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Fast synthesis of $NaNbO_3$ and $K_{0.5}Na_{0.5}NbO_3$ by microwave hydrothermal method

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Abstract

Synthesis of sodium and potassium–sodium niobates ($NaNbO_3$ and $K_{0.5}Na_{0.5}NbO_3$) was achieved by reducing the reaction time via microwave-assisted hydrothermal route. Sodium niobate was synthesized at 180 °C for 15 min using NaOH 6 M. During the synthesis of KNN at 180 °C, the $K_4Na_4Nb_6O_{19}$–$9H_2O$ intermediate phase appeared. By increasing the temperature to 200 and 220 °C, the pure KNN phase was obtained. Potassium–sodium niobate was prepared at 220 °C for 15 min using KOH/NaOH 8 and 10 M. These results were confirmed by X-ray diffraction, Scanning Electron Microscopy and Raman spectroscopy. The $NaNbO_3$ and $K_{0.5}Na_{0.5}NbO_3$ powders consisted of agglomerated pseudo-cubic crystals.

Keywords: B. Electron microscopy; D. Niobates; D. Perovskites; Microwave-hydrothermal synthesis

1. Introduction

Ferroelectric and piezoelectric ceramics are important materials used to produce sensors, actuators, motors, resonators, electromagnetic filters, etc. The most used materials for these applications are those based on $PbTi_{1-x}ZrO_3$ (PZT) and related compositions [1]. Due to environmental concerns related to the high toxicity of lead and lead oxide, some lead-free piezoelectric materials are being studied. Among them are $K_{0.5}Na_{0.5}NbO_3$ (KNN) and its solid solutions with Ta^{5+}, Li^{1+}, Sb^{5+}, Cu^{2+}, Mn^{3+}, ZnO and $BiFeO_3$ [1–6]. Also $Bi_{0.5}Na_{0.5}TiO_3$ (BNT), $Bi_{0.5}K_{0.5}TiO_3$ (BKT), $Ba_{1-x}Ca_xTi_{1-y}Zr_yO_3$ (BCTZ) and several of their compositions are being investigated [7–10]. KNN is interesting because of its high Curie temperature and remnant polarization [5,11]. On the other hand, $NaNbO_3$ (NN) is investigated for its water splitting catalytic properties for [12].

Concerning the synthesis of alkaline niobates, it is crucial to avoid the use of high temperatures in their preparation. The solid state reaction method demands temperatures around 800 °C or higher with prolonged dwell time [5,6]. Under these synthesis conditions, the Na/K volatilization is high, producing secondary phases and oxygen vacancies in detriment of their properties. Therefore, some "soft" chemical routes have been used to overcome these inconveniences, for example sol–gel, hydrothermal, and Pechini methods are reported for the synthesis of KNN, $KNbO_3$ (KN) and NN powders [13–20].

The hydrothermal method is promising because it requires low temperature and gives crystalline powders without further heat treatment. Synthesis of KNN, KN and NN using this technique is reported elsewhere [16–20]. Moreover, hydrothermal synthesis can be assisted by microwave heating, enhancing the reaction kinetics by diminishing the synthesis time. KNN, KN and NN have been

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synthesized by this method [21–23]. Although, the reaction time was reduced as compared to the conventional hydrothermal route, it can be further reduced. In this work, the synthesis of NN and KNN by microwave-hydrothermal method was studied. The influence of concentration, temperature and time on the synthesized powders was monitored by several techniques.

2. Experimental

The synthesis of $NaNbO_3$ (NN) and $K_{0.5}Na_{0.5}NbO_3$ (KNN) ceramic powders was performed using microwave-hydrothermal method. Potassium hydroxide (KOH 90%-Sigma-Aldrich), sodium hydroxide (NaOH 99%-Sigma-Aldrich), niobium oxide (Nb_2O_5 99.99%-Sigma-Aldrich) and deionized water were used as raw materials. First, Nb_2O_5 was dispersed in the desired NaOH or KOH/NaOH (for KNN the KOH/NaOH ratio was kept constant at 3:1) hydroxide solution, and stirred for 30 min. The slurry was poured into a 100 ml teflon lined reactor with a 70% filling ratio. The reactor was cramped by a Kevlar jacket and placed in the equipement carousel. The reaction was carried out in a MARS 6 microwave system (CEM corporation) operated at 2.45 GHz. Several concentrations, temperatures and dwell times were studied. The temperature range studied was 160–220 °C and the reaction time from 5 to 60 min. The alkaline concentration was 3–6 M and 6–10 M for NN and KNN, respectively. The temperature was measured by a fiber optic probe which is introduced into the reactor through a thermowell adapted to the reactor cap. The pressure was monitored by a transducer, also attached to the reactor cap. In Fig. 1 the temperature and pressure behavior versus time for a typical experiment is shown. After the reaction was completed, the precipitates were filtered and washed several times with deionized water and dried for 4 h at 120 °C.

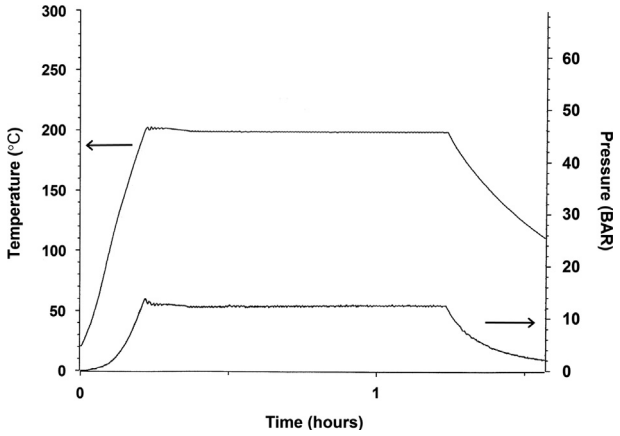

Fig. 1. Temperature and pressure behavior versus time for a typical microwave assisted synthesis experiment.

The powders were structurally and morphologically characterized by X-ray diffraction (bruker D8 advance diffractometer with Cu $k\alpha_1$ radiation), Scanning Electron Microscopy (Field emission JEOL 7600f microscope) and Raman Spectroscopy (Nicolet Almega XR, Dispersive Raman Spectrometer with Nd:YVO laser, $\lambda = 532$ nm).

3. Results and discussion

3.1. Synthesis of $NaNbO_3$

Fig. 2 shows SEM images of NN powders synthesized at different times. It is observed a cubic-like morphology that

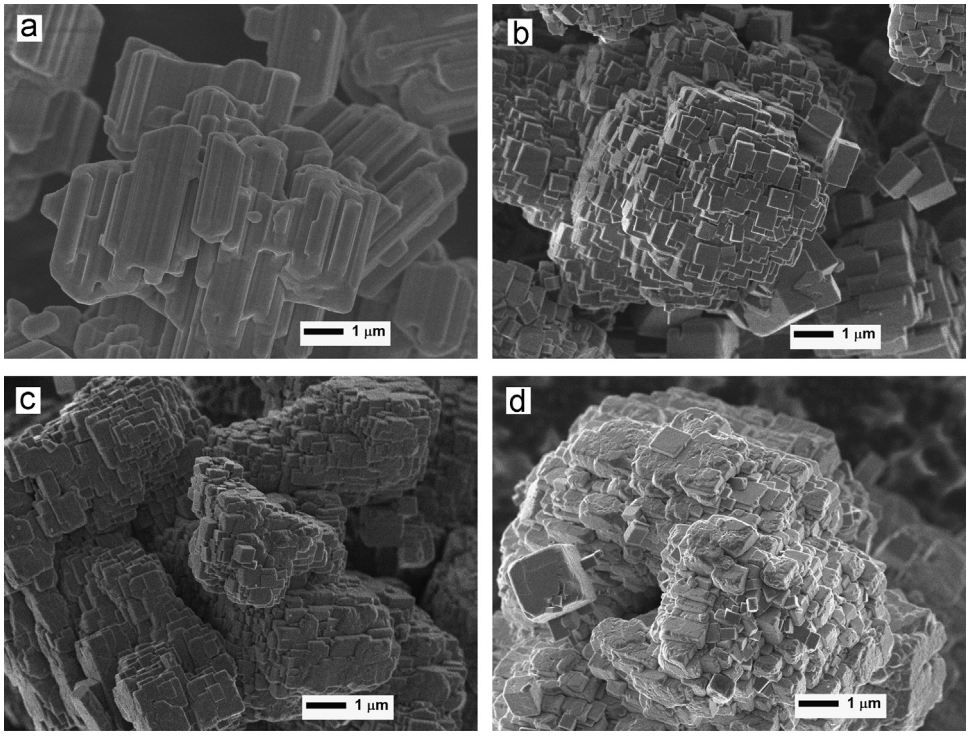

Fig. 2. (a) Nb_2O_5; $NaNbO_3$ powders synthesized at: (b) 180 °C for 15 min, (c) 200 °C for 30 min and (d) 200 °C for 60 min using NaOH 6 M.