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Synthesis and characterization of lead-free piezoelectric $(K_{0.50}Na_{0.50})NbO_3$ powder produced at lower calcination temperatures: A comparative study with a calcination temperature of 850 °C

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ABSTRACT

To prevent the evaporation of alkali elements during the calcination of the lead-free piezoelectric $K_{0.50}Na_{0.50}NbO_3$ (KNN), lower temperatures for the solid-state synthesis of the KNN from a mixture of Na_2CO_3, K_2CO_3 and Nb_2O_5 were investigated with a variety of powder-characterization techniques. The collected data suggested 550 °C as a possible low calcination temperature, as well as being sufficiently high for a completed synthesis of the KNN. The XRD and TEM analyses of double-calcined KNN powder at 550 °C revealed nanocrystalline, cube-shaped particles with a perovskite structure, but without noticeable unreacted precursors or secondary phases. Our investigations revealed that the morphology of the calcined powders underwent a dramatic change from small, differently shaped particles at 600 °C/6 h, to fully rounded, large, spherical agglomerates produced at 1000 °C/6 h. To explain this behavior, a mechanism involving the formation of a liquid phase during the reaction of the alkali elements with the moisture and CO_2 in the atmosphere is proposed.

1. Introduction

Though the initial stimulation for developing lead-free piezoelectric ceramics was the legislative activity of the European Union and some other developed countries, it is not the only reason for the extensive studies over the past 15 years [1,2]. In fact, some unique properties of lead-free piezoceramics, compared to lead-based ones, have made these materials interesting for scientists from all around the world, even if their countries have not yet introduced legislation to eliminate toxic substances from electronic packaging [3–5].

Among the different groups of lead-free piezoelectric ceramics, the potassium sodium niobate $(K_{0.50}Na_{0.50})NbO_3$ (or KNN) family has received significant attention mainly due to its high Curie point, as well as its good electromechanical properties and a low density [6]. However, the main drawbacks when dealing with KNN-based piezoceramics are the hygroscopic nature of the alkali carbonate precursors and the volatility of the alkali elements at elevated temperatures and in humid atmospheres [7–9]. In addition, the sintering-temperature window for KNN is very narrow [10], around 1115 ± 5 °C for undoped KNN, and, according to the $KNbO_3$–$NaNbO_3$ phase diagram, it is very close to the melting point of KNN at 1140 °C [11]. Despite these drawbacks, recent advances in the field further strengthen the attractiveness of KNN [12–17].

A mixed-oxide, solid-state reaction is the most cost-effective and popular method used for the synthesis of KNN-based piezoceramics [18,19]. Since the alkali sources of the raw materials used for the synthesis of KNN are mainly carbonate-based, a calcination step is unavoidable in the synthesis procedure of KNN. Typical calcination temperatures for the synthesis of KNN are reported to be between 750 °C and 950 °C, with different calcination times, mainly 2–6 h [20–23]. But as Popovič et al. [24] have shown thermodynamically, the vapor pressure of the alkali elements over their respective niobates increases by 4–5 orders of magnitude by increasing the temperature from 627 °C to 927 °C. This makes the low-temperature calcination process an easy route to overcoming the off-stoichiometry problem associated with synthesized KNN powder due to the evaporation of alkali elements at elevated temperatures.

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Regardless of the risk of volatilizing the alkali elements during the high-temperature calcination of KNN, using higher calcination temperatures has two different influences on the synthesized KNN powder. On the one hand, it makes the KNN more crystalline and more homogeneous [25] and, consequently, ensures the high purity of the KNN-synthesized powder, which is an important criterion when dealing with advanced ceramics [26]. On the other hand, higher calcination temperatures enable the KNN particles to grow and agglomerate, which is not the preferred situation for sintering. Hence, these contradictory roles should be considered together.

Up to now and by our knowledge, 625 °C was the lowest-reported calcination temperature for KNN precursors from a mixture of alkali carbonates and niobium pentoxide, which resulted in the typical KNN microstructure with a relative density of 93.4% [27]. The aim of this study was, first, to explore whether the calcination temperature could be reduced even further, but still ensure that the formation reaction of KNN ($0.25\ Na_2CO_3\ (s) + 0.25\ K_2CO_3\ (s) + 0.50\ Nb_2O_5\ (s) \rightarrow (K_{0.50}Na_{0.50})NbO_3\ (s) + 0.50\ CO_2\ (g)$) goes to completion. The second aim was to study the physical properties and to perform spectroscopic analyses of this low-temperature-calcined KNN powder and compare them with a typical calcination temperature/time, which was chosen to be 850 °C/6 h. The sintering behavior, the microstructure and the electrical properties of the sintered samples from such a low-temperature-calcined powder will be reported later.

2. Materials and methods

2.1. Powder preparation

In order to synthesize the $(K_{0.50}Na_{0.50})NbO_3$, stoichiometric amounts of Na_2CO_3 (granule, anhydrous, 99.95–100.05%, Sigma–Aldrich, Germany), K_2CO_3 (granule, anhydrous, 99+%, Sigma–Aldrich, Germany) and Nb_2O_5 (325 mesh (< 44 μm), 99.9%, Sigma–Aldrich, Germany) were carefully weighed and homogenized. All the raw materials were dried overnight at 200 °C before weighing. For the homogenization, planetary milling was performed for 8 h at 165 rpm using a polyethylene jar and 3–5 mm zirconia balls. The medium was ethanol and the ball-to-powder ratio was chosen to be 10:1. The homogenized mixture of KNN precursors was dried for 12 h at 80 °C and 4 h at 150 °C (hereafter, the HOM powder) and stored in a desiccator.

HOM powder batches of ~5 g were calcined at different temperatures in a 2-l box furnace. The heating rate and the dwell time were 2 °C/min and 6 h, respectively. The weight losses of the heat-treated HOM powders were tracked carefully for each temperature. If the weights of the 110 °C-dried powder and crucible, before and after calcination, are considered as W_i and W_f, respectively, the weight-loss percentage can be calculated as $(W_i - W_f)/(W_i - W_c) \times 100$, where W_c is the weight of the 110 °C-dried crucible. The measurement error for this test was estimated to be ±0.06%.

2.2. Powder characterization

Differential Thermal Analysis (DTA) and Thermo-Gravimetry (TG) of the HOM powder were recorded in 3 steps: (1) from room temperature to 200 °C, (2) an isotherm for 3 h at 200 °C, and (3) from 200 °C to 750 °C. All the steps were performed with a heating rate of 10 °C/min using a Netzsch STA 409C/CD (Waldkraiburg, Germany). The DTA/TG tests were conducted under a constant flow rate of 100 cm^3/min of dried synthetic air. The DTA/TG plots that are presented here are actually from the third step with a normalized TG curve to 100%. In addition, the corresponding Differential Thermo-Gravimetric (DTG) curve is also calculated and shown.

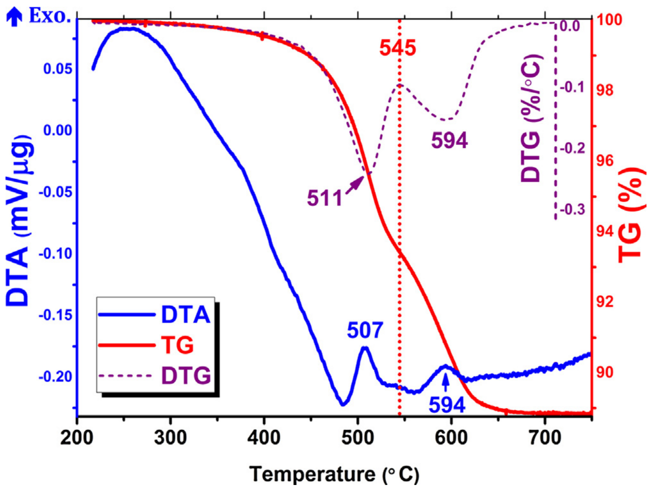

Fig. 1. Results of thermal analysis of a homogenized mixture of KNN precursors (HOM powder) presented as DTA, TG and DTG curves. The temperatures of the extrema are written in °C next to each peak.

The X-ray Diffraction (XRD) patterns of the calcined powders were recorded at room temperature using a PANalytical X'Pert PRO MPD diffractometer (Almelo, The Netherland) with Cu-Kα_1 radiation of 1.5406 Å in the 2θ range of 20–70° with a step of 0.017° and an integration time of 200 s. The phase composition was identified with the PDF-2 database [28]. The morphologies of the HOM and the heat-treated powders were characterized using a Scanning Electron Microscope (SEM—Cambridge Stereoscan 360, UK) operated at 20 kV and a High-Resolution Transmission Electron Microscope (HR-TEM—JEOL JEM-2100, Tokyo, Japan) operated at 200 kV.

The dimensional changes vs. temperature for the HOM powder and the densification behavior of the calcined powders were recorded from 200 °C to 1200 °C with a heating rate of 5 °C/min in synthetic air using a heating-stage microscope (Leitz, version 1A, Wetzlar, Germany). The same amounts of powders were pelletized in a 100-MPa uniaxial press in the same manner for each of the powders. The geometrical green density of the HOM powder compact was 2.56 g/cm^3.

The density of the powders was measured using helium-gas pycnometry with a Micromeritics, AccuPyc 1330, GA, USA. The mass of measured powder was ~5 g. The specific surface areas of the powders were analyzed by nitrogen adsorption/desorption at −196 °C (BET method, Belsorp-mini II, BEL, Osaka, Japan) using an automated gas-adsorption analyzer. Prior to the measurement, the powders were degassed under vacuum for 2 h at 250 °C. The particle size distribution of the powders was analyzed using a static light-scattering particle size analyzer (Microtrac S3500, PA, USA). The results were interpreted as a volumetric particle size.

3. Results and discussion

The course of the reaction between the starting precursors was analyzed using thermal analyses of the HOM powder. Fig. 1 shows two pronounced exothermic peaks in the DTA curve at 507 °C and 594 °C. The positions of these peaks agree with the position of the negative peaks of the first derivative of the TG (DTG) at 511 °C and 594 °C, respectively, indicating that the DTA peaks correspond to different stages of the reaction between the alkali carbonates and the Nb_2O_5 [29]. This is similar to the reaction course that was investigated by Buscaglia et al. [30], where the formation of $BaTiO_3$ from nanocrystalline $BaCO_3$ and TiO_2 was studied.

According to the TG curve, the weight loss of the HOM powder in the temperature ranges 200–545 °C, 545–750 °C and 200–750 °C are 6.57, 4.59 and 11.16%, respectively. If the second heating step (a

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