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Synthesis, doping and electrical bulk response of $(Bi_{1/2}Na_{1/2})_xBa_{1-x}TiO_3$ + CaO –based ceramics with positive temperature coefficient of resistivity (PTCR)

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ABSTRACT

$(Bi_{1/2}Na_{1/2})_xBa_{1-x}TiO_3$ samples were prepared using the mixed-oxide route; their tetragonal to cubic phase transition temperature increases from 125 °C for x = 0–190 °C for x = 0.2. $(Bi_{1/2}Na_{1/2})_{0.10}Ba_{0.90}TiO_3$ ($x = 0.10$) ceramics with CaO addition sintered in air exhibit a positive temperature coefficient of resistivity (PTCR) behavior. Dense PTCR thermistor ceramics with low room-temperature resistivity and resistivity change ρ_{max}/ρ_{min} of 3.5 orders of magnitude at the Curie temperature were prepared using 3.5 mol% CaO, 0.05 wt% SiO_2 addition as sintering aid, and Mn+Fe acceptor doping. Sintering at 1235 °C with two hours holding time were found as optimum synthesis conditions for achieving a good electrical thermistor performance. Impedance spectroscopy confirms that the resistance change is a grain boundary phenomenon, since the grain interior exhibits semiconducting behavior across the phase transition.

1. Introduction

Positive temperature coefficient of resistivity (PTCR) materials are typically donor-doped, semiconducting $BaTiO_3$ (BT) ceramics that exhibit an abrupt increase of resistivity at the transition from the tetragonal into the cubic perovskite phase at the Curie temperature Tc [1,2]. This particular resistance behavior is caused by the formation of Schottky barriers at grain boundaries. According to Verwey's model, the charge transport is dominated by a depletion layer at grain boundaries, which forms as result of an acceptor and/or cation vacancy concentration gradient in the vicinities of grain boundaries [1,2]. Applications of PTCR ceramics, or PTC thermistors, include current limiters, sensors, or constant-temperature heaters. The latter application, in particular, requires PTCR ceramics with high T_c, since the transition into a high-resistivity state above T_c self-regulates the power consumption of the heater. PTCR heaters are used as automotive auxiliary heaters; however, they will play an important role in electric vehicles. Typical Curie temperatures of PTCR ceramics for heaters are within the range of 160 °C–220 °C. Since T_c of $BaTiO_3$ is at 125 °C, the T_c shift to higher temperatures is achieved through cation substitutions. Currently PTCR heater ceramics are prepared through isovalent A-site substitution with lead, and compositions of the system $PbTiO_3$-$BaTiO_3$ with significant Pb concentrations are used [3]. Because of environmental hazard, lead-free PTCR materials with operating temperatures up to 200 °C are needed. However, other A-site substituents in $BaTiO_3$ (e.g. Ca, Sr, Zr, Hf) tend to decrease T_c [2,4]. Some years ago, Takeda et al. proposed as an alternative the BT-rich side of the x $(Bi_{0.5}Na_{0.5})TiO_3$ – (1-x) $BaTiO_3$ (BNBT) system as candidate for high-T_c lead-free PTCR ceramics; a La donor-doped BNBT material with x = 0.05 was shown to exhibit a strong resistivity increase at about 160 °C [5]. PTCR behavior was also demonstrated to exist in samples with x = 0.02 and x = 0.04 even without donor dopants after sintering in air at 1360 °C [6]. The tetragonal to cubic phase transition temperature in the BNBT system increases from 120 °C for x = 0 to about T_c = 220 °C for x = 0.2 [7,8]. Moreover, sintering of BNBT without donor dopants at low partial pressure of oxygen also results in samples with PTCR properties [7,8]. It was demonstrated, that ceramics with $0.02 \leq x \leq 0.08$, sintered in nitrogen at 1340 °C and re-oxidized at 800 °C–1100 °C in air, have PTCR characteristics with a 3-4 orders of magnitude resistivity change at T_c [9]. Recently, Zubair et al. [10] showed, that x $(Bi_{0.5}K_{0.5})TiO_3$ – (1-x) $BaTiO_3$

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(BKBT) ceramics, sintered in nitrogen and followed by air anneals, exhibit an excellent PTCR performance. Alternatively, it was discovered that addition of CaO to BNBT and sintering in air represents an alternative and promising route to fabricate lead-free PTCR ceramics with high T_c [11,12]. Preferential evaporation of Na over Bi, subsequent partial filling of cation vacancies by Ca^{2+}, as well as the impact of Bi^{3+} on Ba-positions acting as donor dopant, were identified as key mechanism behind the PTCR effect in those materials [12]. Further optimization of CaO-substituted BNBT thermistor ceramics using sintering aids as well as additional donor and/or acceptor dopants have not been reported yet.

In this paper, we report on the synthesis of CaO-substituted BNBT thermistor ceramics and the effects of SiO_2 sintering aid and Mn and/or Fe acceptors on the electrical performance. It is shown, that $(Bi_{1/2}Na_{1/2})_{0.10}Ba_{0.90}TiO_3$ ceramics with room-temperature resistivity $\rho_{RT} = 4000$ Ωcm and resistivity change over almost 4 orders of magnitude were obtained after sintering in air with 0.05 wt% SiO_2 addition and an acceptor concentration of 0.04% Mn and 0.02%Fe.

2. Experimental

Samples of $(Bi_{1/2}Na_{1/2})_xBa_{1-x}TiO_3$ ($x = 0$; 0.05; 0.10; 0,15; 0.20) and of $(Bi_{1/2}Na_{1/2})_{0.10}Ba_{0.90}TiO_3$ + y CaO (y = 0; 1.5; 2.0; 3.0; 3.5; 4.0 mol%) were prepared by mixing high-purity raw materials TiO_2 (Evonik Aeroxide P90), $BaCO_3$ (Solvay BM040), Na_2CO_3 (Merck) and Bi_2O_3 (Alfa Aesar) in stoichiometric proportions. The mixtures were homogenized in isopropanol for 3 h in polyamide containers with YSZ grinding media (diameter 0.5 mm) using a Fritzsch Pulverisette 6 planetary ball mill (170 rpm). 0.04%, 0.06% acceptors Me (Mn as $MnCO_3$ and/or Fe as Fe_2O_3) were added, i.e. $(Bi_{1/2}Na_{1/2})_{0.10}Ba_{0.90}Ti_{1-z}Me_zO_3$ + 3.5% CaO with z = 0.0004 Mn, z = 0.0006 Mn, and z = 0.0004 Mn + 0.0002Fe. Calcinations were performed at 800 °C for two hours. Next, the calcined powders were milled in acetone for 20 h with ZrO_2 grinding balls (diameter 3 mm), followed by drying in a rotation evaporator and sieving through a 180 μm polyamide sieve. CaO (prepared from calcining $CaCO_3$ at 800 °C) and 0 wt%, 0.05 wt% SiO_2, or 0.2 wt% SiO_2 were added during milling. Pellets were fabricated by uniaxial pressing. The samples were sintered at 1000–1300 °C for 2 h in air with 5 K/min cooling rate.

X-ray patterns were recorded with a Bruker AXS D8 Advance diffractometer using Cu K_α radiation with parallel beam geometry, and a LynxEye detector. The measurements were made at 40 kV and 40 kA with a step size of 0.02° and 0.5 s/step in the range of 20°–90° 2θ. The lattice parameters c_0 and a_0 were calculated by Rietveld refinement of the full XRD-pattern using Bruker Topas R software. Temperature dependent XRD measurements were carried out in a temperature chamber (MRI, Karlsruhe, Germany) up to 250 °C. The samples were mounted on a Pt-Rh heating stripe with a thermocouple directly connected to the heating stripe below the sample position. Samples were heated with a rate of 10 K/min up to a given temperature and held there for 5 min before the start of the XRD run. To avoid temperature inhomogeneity, the ceramics samples were ground to a thickness of 0.5 mm. The temperature uncertainty was controlled to be less than 5 °C. The powder particle size was measured using laser diffraction (Malvern Mastersizer, 2000). The specific surface S of the powders was measured by nitrogen adsorption (BET, Nova, 2000, Quantachrome Instruments); a primary particle size d_{BET} was estimated using the relation $d_{BET} = 6/\rho \cdot S$ (with density ρ; assuming spherical particles). DSC analysis of the powders was performed with a Mettler-Toledo 882 analyzer with heating rate of 10 K/min. Shrinkage measurements were made on cylindrical compacts with a Netzsch DIL402 dilatometer with 4 K/min heating rate. The bulk density of sintered samples was determined using Archimedes method in heptane. The averages chemical composition of the samples was analyzed using inductively-coupled plasma atomic emission spectroscopy (ICP-AES) after dissolution of powdered sintered samples in a mixture of hydrogen peroxide, perchloric acid and hydrochloric acid. The microstructure of the sintered specimen was investigated using an Ultra 55 Field Emission Scanning Electron Microscope (Zeiss). For electrical measurements the pellets were painted with AgZn paste (Ferro 61400016) and fired at 630 °C for 5 min. R(T) curves were measured using a two-probe set-up with a Keithley 2400 sourcemeter. The pellets were immersed in an oil bath during measurements. The relative permittivity was measured with an impedance analyzer (4192 A, HP) in the frequency range f = 10 Hz - 10^7 Hz. Impedance spectra of selected samples were obtained in the same frequency range at temperatures from 120 K to 573 K (Broadband Dielectric Spectrometer, Novocontrol). Separated values for the capacitance and resistance for bulk and GB regions were extracted from the impedance spectra according to the standard method, whereby the impedance data was displayed on ZView software (Version 2.80, Scribner Associates Inc.).

3. Results and discussion

3.1. Properties of BNBT and CaO addition

The phase transformation behavior in the BNBT series $(Bi_{1/2}Na_{1/2})_xBa_{1-x}TiO_3$ within the compositional range $0 \le x \le 0.20$ was investigated using samples sintered at 1235 °C without any additives or dopants. All samples exhibit a single-phase tetragonal perovskite structure with space group *P4mm* at room temperature. Above room temperature, a phase transition from tetragonal into the ideal cubic perovskite structure occurs at T_{tc}. High-temperature XRD measurements were performed to monitor the tetragonal to cubic phase transition. As an example, the diffraction patterns for x = 0.1 in the range 44° ≤ 2θ ≤ 46° are shown in Fig. 1a. The diffraction patterns were recorded at temperature ramps every 5 K up to 250 °C; and a clear transition from the tetragonal (002) and (200) double peaks into a single cubic (200) peak is observed. DSC measurements of powders with composition $0 \le x \le 0.20$ clearly show an increase of T_{tc} with x (Fig. 1b). Temperature-dependent dielectric measurements exhibit a transition from ferro-to paraelectric behavior at the Curie temperature T_c, associated with the crystallographic transition T_{tc}, as peak in the permittivity vs. temperature curves (Fig. 1c). The variation of T_{tc} vs. composition x in the composition range $0 \le x \le 0.20$, based on XRD and DSC measurements, is summarized in Fig. 1d. A clear trend of an increase of T_{tc} from 125 °C for $BaTiO_3$ to about 195 °C for x = 0.2 is confirmed. Similar results have been reported earlier by other groups [8,13].

The addition of CaO to BNBT was studied in detail for the composition with x = 0.1. XRD diffraction patterns of samples of $(Bi_{1/2}Na_{1/2})_{0.10}Ba_{0.90}TiO_3$ + y CaO sintered at 1235 °C show a single perovskite phase with tetragonal symmetry at room temperature (Fig. 2). Addition of CaO does not significantly alter the tetragonal lattice parameters found for $BaTiO_3$ ($a_0 = 3.988(1)$ Å and $c_0 = 4.036(2)$ Å; Fig. 2 inset), in agreement with results in Ref. [12]. Obviously, the Ca^{2+} ions are completely incorporated into the perovskite lattice and occupy both, A- and B-positions. Substitution of Ca^{2+} on A-sites only would shrink the lattice (ionic radii in XII coordination are 1.34 Å, 1.61 Å, and 1.39 Å for Ca^{2+}, Ba^{2+}, and Na^{+}, respectively [14]), whereas substitution on B-sites should increase the cell volume (ionic radii in VI coordination are 1.00 Å and 0.60 Å for Ca^{2+}, and Ti^{4+}, respectively [14]). Partial substitution of octahedral cation sites in BNBT by Ca^{2+} ions was proposed recently [12].