



Short communication

Flash sintering of potassium-niobate

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Abstract

The challenge in creating stable and dense KNbO_3 ceramics is suppressing the K_2O volatility that occurs at elevated temperature and avoiding the formation of unwanted phases. This challenge could be addressed by applying a field-assisted sintering technique. Flash sintering was conducted successfully on KNbO_3 powder, under applied electric field of 600 V/cm at 750 °C. The linear shrinkage of the sample was approximately 18%, and its density was 95% of the theoretical density. Homogeneous dense samples were obtained, containing grains with similar size to that of the green powder. The stoichiometry ratio of potassium to niobium (K/Nb) remains similar to that of the green powder. Flash sintering is proven here as a process which overcomes the main challenge of sintering ceramics with highly volatile species. In addition to its known advantages, we show here that the process is also a breakthrough in the synthesis of dense stoichiometric KNbO_3 .

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1. Introduction

In recent years there is a growing interest in novel field-assisted sintering techniques that enable lowering the temperature of operation while reducing the process time. One of those techniques is flash sintering, an unconventional densification process in which a powder sample is sintered very rapidly at certain threshold conditions that are determined by temperature and applied electrical field. The specimen is a compressed powder with two electrodes at both ends, on which an electrical field is applied directly. Its major advantage is the fact that no pressure is needed during the process. Raj has demonstrated that during flash process the power density rises rapidly and the sample temperature is much higher than the furnace temperature.¹ At the threshold point (nominal DC electrical field and temperature) a rapid fall in the ceramic resistivity occurs and the specimen temperature rises until it reaches a steady-state value above the

furnace temperature. Experimentally, at the threshold point, the current rises to its compliance value and the electrical field source must be switched from voltage control to current control, in order to decelerate the electrical runaway. The phenomenon can be seen in a typical power density plot during the electric field pulse as a noticeable peak, also referred to as power-spike.¹ Flash sintering was performed on several oxides such as yttria-stabilized zirconia (YSZ),² Co_2MnO_4 ,³ MgO doped alumina⁴ and SrTiO_3 .⁵ Moreover, many researchers are trying to get a better understanding about the different mechanisms and the driving forces of the process by addressing questions regarding the coupling of the heat transfer and the electric field,^{1,6–9} the role of defects and mass transfer,^{4,5} the specimen microstructure and grain growth,^{10–12} the temperature distribution,¹³ etc.

Potassium niobate ceramics, KNbO_3 , is a well-studied lead free ferroelectric material that attracted considerable attention due to its piezoelectric and electro-optic properties.¹⁴ Synthesizing highly dense polycrystalline KNbO_3 ceramics is considered to be a difficult task. The main challenge in the synthesis of stoichiometric stable KNbO_3 is that potassium oxide (K_2O) easily volatilizes above 800 °C. Flückiger et al.¹⁵ showed that the weight loss of sample due to K_2O evaporation is enhanced

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in a humid environment. Furthermore, it is noticeable that the difference in weight loss in both environments (humid and dry) increased gradually with temperature. Its phase diagram, demonstrates the eminent influence of K_2O volatility on the $KNbO_3$ structure. Unwanted Nb-rich phases such as $K_4Nb_6O_{17}$ ($2K_2O \cdot 3Nb_2O_5$) and KNb_3O_8 ($K_2O \cdot 3Nb_2O_5$) are readily formed during calcination and sintering and are found in the final product. Various sintering aids and techniques are reported to achieve enhanced densification of $KNbO_3$ with minimal deviations from stoichiometry. High-density polycrystalline samples can be obtained by sintering alkali-niobate in reducing atmospheres; vacuum and/or low oxygen partial pressures that rate limit the surface evaporations.^{16–21} Other techniques have considered fast sintering approaches such as spark plasma sintering.²²

Here, we applied an even faster sintering approach to kinetically control stoichiometry, namely flash sintering. This is to our knowledge the first demonstration of flash sintering on the alkali niobate family, and using $KNbO_3$ for the model system. Unlike other ceramic powders, which can be fully dense when sintered conventionally, the uniqueness of applying flash process on $KNbO_3$ is the reduction of K_2O volatility. The result is a high density ceramic that maintains the stoichiometric ratio of K/Nb.

2. Materials and methods

2.1. Flash sintering and impedance spectroscopy measurements modified system²³

The flash sintering setup is assembled in a modified horizontal dilatometer (BÄHR DIL-801) equipped with 1500 °C furnace, taking advantage of its ability to measure shrinkage in-situ (Fig. 1). Platinum foil electrodes covered the edges of the standard sample holder of the dilatometer, and connected to a power source and an impedance analyzer via a switch system. DC Electrical field is applied to the electrodes via three Keithley 2400 source meters connected in series to achieve maximum voltage of 600 V with limited current of 100 mA. Impedance spectroscopy measurements were carried out in a dual phase lock-in amplifier (SR 830, Stanford Research) used for lower frequencies of 0.01–100 Hz, and precision LCR meter (Agilent 4284A) for high frequencies of 20 Hz–1 MHz.

2.2. HR-SEM

High resolution scanning electron microscopy, HR-SEM, imaging was performed on a Zeiss Ultra Plus high resolution scanning electron microscope, equipped with a Schottky field-emission electron gun and a unique Gemini electron-beam column. Energy dispersive X-ray spectrometer (Oxford Instruments EDX detector with resolution of 127 eV, operated at acceleration voltages of 10 keV) was used for phase verification and chemical compositional analysis.

2.3. Materials

$KNbO_3$ powder synthesis was performed by a hydrothermal process using 6 M KOH (99.99% total alkalinity, Sigma Aldrich USA) and Nb_2O_5 (99.9%, Sigma Aldrich USA) in a 200 ml Teflon flask. The reaction was carried out in a stainless steel reactor (Parr Co., USA) housing the Teflon flask. The solution was mechanically stirred at 300 rpm for 24 h and the product was separated from the solution and centrifuge-washed with deionized water to reach pH = 7. Drying was performed at 100 °C for 24 h, resulting in a powder that was ground and filtered through a 250 mesh.^{24–26} Grain size of the obtained powder was in the range of 1–3 μm . 4 wt% of polyvinyl alcohol (PVA) in water was added to the obtained powder. The binder-powder mixture was milled in air until complete evaporation of the solvent, ground and filtered as described above. The final samples were uniaxially pressed in a 10 mm by 3 mm by 3 mm stainless steel die at 6.9 MPa, followed by a cold isostatic press of 193 MPa. The PVA binder was burnt out at 500 °C for 10 min. The green density of the samples was approximately 60% of the theoretical density of $KNbO_3$. To enable electrical contacts, 10 nm of titanium followed by 100 nm of platinum were evaporated on the sample edges.

3. Results

One of the main challenges in the synthesis of $KNbO_3$ is to create a stoichiometric compound, e.g., K/Nb ratio should be close to unity. In the conventional solid-state reaction, calcination temperature of the precursors is higher than 800 °C. K_2O volatility is inevitable and the stoichiometric ratio changes, sometimes creating an unwanted second phase. Hydrothermal (HT) synthesis is used here to avoid the loss of potassium at the early preparation steps. An HR-SEM image of the HT $KNbO_3$ powder shows a cubic morphology with grain-sizes ranging from ~1 to 3 μm (Fig. 2). The K/Nb ratio as was analyzed by energy dispersive spectroscopy (EDS) is slightly lower than 1 (average values from seven points are given in the inset table of Fig. 2). While this ratio will decrease gradually during conventional sintering, it should remain unchanged when sintered at temperatures lower than 800 °C, or using a rapid process. Initially, the samples were sintered conventionally both in air and in reduced atmosphere ($pO_2 \approx 10^{-11}$) at 1000 °C. Lowering oxygen partial pressure reduces K_2O volatility and should enhance the densification. Indeed, higher density samples have been obtained after 4 h in reduced atmosphere compared to those sintered in air. Nevertheless their density was still low, 87% of the theoretical density (calculated by Archimedes method).

A possible explanation for the effect of pO_2 on K_2O volatility stems from recent considerations in the theory of point defect chemistry of perovskites.²⁷ Reducing pO_2 enhances the concentration of oxygen vacancies and hence promotes concentration enhancements of quasi-free electrons and other negatively charged species such as metal vacancies for charge compensation. Deviation in K/Nb ratio, however, does not always result in acceptor-like behavior (i.e., as if the material is doped by acceptors when the metal vacancies are frozen-in^{28,29}). There is

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