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Elaboration and characterization of potassium niobate tantalate ceramics

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ABSTRACT

In this work three different sintering techniques were used to improve the densification and dielectric properties of $K(Nb_{0.40}Ta_{0.60})O_3$ (KN40T60) lead-free ceramics. Dense samples were obtained using: (1) conventional sintering in air both with and without sintering aids, (2) two-step sintering and (3) spark-plasma sintering. The Curie temperature ranged between −25 and 25 °C for the tetragonal to cubic phase transition, which depend on the microstructure. As the density of pure KN40T60 ceramics was increased, the large dielectric losses obtained by using a conventional sintering process were significantly reduced and reach suitable values. Improvements in the dielectric behavior and densification of KN40T60 ceramics seemed to be related to the sintering process.

1. Introduction

Piezoelectric ceramics are widely used for producing transducers, actuators, and sensors. Nevertheless, most of these materials have lead content such as lead zirconate titanate, PZT [1,2]. In recent years, potassium niobate tantalate $K(Nb_{1-x}Ta_x)O_3$ (or KNT) have appeared as potential environmental-friendly candidates for substituting lead-based materials in such technological devices [3–6]. KNT solid solutions present a perovskite-type structure, which varies at room temperature and room-pressure, from cubic to tetragonal and orthorhombic symmetry as tantalum is substituted by niobium [7]. Consequently, the ferroelectric and piezoelectric properties of KNT, like the Curie temperature or the polarization capability, can be adjusted by controlling the composition.

One major obstacle for technical applications of KNT ceramics is the challenge of processing these materials because of the presence of alkaline elements, which are sensitive to humidity, evaporation at high-temperature, poor sinterability and because of the difficulty involved in controlling the microstructure. These leave a limited number of processing techniques to produce dense ceramics with suitable dielectric, ferroelectric and piezoelectric properties. Various strategies have been carried out to improve the densification of KNT ceramics, such as adding suitable sintering aids [8–12] or using specific sintering processes such as two-step sintering (TSS) in air [13,14], or pressure-assisted sintering in a controlled atmosphere like spark plasma sintering (SPS) and hot pressing [15–17].

The present paper describes and discusses the preparation and characterization of $KNb_{0.4}Ta_{0.6}O_3$ (KN40T60) ceramics, focusing on the influence of different sintering aids, CuO, MnO_2, WO_3, $CuNb_2O_6$, $CuTa_2O_6$ and KF, and the use of TSS, SPS on the morphology, density and dielectric properties. A comparative study using the three-methods mentioned above has never been published before.

2. Experimental details

High purity K_2CO_3, Nb_2O_5 and Ta_2O_5 were chosen as starting raw materials. In the case of conventional sintering, the raw powders were weighed and ground in an agate mortar until a homogeneous mix was obtained. In order to have better reactivity, the mixed powders were uniaxially pressed and calcined at 1150 °C for 4 h. This high calcination temperature was necessary to have well-crystallized KN40T60 powders without residual raw oxides. Applying lower temperatures for longer periods of time or using double-calcination processes did not allow us to obtain full reaction of the raw materials. After the pure phase was obtained, the calcined powders were milled with alumina balls in a planetary grinding machine (Frisch Pulverisette 6) for 30 min. The mixed powders were then passed through 100 μm to remove some un-broken agglomerates and APV/PEG binder aqueous solution was added. The resultant product was sieved again and uniaxially pressed into 13 mm diameter pellets.

The green pellets were placed in an Al_2O_3 crucible and heat-treated in air at 600 °C for 4 h to remove the organic binder. Final firing was performed at 1150 °C for 6 h in sealed alumina crucibles. The pellets were surrounded with powder of the same composition to keep a saturated alkali-species atmosphere during the heat treatment and limiting the volatilization of alkali-oxides. In order to achieve high densities and improve the dielectric properties of the samples, a first strategy consisted of maintaining the ordinary sintering process while

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testing the reliability of different sintering aids. A variety of oxides such as CuO, MnO_2, WO_3 have already been tried to achieve liquid phase sintering of (K, Na)NbO_3 but hardly experimented with KNT. While those oxides gave interesting results in terms of morphology and electrical characteristics [8–12] searching for better sintering aids has been always a focus of the field. Recently, a simple method named liquid phase screening has been proposed by K. Chen *et. al.* to quickly screen potential sintering aids for $(K_{0.5}Na_{0.5})NbO_3$ ceramics and determine their wetting ability [11,18]. We applied this technique by using homemade $CuNb_2O_6$ and $CuTa_2O_6$ mixed oxides and KF, which has not been used before on KNT compounds. These additives appeared interesting as they contain host cations and represent a source of A-site or B-site ions, which might help to reduce some losses of these cations during the sintering process. Sintering aids (CuO, MnO_2, WO_3, $CuNb_2O_6$, $CuTa_2O_6$ and KF) were introduced by mixing 1 wt% of these compounds with KN40T60 powder before pressing and firing the pellets at 1150 °C for 6 h. To further improve the sintering behavior of KN40T60 ceramics two other sintering processes were investigated: the pressure-less TSS and pressure-assisted SPS. Two-step sintering (TSS) is an attractive and cost-effective sintering method that by controlling the heating rate allows an improvement of the densification [19]. In the first step, the sample was kept at a high temperature (1220 °C) between the liquidus and solidus lines of the $KNbO_3$-$KTaO_3$ phase diagram for a very short time (0–1 min). This was done to reach a critical density via a liquid phase formation. The ceramic was then rapidly cooled down to a lower temperature (1150 °C) and maintained for 6 h to ensure densification with limited grain growth. SPS experiments were performed on a Dr. Sinter 515S Syntex machine equipped with a carbon die matrix and carbon punches. In this process, the pulsed DC current directly passes through the graphite die as the powder is compacted. The heat generation is internal, which facilitates a very high heating and cooling rate. The sample was heated at 1100 °C and compacted at 100 MPa for 5 min. Once the sample was removed from the SPS device, an annealing process was performed in air at 700 °C for 12 h to eliminate any carbon traces in the material.

X-ray diffraction (XRD, PANAalytical X'pert Pro diffractometer with Cu-Kα_1 radiation) patters of the calcined KN40T60 powder and KN40T60 ceramics were collected to identified phases and perform a profile matching using FULLPROF software [20].

The composition and microstructure analysis were performed on a cross-section of the pellets by using a Scanning Electron Microscopy (SEM) coupling to an Energy Dispersive X-Ray microanalysis (EDX). Dielectric measurements were performed on polished pellets in where both surfaces were painted with Ag paste. The temperature dependence of dielectric constant (ε_r) and dielectric loss tangent (tgδ) were measured using a Novocontrol analyzer in the [−70 to 200 °C] temperature range and [1 kHz-1 MHz] frequency range.

3. Results and discussion

3.1. Conventional sintering

X-ray diffraction (XRD) pattern of KN40T60 powders is shown in Fig. 1. No impurity peaks other than KN40T60 perovskite peaks were observed. A Le Bail analysis of the XRD was performed using a tetragonal structure (*P4mm* space group); this was previously reported for the single-crystal phase diagram of $KNb_{1-x}Ta_xO_3$ [7,21]. The sample kept the same tetragonal symmetry after a conventional sintering method in air was performed. Complementary to the XRD, a fracture surface of the sintered pellet was observed by SEM. Fig. 2 shows a porous microstructure consisted of grains presenting a bimodal distribution and cubic shape. EDX analysis on different regions revealed a homogeneous composition within the grains without significant changes at the grain boundaries. However, oxygen vacancies were formed and the average value of the measured Nb: Ta ratio was

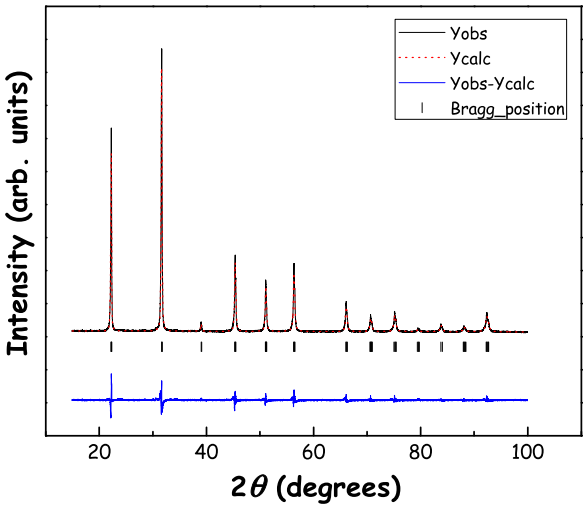

Fig. 1. Experimental (–) and calculated (—) profiles from the Rietveld refinement of the tetragonal (*P4mm*) phase of $KNb_{0.4}Ta_{0.6}O_3$ at room temperature and room pressure. The difference profile is on the same scale. Cell parameters are a=b=3.99285 Å and c=4.00169 Å.

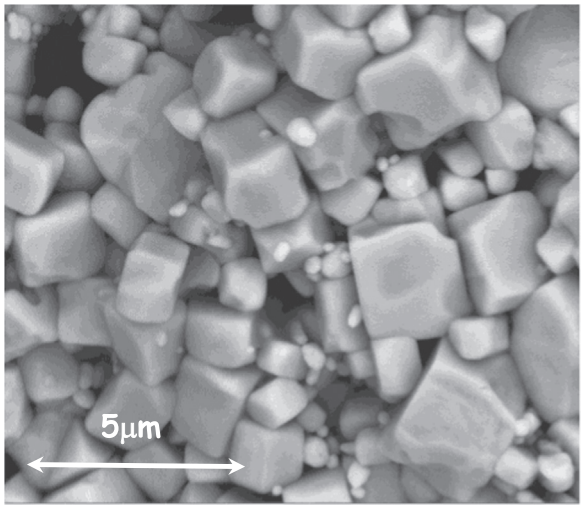

Fig. 2. SEM micrograph of $KNb_{0.4}Ta_{0.6}O_3$ ceramics sintered in air by conventional sintering at 1150 °C during 6 h.

0.7, which is higher than the nominal value of 0.67 for the $KNb_{0.4}Ta_{0.6}O_3$ compound. The difficulty in maintaining the exact stoichiometric ratio of Nb: Ta at the B-site in air-sintered samples has already been reported [17,22].

After confirming the purity and crystal structure of the air-sintered KN40T60 ceramic, dielectric measurements were performed. Fig. 3 shows that the maximum of the dielectric constant appears around 0 °C. This value is lower compared to the Curie temperature (T_C) around 50 °C for a single crystal of the same 40:60 nominal composition [7]. This has already been reported in studies dealing with electrical properties of KNT materials [17,22,23].

This difference in the T_C might be due to the fluctuations between the measured and nominal compositions of the samples but also to the presence of oxygen vacancies. Indeed it has been reported for ferroelectric ceramics like $BaTiO_3$ that the T_C considerably depends on the presence of oxygen vacancies, which tend to remove locally the tetragonal symmetry and the ferroelectric state leading to a reduction of T_C [24,25].

Furthermore, the sample exhibits strong frequency dispersion in the dielectric properties and high dielectric losses, with a peak at low frequency that decays at higher temperatures, before the normal