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Journal of the European Ceramic Society 25 (2005) 2713–2717

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# Chemical synthesis of $KNbO_3$ and $KNbO_3$–$BaTiO_3$ ceramics

Irena Pribošič[a,*], Darko Makovec[a], Miha Drofenik[a,b]

[a] Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia
[b] Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova 17, SI-2000 Maribor, Slovenia

## Abstract

Powders of $KNbO_3$ (KN) and $KNbO_3$–$BaTiO_3$ (KN–BT) solid solution were prepared by the Polymerised Complex Method (PC method), based on the Pechini-type reaction route. The crystallization process of KN and KN–BT solid solution during the calcination of an amorphous precursor was observed, using TGA–DTA analysis and X-ray powder diffraction. After calcination the powders were ball milled, pressed into pellets and sintered. Using this procedure we achieved relatively high-density and very homogeneous KN and KN–BT ceramics.

*Keywords:* Powders-chemical preparation; Sintering; $KNbO_3$; $BaTiO_3$

## 1. Introduction

$KNbO_3$ (KN) is a technologically interesting material because of its high-temperature ferroelectricity and piezoelectricity, especially because it does not contain poisonous lead, which is used in other materials (e.g. PZT). Apart from its applications as a high-temperature ferroelectric or piezoelectric material, it was also tested as a material with a positive temperature coefficient of resistivity (PTCR). The applications of lead-free $BaTiO_3$-based ceramics with a PTCR are restricted to temperatures below $\sim 130\,^{\circ}C$. In order to increase the temperature range of lead-free PTC-resistor operation to higher temperatures, new PTCR materials are needed. Among the possible materials, lead-free ferroelectrics with high Curie temperatures are of particular interest. KN is a ferroelectric material with a Curie temperature ($T_C$) of $415\,^{\circ}C$, thus giving it, and its solid solution with $BaTiO_3$, the potential to be materials for high-temperature PTCR applications.

In our earlier studies the PTC resistors based on $KNbO_3$–$BaTiO_3$ (KN–BT) solid solutions were prepared by conventional ceramic technology using calcination of the appropriate oxides and carbonates.[1] The ceramics were produced in a semiconducting form by atmospheric reduction. Subsequent reoxidation of the grain boundaries in these semiconducting ceramics resulted in the appearance of a significant PTCR effect. However, the PTCR effect degraded at elevated temperatures, most probably due to the fine-grained structure and the non-homogeneity of these ceramics. It appeared that the microstructure of the ceramics needed to be controlled further in order to improve the PTCR effect in KN–BT ceramics.

The preparation of KN–BT ceramics using conventional solid-state technology is relatively difficult due to the large differences in the properties of the cations involved. To prepare ceramics with a microstructure appropriate for PTC resistors, the homogeneity of the starting powder needs to be increased.

Various wet chemical methods have been reported for the preparation of $KNbO_3$.[2–5]

In this study, we report on a Polymerised Complex Method (PC method), based on the Pechini-type reaction route[6] for the preparation of homogeneous KN–BT PTCR ceramics, starting from an aqueous precursor solution of the respective metal complexes.

## 2. Experimental procedure

Niobium (V) chloride ($NbCl_5$, Alfa 51108), potassium carbonate ($K_2CO_3$, Aldrich 20,961-9), barium nitrite

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* Corresponding author. Tel.: +386 1 477 3762; fax: +386 1 477 3875.
*E-mail address:* irena.pribosic@ijs.si (I. Pribošič).

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doi:10.1016/j.jeurceramsoc.2005.03.128

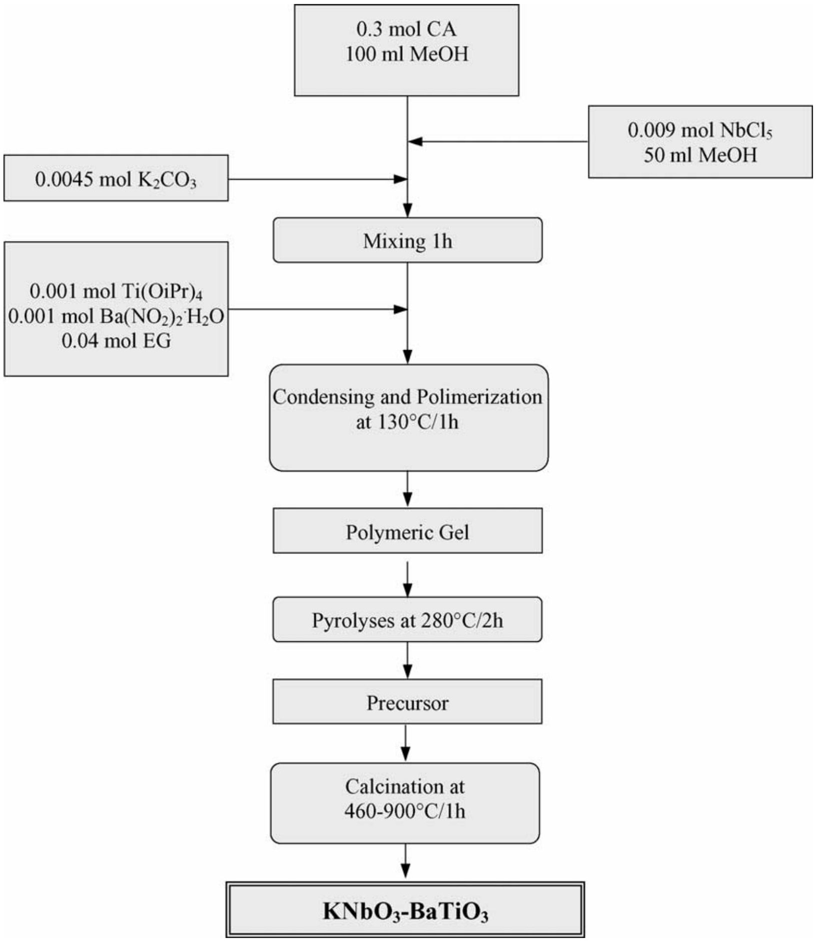

Fig. 1. Flow diagram for preparing $KNbO_3$–$BaTiO_3$ solid solution by the PC method.

$(Ba(NO)_2{\cdot}H_2O$, Alfa 17680), titanium (IV) isopropoxide-$Ti(OiPr)_4$ ($Ti[OCH(CH_3)_2]_4$, Alfa 77115), citric acid (CA) ($C_6O_7H_8$, Alfa 31185) and ethylene glycol-EG ($C_2O_2H_6$, Alfa 31332) were used to synthesize powders of KN and KN–BT solid solution with 10 mol% of $BaTiO_3$ and 90 mol% of $KNbO_3$ (90KN–10BT). A schematic of the experimental procedure is illustrated in Fig. 1.

For the preparation of the powders, CA (0.3 mol) and $NbCl_5$ (0.01 mol) were dissolved in 100 and 50 ml of methanol, respectively. With continuous stirring the $NbCl_5$ solution was slowly added to the solution of CA. $K_2CO_3$ (0.005 mol) powder was added and the solution was magnetically stirred for 1 h, to obtain a clear, colourless solution of metal–citrate complexes. This solution, containing $Nb^{5+}$ and $K^+$ cations, was mixed with the 0.04 mol EG. The mixture was then slowly heated up to 130 °C for 1 h, first to evaporate the methanol and subsequently to promote esterification between the CA and the EG. During condensation of the solution, white precipitates were formed, but the solid substance was dissolved when the temperature reached 130 °C. After esterification, a clear, slightly yellow polymeric gel appeared. This gel remained clear after cooling to room temperature. Charring the resin at 280 °C for 2 h resulted in a black, highly porous, solid precursor.

For the preparation of the KN–BT solid solutions, appropriate amounts of $Ti^{4+}$ and $Ba^{2+}$ cations were added to the metal–citrate complex solution with the previous dissolution of $Ti(OiPr)_4$ and $Ba(NO_2)_2{\cdot}H_2O$ in EG (Fig. 1).

Later on the precursors were calcinated for 1 h at temperatures from 460 to 900 °C. The thermal decomposition and crystallization of the precursor were investigated by thermogravimetry and differential thermal analysis (TG–DTA, Netzsch, STA 409) in static air with a heating rate of 1 °C/min and X-ray powder diffraction (Model D4 Endeavor, Bruker AXS). The specific surface area of the powders was determined using the BET method (Micromeritics Gemini 2370).

Powder calcined at 900 °C was used for the sintering experiments. The powder was deagglomerated by milling in a zirconium ball mill in ethanol for 3 h. The deagglomerated powders were pressed into pellets, 6 mm diameter and 2.5 mm thick, and sintered for 1 h at the optimum sintering temperature. The temperature at which the maximum density was achieved was assumed to be the optimum sintering temperature.

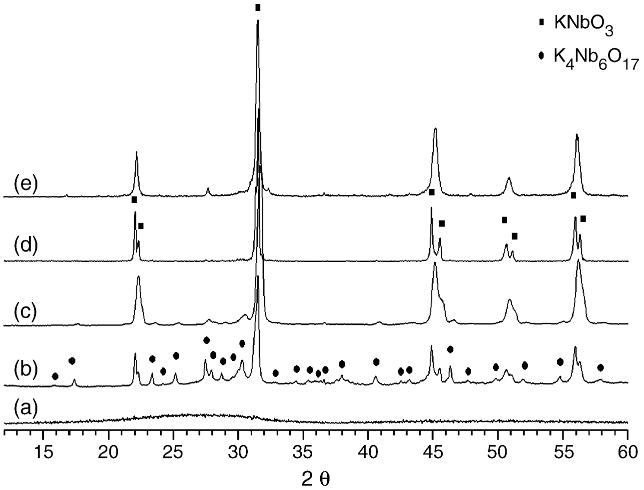

Fig. 2. XRD patterns of KN (a–d) and 90KN–10BT (e) powders precursors calcinated for 1 h at: (a) 460 °C, (b) 540 °C, (c) 600 °C and (d), (e) at 900 °C.

The densities of the sintered samples were measured using Archimedes principle, whereas their microstructures were characterized using an SEM (Model 4800, JEOL, Tokyo, Japan).

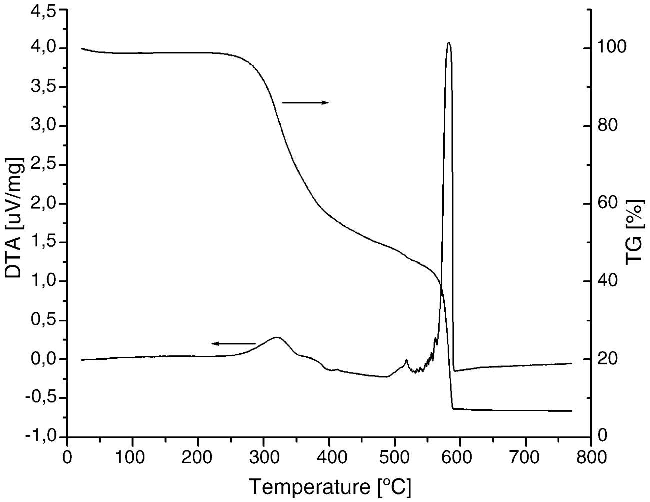

Fig. 3. TG–DTA curves of the KN precursor in static air with a heating range of 1 °C/min.

## 3. Results and discussion

The X-ray diffraction (XRD) patterns of the KN powders heated for 1 h at different temperatures are shown in

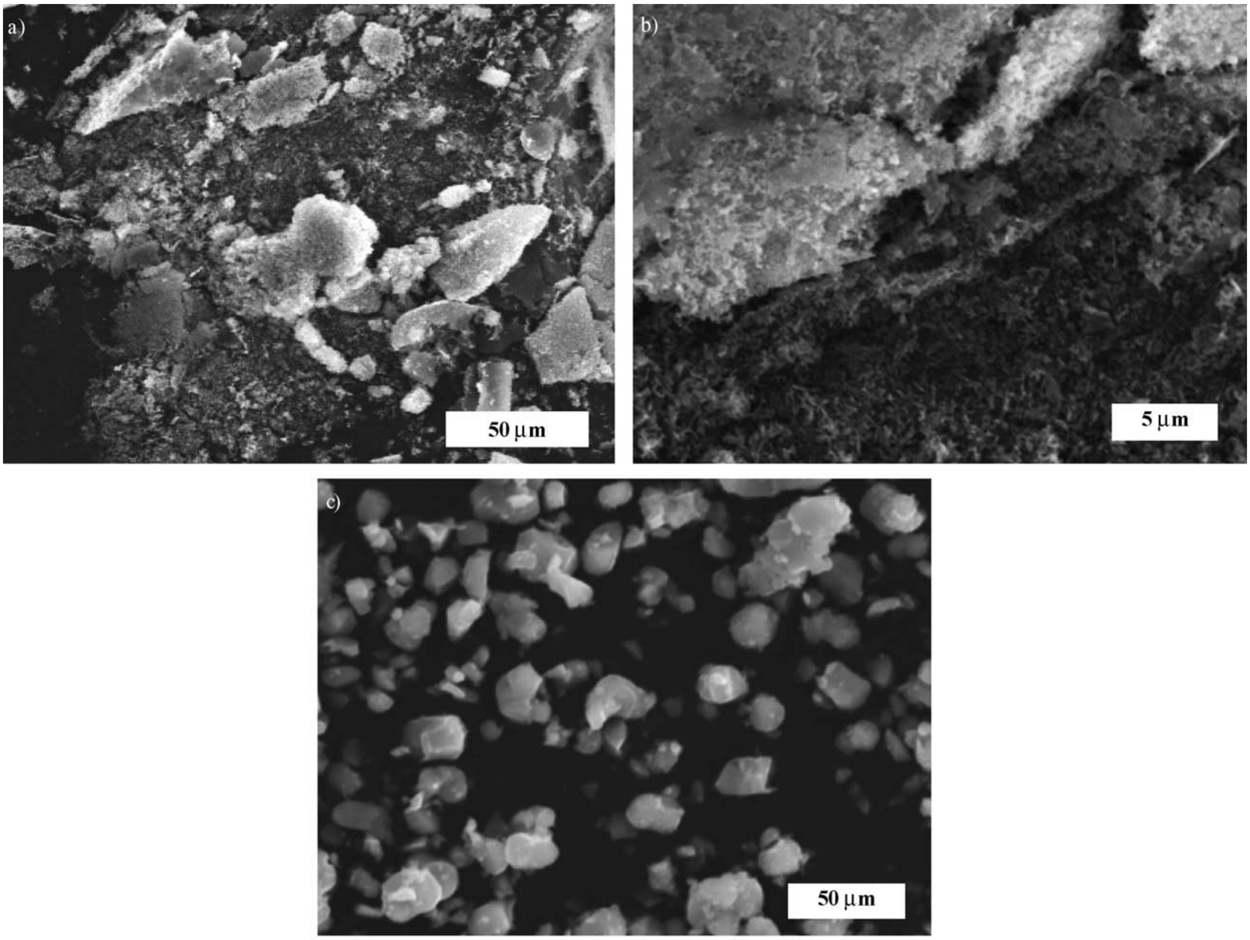

Fig. 4. SEM micrographs of the KN precursor powder prepared using the PC-method (a and b) calcined at 900 °C for 1 h, and calcined powder prepared using the solid-state method (c).

Fig. 2. After 1 h at 460 °C no crystalline phase could be detected with XRD. The XRD spectrum of the powder heated at 540 °C shows the presence of reflections, which could be ascribed to crystalline phases: the KN perovskite and $K_4Nb_6O_{17}$ ($K_4N_6$—orthorhombic, space group: $P2_1nb(33)$)[7] compounds. With increasing temperature the amount of $K_4N_6$ decreased while the amount of KN increased. After a calcination at 900 °C only the KN compound was present. Therefore we believe that in the first stage $K_4N_6$ is formed from an amorphous precursor and subsequently it reacts to form KN. Because of the stoichiometry of $Nb^{5+}$ and $K^+$ cations in the $K_4N_6$ compound, the presence of a potassium-rich phase is expected. However, no such phase was visible on the XRD pattern, most probably due to its relatively small content (the peaks for potential K-rich phases can be hidden behind the peaks of the $K_4N_6$ and KN compounds). The cell parameters of the orthorhombic KN cell were determined to be $a = 0.5696$ nm, $b = 0.5709$ nm and $c = 0.3983$ nm, which is close to those reported for that compound.[8]

The XRD analysis of the 90KN–10BT powder calcined at 900 °C (Fig. 2e) revealed a few small unidentified peaks besides the peaks corresponding to the matrix perovskite phase. Also, in the case of KN–BT, the perovskite phase appeared between temperatures of 460 and 540 °C. However, the peaks of perovskite phase in the KN–BT samples showed an increase in the symmetry of that phase compared to pure KN. For example, the split peak of pure KN around $2\theta = 22.2°$ corresponding to the (0 1 1) and (1 0 0) reflections changed into one broad peak in the diffractogram of the KN–BT sample (Fig. 2d and e). The change in the cell of the perovskite phase in the KN–BT sample compared to pure KN strongly suggests the formation of the solid solution of $BaTiO_3$ in $KNbO_3$. The XRD suggested a tetragonal cell for the solid solution, with $a = 0.4034$ nm and $c = 0.4017$ nm after the calcination at 600 °C, and $a = 0.4016$ nm, $c = 0.4003$ nm after calcination at 900 °C. However, it is not clear whether a single-phase KN–BT solid solution was formed during the calcination. In the 90KN–10BT sample prepared with the solid-state process, two solid solutions were detected after sintering at 1125 °C: a solid solution of $BaTiO_3$ in $KNbO_3$ and a solid solution of $KNbO_3$ in $BaTiO_3$.[1]

The results of the XRD analyses were in agreement with the TGA/DTA analyses. Fig. 3 shows the TG/DTA curves of the KN powder precursor obtained by the PC method. The TGA curve shows two regions of weight loss, while the DTA curve shows three exothermic effects with maxima at 320, 518 and 582 °C. The first broad peak in the DTA curve around 320 °C, associated with the large weight loss of approximately 49.5%, can be related to the burnout of organic species involved in the precursor powder. The XRD analysis suggested the appearance of $K_4N_6$ as the first crystalline phase between 460 and 540 °C. Thus, the second small peak in the DTA curve at 518 °C is most probably related to crystallization of K4N6. The largest peak in DTA curve at 582 °C was associated with the second step in TGA curve (42.6%). This sharp peak can be attributed to the crystallization of KN. Above 590 °C there is no further weight loss and no thermal effect up to 780 °C.

Fig. 4 shows SEM images of the KN powder prepared using the PC-method and calcined at 900 °C (a and b), and KN powder prepared using the solid-state method (c). The powder prepared by the chemical method is strongly agglomerated. The agglomerates are composed of smaller nano-sized particles. In contrast, with the solid-state method the calcined powder is not agglomerated; however, the particle size is much bigger. The surface area of this powder was only 1.78 $m^2$/g. For the sintering experiments the calcined powders were deagglomerated by milling; however, some smaller agglomerates remained in the powder. After milling the surface area of the powder was 14.5 $m^2$/g.

Fig. 5 shows a fracture surface of the KN ceramics, sintered for 1 h at 1055 °C. The ceramic is relatively dense, 89% of theoretical density. In the dense matrix some large elongated pores are distributed. Such pores are typical for differential sintering of the powder with agglomerates. The grain size was around 3 µm, similar to that obtained by solid-state processing,[1] where the density of the sintered KN ceramics reached only 83% of theoretical density.

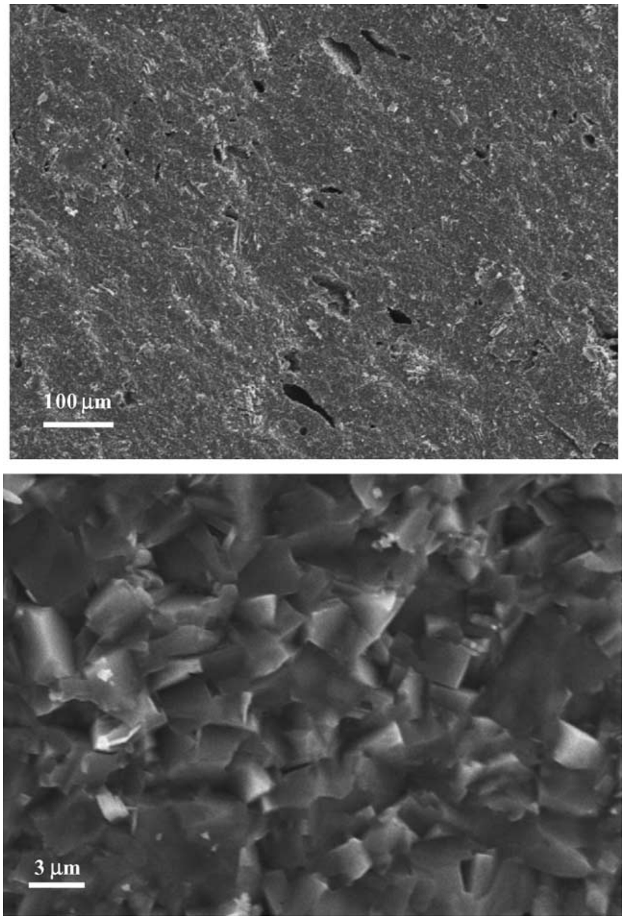

Fig. 5. Fracture surface of the KN, sintered for 1 h at 1055 °C.

## 4. Conclusions

The PC method, based on a Pechini-type reaction route was used to prepare KN and KN–BT powders. The observations indicate that the crystallization of KN proceeds via the $K_4N_6$ intermediate phase. The perovskite KN is obtained already after heating at temperature of ~600 °C. In the case of the KN–BT precursor, a solid solution between the perovskites KN and BT is already formed at temperatures below 900 °C.

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