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Original Article

High-temperature solid-state reactions in the (1-x)$Na_{0.5}Bi_{0.5}TiO_3$–x$SrTiO_3$ system

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ABSTRACT

High-temperature reactions during the solid-state synthesis of samples from the (1-x)$Na_{0.5}Bi_{0.5}TiO_3$–x$SrTiO_3$ system were investigated. Due to the number of chemically different elements, the processing of these ceramics is delicate and requires several firing steps under specific conditions to obtain phase-pure samples. Sintering in an air atmosphere resulted in a macroscopically inhomogeneous microstructure, which is a consequence of incomplete reaction between different secondary phases. However, prolongation of the sintering time aggregated the pores in the sample, while at a higher firing temperature the sample's secondary phase melted. As a result, the nominal composition was altered, leading to the formation of the $Na_2Ti_6O_{13}$ secondary phase. Sintering under an increased oxygen pressure of 1 MPa limited the evaporation of the secondary phase. This allowed the completion of the reaction, forming a homogeneous and dense sample. The study provides a set of experimental conditions for the successful preparation of ceramics from the investigated system.

1. Introduction

The (Ba,Sr)TiO_3 system has been extensively investigated for electronic applications since it exhibits high permittivity maxima, which depending on the barium content range from 0 to 390 K [1]. The permittivity maxima correspond to the displacive phase transition, which, however, also increases the dielectric losses and the temperature coefficient of the dielectric constant. The doping of (Ba,Sr)TiO_3 and the formation of composites can improve a material's figure of merit, as was demonstrated for different voltage-tunable applications. However, such intrinsic and extrinsic modifications of the material's structure imply difficulties in ceramics or thin-film preparation as well as controlling the properties. In order to overcome these difficulties, other materials systems have also been investigated, including relaxor ferroelectrics, like Ba(Ti,Zr)O_3 [2]. For such systems the temperatures of the phase transitions can also be gradually decreased using incipient ferroelectric or incipient antiferroelectric materials, analogous to the (Ba,Sr)TiO_3 system, and thus a relaxor's functional properties can be correspondingly adjusted. In our research group we have modified the relaxor $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) with three different systems, i.e., with $NaTaO_3$ and $KTaO_3$, which are both incipient ferroelectrics, as well as with $Li_{3x}La_{(2/3)-x(1/3)-2x}TiO_3$ [3,4], the properties of which are characteristic for an incipient antiferroelectric. In contrast to the (Ba,Sr)TiO_3 system, the tunability of which is based on ferroelectric instability, relaxor-type systems base their dielectric tunable response on polar nano-regions and their electric-field-dependent dynamics [5]. They are not attractive for microwave dielectric applications since their dielectric losses shift across a wide temperature range as a function of the operating frequency, but can exhibit promising tunable properties in the radio-frequency range [6]. Furthermore, for solid solutions with a higher content of relaxor material, attractive piezoelectric properties can also be obtained [7]. Based on the polar order of the end members these materials systems can form a morphotropic phase boundary (MPB) between the polar and nonpolar phases. Such a compositionally driven phase transition would lead to an enhancement of the piezoelectric response due to the polarization extension, which is an important mechanism, typically observed during a temperature-driven, ferroelectric-paraelectric phase transition [8].

The (1-x)$Na_{0.5}Bi_{0.5}TiO_3$–x$SrTiO_3$ (NBT-xST) system was first investigated in 1974, by Sakata and Masuda, who prepared ceramics with different solid solutions and determined their basic electrical properties [9]. The interest in the system has increased only recently, with most of the studies being focused on the system's piezoelectric properties [10,11], which were improved by doping with Nb [12] or by creating ceramics with a core-shell structure [13]. It was also determined that $Na_{0.5}Bi_{0.5}TiO_3$ forms solid solutions with $SrTiO_3$ across the whole concentration interval, with a MPB between the rhombohedral and pseudocubic phases at x = 0.25–0.26 [14]. However, the voltage-

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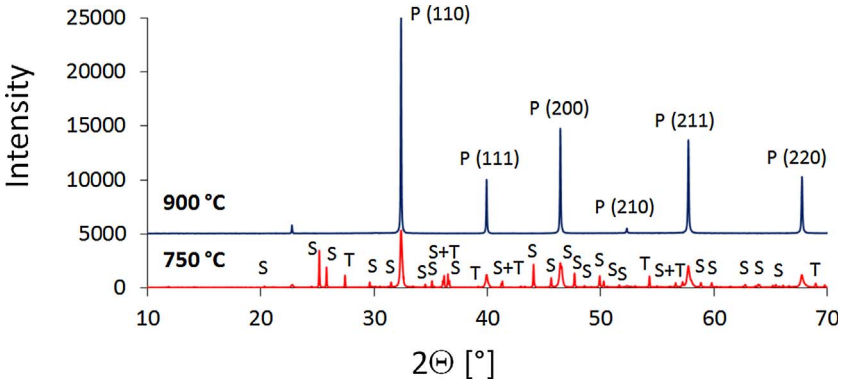

Fig. 1. XRD patterns of the NBT-xST sample with x = 0.7 after the firing at 750 °C and the second subsequent firing at 900 °C. P, S and T correspond to perovskite, $SrCO_3$ and TiO_2 phases, respectively.

tunable properties of NBT-xST have not been determined yet and are the focus of our forthcoming study.

Despite many recent reports on NBT-xST functional properties, solid-state synthesis of the ceramics with homogeneous microstructure has not been accurately determined yet. The present study thus focuses on the solid-state reactions in NBT-xST system with compositions across the whole concentration range. The results of the study revealed that during the sintering of the ceramics a high pressure of oxygen is needed to successfully complete the corresponding high-temperature reaction and to simultaneously achieve a high relative density of the ceramics. This is due to the presence of volatile elements in the system, which impose additional demands on the processing conditions.

2. Materials and methods

Samples from the (1-x)NBT–xST system were prepared by a conventional solid-state reaction method (x = 0.1, 0.3, 0.5, 0.7, 0.9). Corresponding amounts of reagent-grade powders of Bi_2O_3 (Alfa Aesar, 99.975%), TiO_2 (Alfa Aesar, 99.8%), Na_2CO_3 (Alfa Aesar, 99.997%), and $SrCO_3$ (Alfa Aesar, 99.99%) were weighed and milled for 1 h at 200 rpm in a planetary ball mill with ethanol and 3-mm Y-stabilized ZrO_2 balls. The obtained powders were dried, uniaxially pressed into pellets with 100 MPa and calcined at 750 °C and 900 °C for 10 h, with intermediate cooling and grinding. After calcination the samples were milled again under identical conditions. Using a laser granulometer (Cilas, 850) the median size of the particles after the milling was measured and in all the experiments it totalled less than 1 μm. The milled powders were pelletized uniaxially with 100 MPa and sintered under conditions specified in the section covering the results and discussion. For all the firings the same tube furnace was used to fire in an air atmosphere with cooling and heating rates of 10 °C/minute. To reduce the evaporation of the elements during the sintering a furnace that can operate at 1 MPa of oxygen (Thermal Technology) was also used in specific cases, which are specified in the results and discussion section. However, due to the limitations of the furnace the heating rate had to be decreased to 5 °C/min.

Room-temperature X-ray diffraction (XRD) patterns of the samples were recorded after each firing using a diffractometer with an incident-beam Johannson's monochromator (PANalytical X'Pert PRO) with Cu–Kα1 radiation, in the 2θ range from 10° to 80°, a measurement step of 0.0167° and a step time of 300 s. For the purposes of the symmetry determination, the patterns were also collected using a diffractometer with an incident-beam hybrid monochromator (PANalytical Empyrean) for a parallel beam geometry and Cu–Kα1 radiation, in the 2θ range from 10° to 140°, a measurement step of 0.0131° and a step time of 1500 s. The XRD pattern was fitted using High Score Plus software (PANalytical). A scanning electron microscope (SEM, Jeol JSM 5800) equipped with an energy-dispersive X-ray spectrometer (EDS, Oxford-Link, Isis 300) was used for the microstructural analysis and the phase identification, after the sample surfaces were polished. A Hesse Instruments heating microscope was used to determine the linear shrinkage of the pellets, during their heating with a rate of 10 °C/min in air. The pellets were prepared in the same way as for the sintering study. The thermogravimetric analyses (TGA) were made using a NETZSCH STA 449C in an Al_2O_3 crucible and an atmosphere of air. The samples were heated with a rate of 10 °C/min before the high-temperature isothermal part of the measurement was reached. The densities of the sintered samples were determined using Archimedes' method in an ethanol medium.

3. Results and discussion

Initially, a detailed study of the solid-state reactions was performed for a sample with x = 0.7, as according to the literature this solid solution exhibits radio-frequency dielectric relaxations that are slightly below room temperature and so this sample is foreseen to be most appropriate for tunable applications. After the calcination at 750 °C the XRD analysis of the sample shows that the NBT-ST solid solution with the perovskite crystal structure is already formed and is present in the sample in addition to the $SrCO_3$ and TiO_2 secondary phases (Fig. 1). After the subsequent firing at 900 °C only the matrix phase is present in the sample, with respect to the detection limits of the XRD method (Fig. 1).

The sintering behaviour of the pre-reacted and milled powders was analysed using a heating microscope. The shrinkage of the pellet was 20% and this occurs in the temperature range between 1000 °C and 1250 °C (Fig. 2). Based on the pellet's shrinkage the initial sintering temperature was selected as 1200 °C. After 1 h of sintering at the selected temperature we investigated the sample using the SEM to reveal its composition and homogeneity. The EDS results show that the sample contains mainly the matrix phase with a stoichiometric composition, within the experimental error of the technique (Table 1). However, the matrix is accompanied by white and to smaller extent also by dark inclusions, as seen by the backscattered electron (BSE) image of the sample's surface (Fig. 3a). Due to the small volume fraction of the

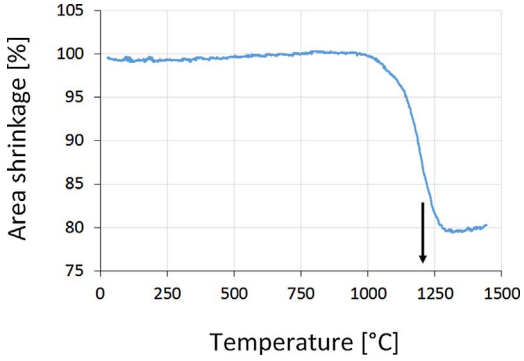

Fig. 2. Shrinkage of NBT-xST sample with x = 0.7.