

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

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Abstract

Potassium tantalate (KTaO₃ – 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.

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1. Introduction

With the increasing demand of oxide ferroelectrics, (Ba,Sr)TiO₃ is currently considered as the main candidate for tunable electronic applications due to the high tunability of the dielectric permittivity of ferroelectric BaTiO₃ and low dielectric loss of incipient ferroelectric SrTiO₃.¹ However, the dielectric loss of another incipient ferroelectric with a cubic perovskite structure KTaO₃ (KT) is even lower than that of SrTiO₃.² 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 KTaO₃ single crystals have been extensively investigated,⁴ the studies on KTaO₃-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 KTaO₃ 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 SrTiO₃ ceramics are widely studied,⁷ to the best of 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 KTaO₃ phase,⁵ whereas Axelson et al.⁶ report formation of the K₆Ta_{10.8}O₃₀ 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 KTaO₃ 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, K₂CO₃ and Ta₂O₅ reagents were weighed according to the compositions KTaO₃, K_{1.02}TaO_{3.01}, and K_{1.05}TaO_{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/cm³, as shown in Table 1, i.e., it is ~87–90% of theoretical density of KTaO₃. 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 2θ = 20° and 110°, using WinPLOTR software. The microstruc-

ture 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 KTaO₃. No distinct secondary phases are detected for ceramics with K/Ta = 1.05. If the small peak at

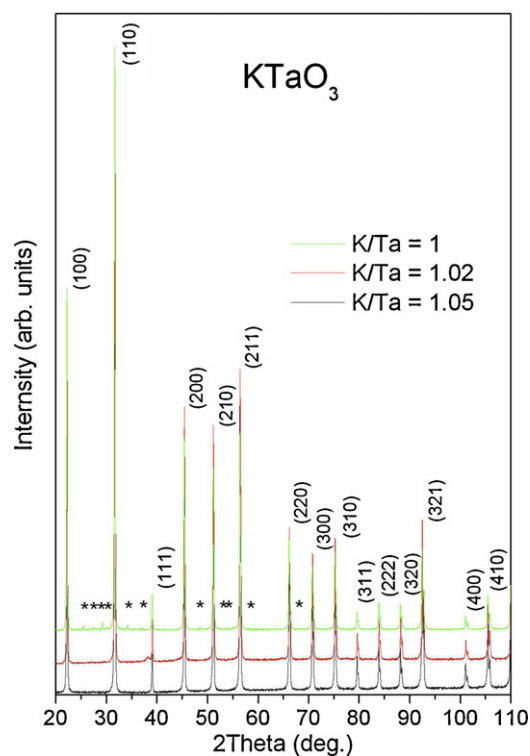


Fig. 1. XRD patterns of sintered potassium tantalate ceramics, prepared with initial K/Ta ratio of 1, 1.02, and 1.05. Reflections of KTaO₃ phase are marked by corresponding indexes and reflections of K₆Ta_{10.8}O₃₀ secondary phase are marked by *.

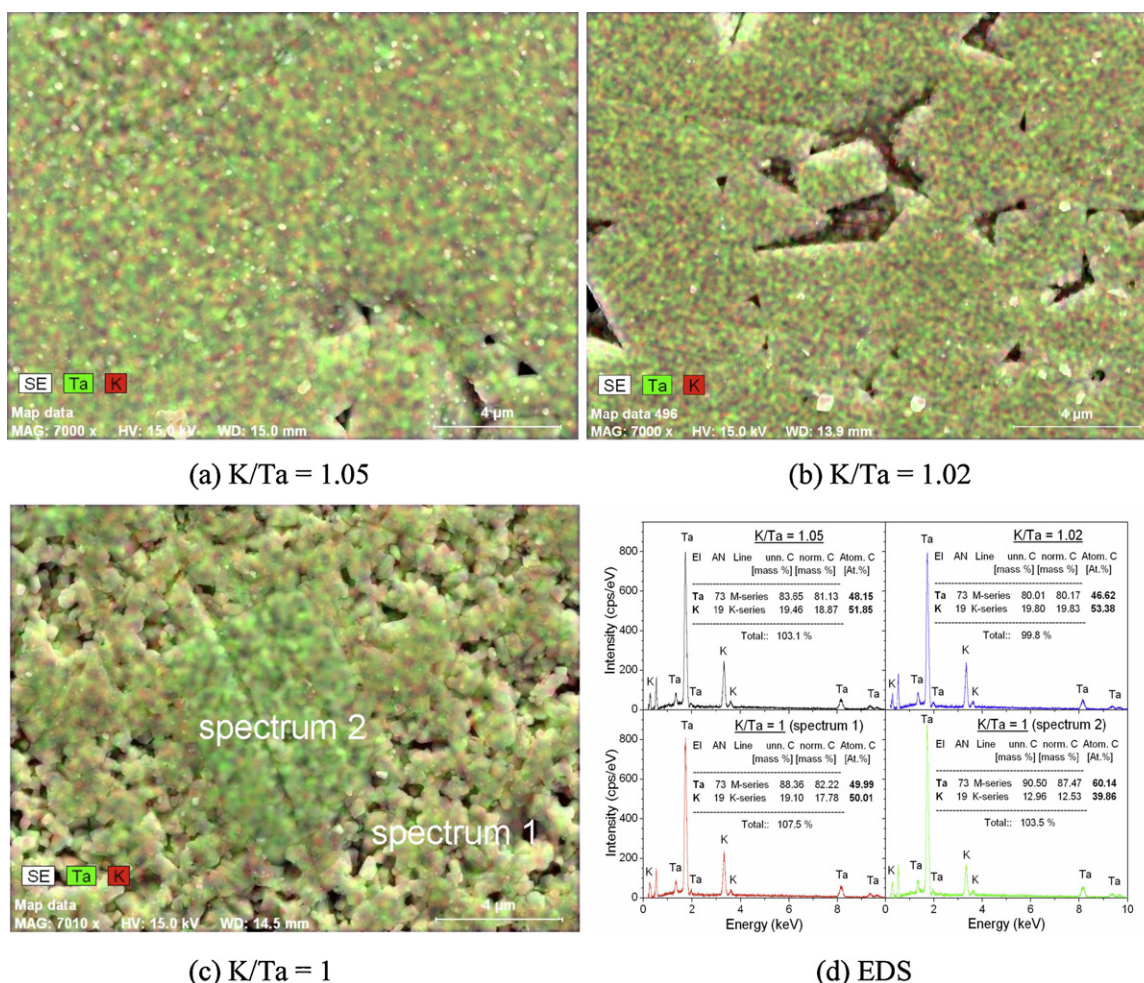


Fig. 2. Tantalum (green) and potassium (red) distributions over microstructure of KT ceramics, prepared with initial K/Ta ratios of 1.05 (a), 1.02 (b), and 1 (c), as well as corresponding energy dispersive spectra (d). For K/Ta = 1, two local spectra were taken on the positions marked as spectrum 1 and spectrum 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

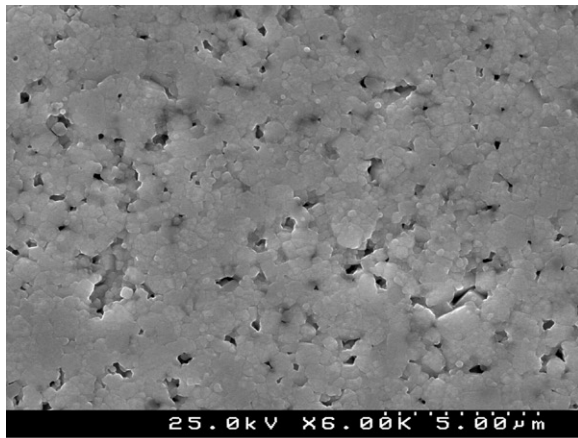
$2\theta = 38^\circ$ observed for K/Ta = 1.02 is not much significant, an almost pure single-phase state was also reached. Conversely, additional diffraction lines observed in the spectrum for K/Ta = 1, evidence the existence of a secondary phase, which was assigned to potassium-poor $K_6Ta_{10.8}O_{30}$ phase. This observation is in agreement with the work by Axelsson et al.⁶ contrarily to the single phase in ceramics conventionally sintered by Chen et al.⁵ Moreover, it is evident that the loss of potassium is reached due to its high volatility during the sintering process, since the XRD patterns of KT powders recorded after their calcination (not shown) did not reveal any secondary phase for all the samples, including K/Ta = 1.

The lattice parameter of $KTaO_3$ phase, deduced from XRD patterns and presented in Table 1, varies with the initial K/Ta ratio (within the experimental error) from $3.9896(1)\text{ \AA}$ for K/Ta = 1 via $3.9895(1)\text{ \AA}$ for K/Ta = 1.02 to $3.9893(1)\text{ \AA}$ for K/Ta = 1.05, being all the values close to 3.989 \AA , like it has been reported for $KTaO_3$ single crystals.⁸

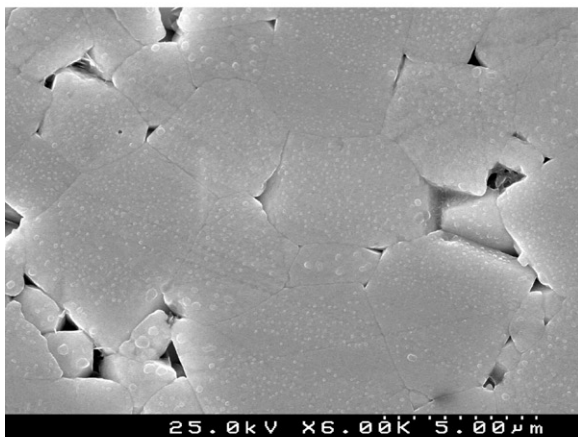
Fig. 2 depicts the elemental distribution obtained by SEM/EDS and corresponding energy dispersive spectra, revealing the presence of potassium and tantalum in KT ceramics

with the initial K/Ta ratio = 1.05, 1.02, and 1. Whereas a homogeneous distribution of both potassium and tantalum over the grains of KT ceramics with initial K/Ta ratio = 1.05 (Fig. 2a), 1.02 (Fig. 2b) is evident, some Ta-rich areas, which looks to have a higher density, are detectable in the ceramics with K/Ta = 1 (Fig. 2c). The semi-quantitative analysis of the energy dispersive spectrum recorded from this Ta-rich area (marked as spectrum 2 in Fig. 2c and d), yields Ta/K ratio of 1.5 that agrees well with the value of 1.8 for potassium-poor $K_6Ta_{10.8}O_{30}$ secondary phase, earlier detected by XRD. Regarding the other areas of KT ceramics with initial K/Ta ratio = 1, as well as all the studied areas of the ceramics with K/Ta = 1.02 and 1.05, the semi-quantitative analysis of their energy dispersive spectra yields Ta/K ratio close to 1.

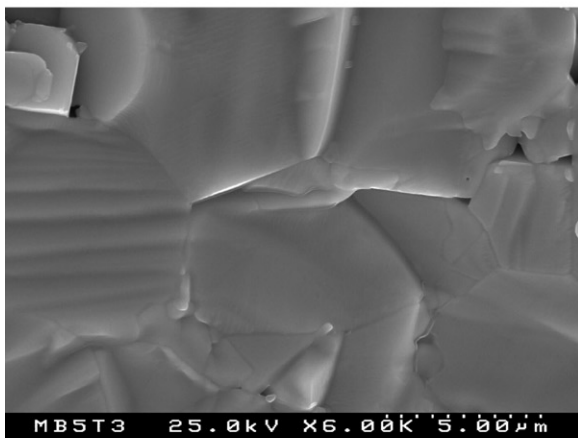
The SEM micrographs, shown in Fig. 3, reveal well defined porosity, not so well defined grain boundaries, and cubic-type grain shape for all KT ceramics under study. These features are in agreement with the density about 88%, measured by Archimedes' method and with the statement that melting of KT ceramics starts before the densification process.⁵ Moreover, Fig. 3 reveals that the grain size strongly increases with K/Ta



(a) K/Ta = 1



(b) K/Ta = 1.02



(c) K/Ta = 1.05

Fig. 3. SEM micrographs of KT ceramics with K/Ta=1 (a), 1.02 (b), and 1.05 (c).

ratio from the submicron range for K/Ta = 1 to the range of several microns for K/Ta > 1. The average grain size of 0.7 μm was determined for the ceramics with initial K/Ta ratio = 1, 4.9 μm for K/Ta = 1.02, and 6.5 μm for K/Ta = 1.05, as displayed in Table 1. It is worthwhile to mention that comparing our SEM micrograph for K/Ta = 1.05 with those obtained by Axelsson

et al. on equivalent ceramics conventionally sintered at 1340 $^{\circ}\text{C}$ for 1 h, it is evident that the grain size in our ceramics is larger. On the other hand, Chen et al. reported the submicron grain size for KT ceramics conventionally sintered at 1330 $^{\circ}\text{C}$ for 1 h and grain size of 1–8 μm for KT ceramics hot-pressed at 1310 $^{\circ}\text{C}$ for 1 h.⁵

In contrast to KT, the grain size of SrTiO₃ ceramics, which also possess an ABO₃ perovskite structure in which Sr occupies A site and Ti occupies B site, was found to increase strongly when Sr/Ti ratio is <1.⁷ According to the phase diagram between SrO and TiO₂, an eutectic liquid phase exists on the titania-rich side that promotes the grain growth during sintering. In the case of KTaO₃, a liquid phase appears for K/Ta >1,⁹ i.e., the grain boundaries become wet close the eutectic temperature,⁶ the grain boundary diffusion increases, and the grain growth is promoted by means of K₂O excess.

Radio-frequency dielectric permittivity and loss of KT ceramics, with initial K/Ta ratio = 1, 1.02, and 1.05 are presented in Fig. 4 as a function of the temperature. The temperature dependence of the dielectric permittivity (ϵ') at the frequencies of 0.1, 10, and 1000 kHz is shown in Fig. 4a. The steadily increase of $\epsilon'(T)$ and its levelling-off at high values as the temperature approaches 0 K, without any apparent anomaly for all the samples, are typical of quantum paraelectrics.⁴ No considerable frequency dispersion was found over the frequency range of 10²–10⁶ Hz. Furthermore, potassium excess raises the dielectric permittivity monotonously in the range of initial K/Ta ratio under study, in spite of the small difference between the low-temperature dielectric permittivity for K/Ta = 1.02 and K/Ta = 1.05. Such a variation in the permittivity cannot be predominantly influenced by porosity by two reasons. First, as shown in Table 1 the density variation for the studied ceramics is rather small. Second, the highest permittivity is observed for K/Ta = 1.05 ceramics with the medium density, while the lowest permittivity is found on K/Ta = 1 ceramics with the highest density (see Table 1). The dielectric permittivity of KT ceramics with initial K/Ta ratio of 1 is about 2300, which is close to that reported by Chen et al.⁵ but much smaller than that of KT single crystal.² Such decrease of permittivity can be explained by contributions of pores (low density), grain boundaries (small grain size) and secondary phases in the ceramics, which are less polarizable than crystalline grains of KT. All these features, including the presence of the secondary phase, can be addressed to ceramics prepared by Chen et al.⁵ Since the density and grain size of their ceramics are reported to be similar to that of our KT ceramics with initial K/Ta ratio of 1, the similarity in the dielectric permittivity suggests that ceramics prepared by Chen et al. were not monophasic. On the other hand, the dielectric permittivity of KT ceramics with initial K/Ta ratio of 1.05 reaches value about 4000, which is much higher than 1000 and 2000, reported by Chen et al.,⁵ is higher than 3100, as it was reported by Axelsson et al.,⁶ and is not much below 5000, which was reported for KT single crystal.² The larger value of the permittivity for ceramics with initial K/Ta = 1.05, as compared to that reported by Axelsson et al.,⁶ can be apparently explained by the larger grain size of KT ceramics obtained in

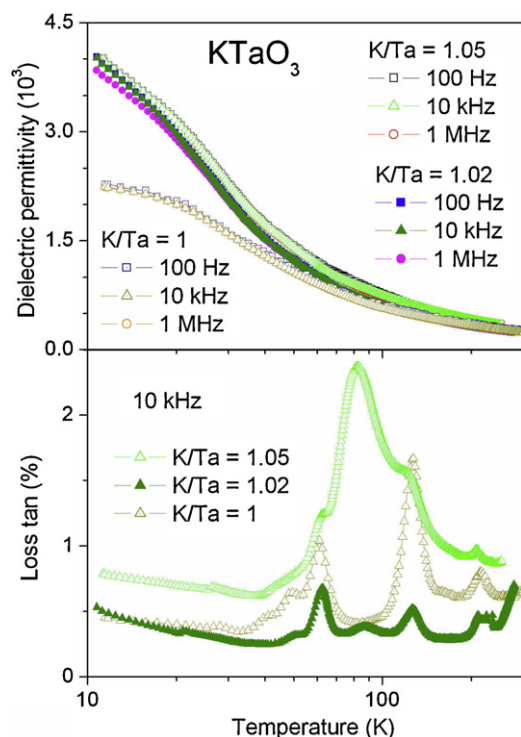


Fig. 4. Temperature dependence of the real part of the dielectric permittivity ϵ' (a) and of the dielectric loss $\tan \delta$ (b) of potassium tantalate ceramics with initial K/Ta ratio of 1, 1.02, and 1.05 at selected frequencies.

this work and hence smaller contribution of less polarizable grain boundaries.

Fig. 4b shows the temperature dependence of the dielectric loss ($\tan \delta$) at 10 kHz for KT ceramics with initial K/Ta ratio = 1, 1.02, and 1.05. For K/Ta ratio = 1, five peaks are clearly seen about 27, 49, 62, 127, and 214 K, probably related to formation of $K_6Ta_{10.8}O_{30}$ secondary phase. Similar peaks are observed for K/Ta ratio = 1.02, but with two differences: firstly, the intensity of the peaks becomes much smaller; secondly, another less intense peak emerges about 89 K. For K/Ta ratio = 1.05, the later peak, slightly shifted to 83 K, becomes dominant, while all other peaks decrease in intensity, mostly transforming into shoulders. Thus, potassium excess first decreases the dielectric loss down to 0.25%, reducing the peak intensities, but then strongly increases the loss up to 2.37%, inducing a strong peak close to 83 K.

It is well known that for quantum paraelectrics, $\epsilon'(T)$ can be described by Barrett's relation,¹⁰ which is based on the mean-field theory taking quantum fluctuations into account: $\epsilon'(T) = C/[(T_1/2)\coth(T_1/2T) - T_0] + \epsilon_1$. C stands for the Curie–Weiss constant, T_1 for the temperature of the crossover between classical and quantum behaviour, T_0 for the transition temperature at which the lattice instability would occur in the absence of quantum fluctuations, and ϵ_1 for the temperature independent component of permittivity. Fig. 5 shows $\epsilon'(T)$ measured at 10 kHz, along with the Barrett's law fitting curves for K/Ta = 1, 1.02, and 1.05. The fitting parameters are indicated in Table 1. The most significant feature is that C increases with increasing initial K/Ta ratio. The increase of C reflects the

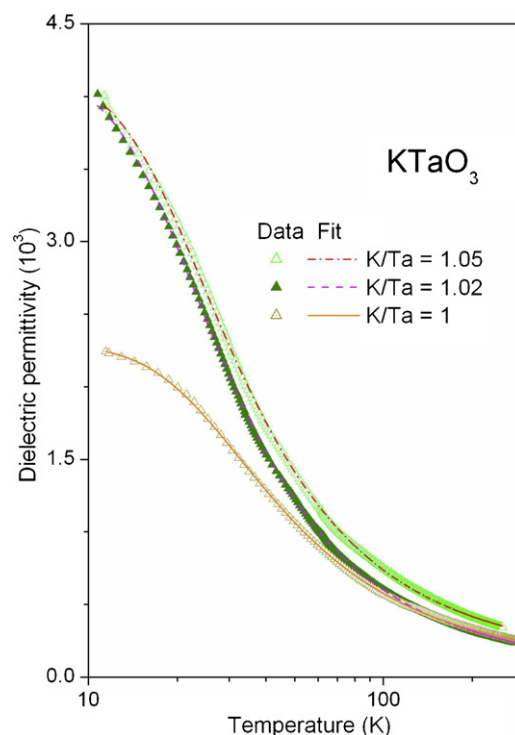


Fig. 5. Temperature dependence of the real part of the dielectric permittivity ϵ' of potassium tantalate ceramics with initial K/Ta ratio of 1, 1.02, and 1.05 and the fit of the Barrett relation to the experimental data.

increase of the $\epsilon'(T)$ amplitude. Such increase can be tentatively explained from two reasons. On one hand, the reduction and final disappearance of the less polarizable potassium-poor secondary phase with increasing K/Ta ratio, and on the second hand, the strong increase of the grain size and decrease of the grain boundary contribution to the dielectric permittivity for K/Ta > 1. Contrarily, no significant effect of K/Ta ratio is apparent on the T_0 and T_1 parameters. In $SrTiO_3$ ceramics with Sr/Ti ratio from 0.997 to 1.02, nonstoichiometry did not affect transition temperature T_0 , as well.⁷

4. Conclusions

The effect of initial K/Ta ratio (1–1.05) on the crystallographic structure, microstructure and dielectric response of $KTaO_3$ ceramics is reported. Initial excess of potassium is shown to be necessary to yield by solid state reaction process single-phase ceramics with lattice parameters close to that of KT single crystals. Moreover, potassium excess favours the grain growth in KT ceramics. Combination of the absence of secondary phases with increased grain size in KT ceramics with initial potassium excess of 5% yields an increase of the lowest temperature dielectric permittivity value up to ~ 4000 , the highest ever reported for KT ceramics. For K/Ta ratio = 1.02, the dielectric permittivity is not much lower than 4000, but the dielectric loss has the lowest amplitude. Contrarily, the highest value is reached for K/Ta = 1.05, mainly due to the strong peak emerging about 83 K. Furthermore, the variation of K/Ta ratio did not change the quantum-paraelectric nature of KT, though changes

in the temperature behaviour of the dielectric constant were evidenced by fitting the Barrett relation to the experimental data.

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