prepared by the conventional solid-state reaction route. High purity chemicals of K_2CO_3 (99.99%), Bi_2O_3 (99.99%) and TiO_2 (99.9%) (all of Aldrich) were used. The K_2CO_3 was previously dried at 200 °C for 1.5 h (in order to remove the absorbed water) and cooled to room temperature in desiccator. The mixture of starting powders, weighted in stochiometric proportions, was homogenized in a mortar and milled in ethyl alcohol medium in a planetary ball mill. The powders were dried, uniaxally pressed into pellets at 150 MPa and calcinated at 700 °C for 1.5 h, at 800 °C for 2 h and at 820 °C for 5 h with intermediate grinding. Products of the third calcination were again crushed into fine powders and pressed into pellets at 150 MPa. They were successively sintered at 900 °C for 1.5 h, at 1000 °C for 1.5 h and at 1020 °C for 1.5 h. Then the products were again pulverized and milled before further sintering. The powders were uniaxially pressed into cylindrical discs with thickness of 6 mm and 12 mm in diameter under a pressure of 300 MPa. They were finally successively sintered at 1030 °C for 5 h and at 1040 °C for 1 h. We realize that above described technology with many heating/cooling cycles is not convenient for industrial applications. However, it has been experimentally proved that multiple calcinations and sintering processes with intermediate milling prevent of the appearance of the undesired secondary phases. All calcination and sintering processes were carried out in enclosed aluminum crucible, with of pre-sintered KBT powder over the samples. The above mentioned precaution was undertaken in order to avoid any possible loss of potassium and bismuth in the sintered samples. Ceramics obtained in these technological conditions were cream-coloured and translucent. They had density greater than 97% of their theoretical value (measured by Archimedes method), and of very good mechanical properties. The room-temperature resistivity of samples was of the same order as in Ref. [8], of 10^{13} Ωcm.

X-ray diffraction (XRD) measurements of the KBT sample were performed on the X'PERT PRO Panalytical diffractometer in standard Bragg − Brentano geometry with fixed slits and using Cu Kα1, α2 doublet radiation (λKα1 = 0.154060 nm, λKα2 = 0.1544430 nm). In order to eliminate the Cu K_β line and improve the quality of the XRD pattern (background) the Ni-filter and the graphite monochromator were used, respectively. Temperature-dependent X-ray studies were performed using the HTK 1200N (Anton Paar) High-Temperature Oven-Chamber in which the air pressure was kept below 10^{-3} mbar (Pfeiffer TMH 071 pump). The sample, polished slice of 0.8 mm thickness and ca. 12 mm diameter, was set on the ceramic container. The data were collected in a heating process, from 25 to 600 °C with step of 25 °C and accuracy of ± 1 °C. At each step the temperature was stabilized at least 30 min in order to reach the thermal equilibrium. Obtained data were processed using Le Baill and Rietveld method implemented in program FullProf [15].

Microstructures of sintered samples were observed using a scanning electron microscope (Model Hitachi S4700). The chemical composition of the samples was determined with an electron-probe microanalysis using an energy-dispersive (EDS) X-ray spectroscopy. The EDS standardless quantitative analyses were performed employing the Noran-Vantage system.

The Raman scattering experiments were carried out in Bio-Rad FTS 6000 spectrometer and a high temperature chamber was used. The Nd-YAg laser line of 1064 nm and of 200 mW power was selected as excitation beam. The spectra were collected with resolution of 4 cm^{-1}.

The differential scanning calorimetry (DSC) studies were performed using a Netzsch DSC F3 Maia scanning calorimeter in the temperature range from room temperature to 400 °C under the argon atmosphere at a flow rate of 30 ml/min. The specimen, a single piece of ceramic of an average mass of 122 mg was placed in an aluminum container. The data were collected upon heating and cooling of samples with a constant rate of 10 °C/min.

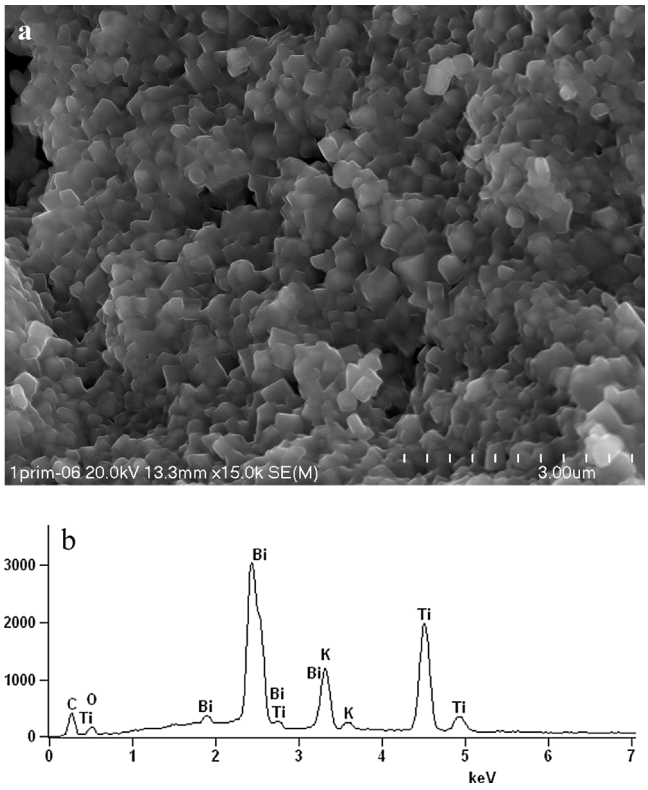

Fig. 1. SEM micrograph of cross section of KBT ceramics.

Dielectric studies were carried out for silver electroded samples using an GW 8110G meter in the temperature range of 30–550 °C. The measuring electric field of strength of 20V$cm^{-1}$and frequency ranging from 100 Hz to 1 MHz were applied. The apparatus was set in capacity C and conductivity G mode. In order to reduce any ageing influence, the samples were annealed for 1 h at 550 °C prior to the measurements. The data were collected regularly with a step of 0.1 °C upon heating and cooling, with the temperature change at a rate of 2 °C/min., using an automatic temperature controller.

The pyroelectric current for the prior polarized sample was recorded by a quasi-static method on heating at a rate of 10 °C/min. The polarizing procedure proceeded from 250 °C down to room temperature in the dc electric field of 15 kV/cm.

The polarization versus electric field (P-E) hysteresis loops were obtained at 50 Hz with the aid of a Sawyer-Tower circuit.

3. Results and discussion

Fig. 1 shows the SEM micrograph (a) of fractured KBT ceramic and its EDS spectrum (b). Dense and nearly pore-free microstructures were observed, in agreement with their high density. Uniformly shaped and distributed grains with average size of 0.35 μm were also revealed. Similar microstructures of KBT ceramics were observed in papers [7,8]. EDS analysis indicates a homogeneous distribution of all the elements throughout the grains and nominal chemical composition of the material.

The XRD patterns (full angle scans) obtained as a function of temperature for the KBT ceramics are presented in Fig. 2. They are indexed according to the rules for a pseudo-cubic cell. For better visualization, the evolution of chosen structural lines in the narrower angle ranges are presented in Fig. S1(a–b) (in the online version at DOI: http://dx.doi.org/10.1016/j.jeurceramsoc.2017.09.036). For the majority of diffraction lines (as $(110)_c$, $(200)_c$, $(211)_c$ and $(220)_c$) one can distinguish three characteristic temperature ranges. Upon heating, in the first range of (30–200 °C) a slow decrease of peak splitting and a