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Journal of Alloys and Compounds 424 (2006) 231–236

Journal of ALLOYS AND COMPOUNDS

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Mechanosynthesis of the ferroelectric materials $Ba_2ANb_5O_{15}$ (A = K, Na, Li)

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Received 15 September 2005; accepted 19 October 2005

Available online 24 January 2006

Abstract

A novel mechanochemical activation route was applied in order to obtain the $Ba_2ANb_5O_{15}$ (A = K, Na, Li) ferroelectric materials. The evolution of the $4BaO_2$:A_2CO_3:$5Nb_2O_5$ powder mixtures during mechanical treatment and subsequent annealings, was followed by X-ray powder diffraction (XRD), thermal analysis and scanning electron microscopy (SEM). The sought bronze-type phases were mechanosynthesized after 48 h of treatment in a planetary mill. Very crystalline phases can be obtained with very important decreases in the temperatures and reaction times as compared with the traditional ceramic method. Dense ceramics were processed from mechanosynthesized precursors at relative low temperature, by a conventional-sintering route, and their dielectric properties characterized.

Keywords: Ferroelectrics; Mechanochemical synthesis; X-ray diffraction; Scanning and transmission electron microscopy; Dielectric response

1. Introduction

Mixed oxides belonging to the tetragonal tungsten bronze structural type (TTB) are a technologically important family of materials because of their ferroelectric and highly nonlinear properties [1,2]. $Ba_2ANb_5O_{15}$ (A = K, Na, Li) mixed oxides are representative of TTB materials that can be considered a good alternative for the substitution of commercial piezoceramics by lead-free materials. The $Ba_2NaNb_5O_{15}$ (BNN) oxide is the best known member of this family; at about 590 °C it undergoes a phase transition to a tetragonal ferroelectric phase. Then, at about 300 °C, a ferro-paraelastic transition occurs to an incommensurate orthorhombic structure and, finally, at −160 °C another phase transition takes place in which the structure reverts to a tetragonal ferroelectric phase [2].

Powdered samples of these oxides are usually prepared by the conventional ceramic method, but high temperatures and long reaction times are required, which yield precursors that are not suitable for the preparation of high performance ceramics. This is so because very large inhomogeneous particle sizes are obtained and a certain level of impurity content is difficult to avoid. Thus, alternative synthesis routes need to be developed in order to facilitate the successful preparation of these oxides, with a controlled stoichiometry and particle size, and to process good ceramics of this system.

Mechanochemical activation techniques were developed for the synthesis of alloys and intermetallic compounds [3]. More recently solid-state mechanochemistry has been used to prepare new oxides, or to improve the properties of known functional materials [4–10]. Mechanical activation is usually the result of disorder of the crystal and generation of defects that cause the decrease of the activation barrier for reaction [11]. Mechanical treatment is a way to modify the conditions in which chemical reactions usually take place. During the high energy milling, the particle size of the crystals is reduced, the homogeneity of the mixture is increased, and in most of cases the solid becomes more reactive [12]. Furthermore, the obtained high reactivity and low particle size facilitate the sintering process, being possible to obtain high density ceramics at low temperatures [6,10].

A previous study of the effect of the mechanical activation on the preparation of the $Ba_2NaNb_5O_{15}$ oxide has been reported by van Hal et al. [13]. However, no mechanosynthesis was detected by these authors up to 168 h of mechanical milling, when the phase is detected by XRD besides an amorphous background.

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0925-8388/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2005.10.083

On the contrary, neither $Ba_2KNb_5O_{15}$ nor $Ba_2LiNb_5O_{15}$ have been obtained by a similar procedure.

This article reports on the synthesis of $Ba_2ANb_5O_{15}$ (A = K, Na, Li) TTB oxides prepared by direct mechanosynthesis, achieved by milling in a planetary system. Moreover, the processing of dense ceramics of these materials has been carried out at relative low temperatures and their electrical characterization is also reported.

2. Experimental procedure

Mechanical activation techniques have been applied to the preparation of $Ba_2ANb_5O_{15}$ (A = K, Na, Li) powders. About 3 g of the stoichiometric mixtures of analytical-grade BaO_2, A_2CO_3 and Nb_2O_5 were mixed by hand in a agate mortar. Then, the initial mixtures were mechanically activated using vibrating (only for BKN preparation) or planetary mills (Fristch, Pulverisette models 0 and 6, respectively). In both cases, the mixture was placed in a stainless-steel vessel, using one ball of 5 cm diameter for the vibrating mill, whereas for the planetary mill five balls of 2 cm diameter each were utilized. The milling bowl of the planetary system was rotated at 300 rpm.

For the sake of comparison, these phases were also prepared by solid-state reaction, from the same starting mixtures of reagents, by successive thermal treatments at increasing temperatures from 400 up to 1200 °C (A = K, Na) or 1000 °C (A = Li), followed by slow cooling into the furnace.

The milled powders were characterized by thermogravimetric (TG) and differential thermal analysis (DTA) and X-ray powder diffraction (XRD) at room and increasing temperatures. The effects of both milling and thermal treatments in the particle morphology were investigated by standard scanning electron microscopy (SEM).

The DTA and TG measurements were taken in air, with a Seiko 320 instrument, with α-Al_2O_3 as the inert reference material, between room temperature and 1000 °C, at 10 °C min^{-1}, in the heating and cooling process and the quantity of sample used was about 10 mg. The evolved gases were analyzed with a Pfeiffer ThermoStar GSD 301T (quadrupole mass spectrometer) with argon as gas carried to determine the molar mass.

XRD patterns at room temperature were measured in a Bruker AXS D8 Advance Diffractometer, between 5° and 80° (2Θ), with 2Θ increments of 0.05° and counting time of 4 s per step. For high temperature measurements, a Philips PW1310 diffractometer, coupled with an Anton Paar HTK 10 attachment to stabilize the temperature, was used. The patterns were obtained by depositing a small quantity of powder onto a platinum sheet placed on a tantalum strip, which was the heating element. The recordings were taken from 5° to 70° (2θ) with a scan rate of 0.02° s^{-1}. The temperature was monitored by a Pt–Pt 13% Rh thermocouple welded in the center of the platinum sheet. The heating rate was 10 °C min^{-1}. Care was taken in order to stabilize the temperature before the measurement. The Cu Kα doublet (λ = 1.5418 Å) was used in all X-ray experiments.

SEM images were taken in the range of 10–20 kV in a Digital Scanning Microscope DSM 960 Zeiss. For this purpose, dispersed particles of the milled and thermally treated powders were placed in a carbon film and a gold layer was sputtered onto it.

Some powders were shaped by uniaxial pressing at 210 kg cm^{-2} as thin disks of ∼10 mm diameter and 2 mm thickness. Disks were isostatically pressed at 2000 kg cm^{-2} and then conventional sintering was carried out on a Pt foil. Ceramics with $Ba_2LiNb_5O_{15}$ composition were processed by sintering at 1200 °C of precursors obtained by classical solid-state reaction. Pellets of $Ba_2KNb_5O_{15}$ and $Ba_2NaNb_5O_{15}$ composition were prepared from milled powders by sintering at 900 °C. They all present similar porosity, ∼8–10% as measured by the Archimede's method.

The temperature dependence of the dielectric permittivity and losses was measured by impedance spectroscopy with a HP4194A analyser at several frequencies between 1 kHz and 1 MHz, and up to 700 °C. Measurements were accomplished on ceramic discs on which Pt electrodes were painted and sintered at 700 °C. The experimental setup for the temperature control is described elsewhere [14]. One degree Celsius per minute heating and cooling rates were used.

3. Results and discussion

3.1. $Ba_2KNb_5O_{15}$ phase

In both milling processes (planetary and vibrating mills), two steps were observed: an initial diminution in particle size of the starting oxides, and a subsequent solid-state reaction in the activated mixture, which leads to the formation of nanocrystalline phases. In the vibrating mill, after the first day of mechanical activation the formation of $K_4Nb_6O_{17}$ and $BaNb_6O_{16}$ started, and they remained stable after 12 days of grinding (not shown here). Only the annealing of such precursor sample at 1000 °C allows the preparation of a single $Ba_2KNb_5O_{15}$ phase to be managed, so it can be say that the vibrating treatment gives rise to a mechanoactivation process. However, when the starting mixture was mechanically treated in the planetary mill, after 10 h of grinding the formation of the sought TTB oxide is observed (Fig. 1) and further milling only produces an increase in the crystallinity, this being the unique detectable phase after a treatment as long as 48 h. In this case an actual mechanochemical reaction, or mechanosynthesis, occurs.

Fig. 2a shows the TG and DTA curves of the mechanosynthesized $Ba_2KNb_5O_{15}$, acquired from a heating/cooling cycle of the powder milled for 48 h in the planetary mill, displaying three weight-loss steps in the temperature ranges: room temperature to 450, 530–650 and 680–950 °C, respectively. The first weight loss was attributed to the elimination of H_2O, which the powder takes during milling, as has been observed in other mechanosynthesis processes [15]. The remaining processes were attributed to the elimination of CO_2, as corroborated by mass spectrometric measurements. The DTA curve exhibits also three exothermic peaks on heating, centered at 340, 578 and 679 °C, corresponding to the weight losses detected. In order to interpret the TG and DTA recordings and to isolate each possible phase at room temperature, this precursor milled for 48 h was heated in a furnace, at increasing temperatures. XRD patterns show no noticeable

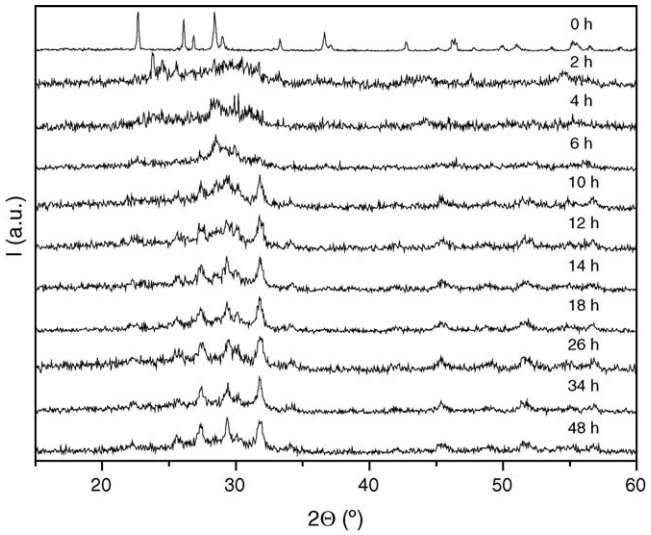

Fig. 1. XRD patterns of the mixture $4BaO_2$:K_2CO_3:$5Nb_2O_5$ after different mechanochemical activation times in a planetary mill.