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Role of initial potassium excess on the properties of potassium tantalate ceramics

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Abstract

Potassium tantalate ($KTaO_3$ – KT) ceramics with controlled initial K/Ta ratio = 1, 1.02 and 1.05 were synthesised by solid-state reaction. Crystal structure and microstructure of the sintered ceramics were examined by XRD and SEM/EDS, respectively. Their dielectric properties were then studied as a function of the temperature over the radio frequency range. Ceramics with K/Ta ratio = 1 exhibits potassium-poor secondary phases, in contrast to ceramics with initial K/Ta ratio = 1.05, where no secondary phases are detected. Moreover, the grain size increases dramatically with K/Ta ratio >1. The quantum paraelectric behaviour of KT ceramics is weakly affected by the variation of K/Ta ratio and their dielectric response is well described by Barrett's equation. Though, no anomaly is induced in the dielectric permittivity by potassium excess, it yields an increase of its lowest temperature magnitude up to ~4000, which is to the best of our knowledge, the highest value ever reported for KT ceramics.

Keywords: Tantalates; Ceramics; Powders-solid state reaction; Defects; Dielectric properties

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1. Introduction

With the increasing demand of oxide ferroelectrics, $(Ba,Sr)TiO_3$ is currently considered as the main candidate for tunable electronic applications due to the high tunability of the dielectric permittivity of ferroelectric $BaTiO_3$ and low dielectric loss of incipient ferroelectric $SrTiO_3$.[1] However, the dielectric loss of another incipient ferroelectric with a cubic perovskite structure $KTaO_3$ (KT) is even lower than that of $SrTiO_3$.[2] KT single crystals possess loss $\tan\delta \sim 10^{-4}$ in GHz range, whereas the dielectric permittivity continuously increases to ~5000 on cooling toward 0 K, becoming dc-electric-field tunable in the low-temperature range.[3] However, whereas low-temperature properties of $KTaO_3$ single crystals have been extensively investigated,[4] the studies on $KTaO_3$-based ceramics are not frequent,[5,6] although ceramics are cheaper to produce than single crystals. This scarcity probably stems from the fact that polycrystalline $KTaO_3$ is hard to achieve as a monophasic stoichiometric compound with high relative density, with the drawback of being easy to melt above 1350 °C.[6] On the other hand, the optimisation of the dielectric response in functional materials is evidently associated with the precise control of the composition (stoichiometry). Whereas the properties of nonstoichiometric $SrTiO_3$ ceramics are widely studied,[7] to the best our knowledge, no such systematic studies have been dedicated to the role of nonstoichiometry on the structure, grain size and dielectric response of KT ceramics. In Ref. 5, Chen et al. obtained KT ceramic samples by both conventional sintering at 1330 °C for 1 h and by isostatic hot-pressing at 1300–1310 °C under 20.7 MPa in argon for 1 h. Samples obtained from the former method showed density about 87%, dielectric permittivity up to 1000 and dissipation factor about 7.5% at 100 kHz, whereas those processed by the latter method revealed density about 92%, dielectric permittivity up to 2000 and dissipation factor about 1% at 100 kHz.[5] Axelsson et al. obtained KT ceramics with density about 85% and dielectric permittivity up to 3100 at 3.6 GHz by conventional sintering at 1340 °C for 1 h with the aid of 5% excess of potassium.[6] It is worthwhile to note the discrepancy between the density and the dielectric permittivity values reported in these two early works on KT ceramics. It is surprising that the more dense ceramics showed the lower dielectric permittivity. Moreover, the two aforementioned works oppose

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Table 1
Density, lattice parameter, average grain size, and Barrett relation parameters of KT ceramics with initial K/Ta ratio = 1, 1.02, and 1.05.

Initial K/Ta ratio	Density (g/cm^3)	Lattice parameter (Å)	Average grain size (μm)	Barrett relation parameters			
				T_0 (K)	T_1 (K)	$C/10^3$ (K)	ε_1
1	6.3	3.9896(1)	0.7	14	66	38	123
1.02	6.1	3.9895(1)	4.9	12	48	49	58
1.05	6.2	3.9893(1)	6.5	10	48	57	120

each other regarding the phase formation process in KT ceramics, conventionally sintered at similar conditions and analysed by XRD: Chen et al. report only $KTaO_3$ phase,[5] whereas Axelsson et al.[6] report formation of the $K_6Ta_{10.8}O_{30}$ secondary phase, if ceramics were prepared without potassium excess.

This work is aimed at clarifying the effect of initial K/Ta ratio on the properties of $KTaO_3$ ceramics. In order to better compare our results with the ones from earlier works, K/Ta ratio were chosen as 1 (as in Ref. 5), 1.05 (as in Ref. 6) and 1.02, as an intermediate between 1 and 1.05. X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS) analysis are used for the crystallographic, microstructural, and local elemental characterisation. Dielectric behaviour of the as-processed KT ceramics is evaluated from 10 K to room temperature over the radio-frequency range.

2. Experimental procedure

Ceramic samples were prepared by conventional mixed oxide method. After drying for dehydration, K_2CO_3 and Ta_2O_5 reagents were weighed according to the compositions $KTaO_3$, $K_{1.02}TaO_{3.01}$, and $K_{1.05}TiO_{3.025}$. After ball milling in alcohol for 5 h using Teflon pots and zirconia balls in a planetary mill, the powders were dried, and then calcined at 875 °C for 8 h. The calcined powders were milled again for 5 h to obtain powders with particle size lower than 5 μm. Pellets of 10 mm in diameter were uniaxially pressed at 100 MPa, covered by powder of the same composition to decrease the loss of potassium, and sintered in closed alumina crucibles at 1350 °C for 1 h with a heating and cooling rate of 5 °C/min. In order to quantify the potassium loss during sintering, thorough weight loss and inductively coupled plasma spectroscopy analyses were performed on calcined and sintered samples. Thorough weight loss analysis, revealing the weight difference of the calcined sample after drying at 200 °C and after sintering at 1350 °C, indicated the potassium loss of about 3%. At the same time, fully quantitative analysis, performed by inductively coupled plasma spectroscopy, presented the potassium loss of about 4%.

The density of all the sintered samples, measured by the Archimedes' method using diethylphthalate as the immersion liquid, varies within 6.1–6.3 g/cm^3, as shown in Table 1, i.e., it is ∼87–90% of theoretical density of $KTaO_3$. Room temperature XRD analysis (Rigaku D/Max-B, Cu Kα) was conducted on some of the grounded sintered samples with a scanning speed of 1°/min and a step of 0.02°. Lattice parameters were refined by the least square fitting to the observed XRD data, between $2\theta = 20°$ and $110°$, using WinPLOTR software. The microstructure of ceramics was observed on polished and thermally etched sections using SEM/EDS (Hitachi S-4100, Hitachi SU-70). The average grain size of the sintered pellets was measured on at least 100 grains by AnalySIS (Soft Imaging System GmbH) software. For the dielectric measurements, gold electrodes were sputtered on both sides of polished sintered samples. The dielectric permittivity and loss were measured at different frequencies between 100 Hz and 1 MHz, using Precision LCR Meter HP 4284A and a Displex APD-Cryogenics cryostat of He closed cycle during heating in the temperature range from 10 to 300 K.

3. Results and discussion

XRD patterns of the sintered potassium tantalate ceramic samples with initial K/Ta ratio = 1, 1.02, and 1.05 are shown in Fig. 1. For all the compositions the observed X-ray diffraction lines are consistent with the cubic crystallographic structure of stoichiometric $KTaO_3$. No distinct secondary phases are detected for ceramics with K/Ta = 1.05. If the small peak at

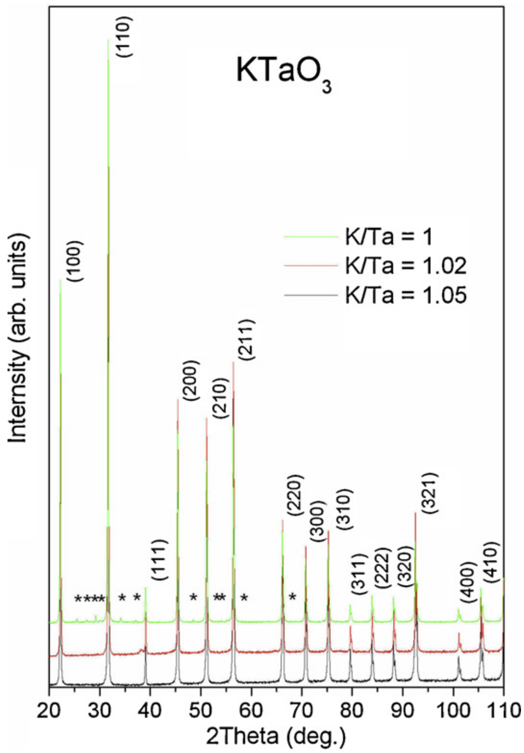

Fig. 1. XRD patterns of sintered potassium tantalate ceramics, prepared with initial K/Ta ratio of 1, 1.02, and 1.05. Reflections of $KTaO_3$ phase are marked by corresponding indexes and reflections of $K_6Ta_{10.8}O_{30}$ secondary phase are marked by *.