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Influence of point defects in $KTaO_3$ on low-temperature dielectric relaxation

Anna-Karin Axelsson [a], Matjaz Valant [a,b,*], Neil McN. Alford [a]

[a] *Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, UK*
[b] *Materials Research Laboratory, University of Nova Gorica, Vipavska 13, 5000 Nova Gorica, Slovenia*

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Abstract

Substituted $KTaO_3$ ceramics were synthesized, sintered and studied using low-temperature microwave dielectric analysis and Raman spectroscopy. Because of a fundamentally different nature of aliovalent Mn- and isovalent Na-substitution mechanisms, significant differences in processing and dielectric properties were identified. The properties were correlated to the defect structure of the substituted $KTaO_3$ lattices. Characteristics of the induced polar domains were clearly different for the two substitutional mechanisms, which further reflects in a significantly different dielectric behavior. Linear response of changes in the Raman spectra corresponds to evidence of the formation of symmetry-breaking regions.

Keywords: Defects; Dielectric properties; Ferroelectric properties; Tantalates; Polar domains

1. Introduction

$KTaO_3$ is an incipient ferroelectric and displays a continuous increase in the dielectric constant with decreasing temperature. $KTaO_3$ exhibits many technologically interesting properties. It can be used in optoelectronics for optical waveguides. In combination with low-loss superconductors it has been considered for applications in tunable microwave components and fatigue-free nonvolatile memories.[1] Additionally, it possesses a combination of a high permittivity and relatively low dielectric losses at room temperature, which makes it an attractive candidate for application in microwave devices.[2] It exhibits semiconductor properties with a band gap suitable for photocatalytic water splitting.[3] In many applications it is used in a form of powders and single crystals but ceramic elements are frequently required to reduce production and machining cost, increase design flexibility and functionality. Sintering of $KTaO_3$ powder is very difficult mainly due to the high covalent bonding within this crystal structure.[4,5] More effective sintering has been obtained with an aid of dopants.[6,7] However, the dopants can significantly change functional properties (e.g. optical and dielectric) and cannot be tolerated for particular applications. Especially sensitive to the presence of dopants are dielectric properties. The presence of additional polarization mechanisms can significantly alter the dielectric relaxation processes in such a material. Consequently, this can result in a significant increase in dielectric losses and a reduced technological value of the material.

One type of defect that occurs at aliovalent substitutions is dipoles, generated by e.g. a Columbic attraction of oppositely charged species. This type of random lattice disorders would cause a dielectric anomaly and pronounced relaxation when exposed to an electromagnetic field. Most commonly, this type of local ferroelectric phase transition is induced by different types of defect such as local symmetry-breaking defects (SB) or the soft non-symmetry-breaking (NSB) defects that increase the local ferroelectric transition temperature.[8] Raman spectroscopy and inelastic neutron scattering studies have revealed the effect of the oxygen vacancies on the ferroelectric soft mode in reduced $SrTiO_3$. Similar results have been obtained for $KTaO_3$.[9] In these cases, the oxygen vacancies act as very hard local NSB defects, which affect the local ferroelectric transition temperature.

In practice this may mean that for polycrystalline substituted $KTaO_3$ systems, the physics, which is governing the behavior of the single crystals, is changed. By solid state synthesis, deviation of the phonon fluctuations comes from a number of sources including grain boundaries, impurities, vacancies. Therefore, the dielectric loss, especially in low temperatures, is linked to

* Corresponding author at: University of Nova Gorica, Vipavska 13, 5000 Nova Gorica, Slovenia. Tel.: +386 53653502; fax: +386 53653527.
E-mail address: matjaz.valant@ung.si (M. Valant).

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mixing of the modes not observed in very high quality single crystals.[10] The information about the interaction between the low frequency modes can be obtained directly by Raman spectroscopy, far infrared spectroscopy and indirectly by dielectric measurements.

In the present contribution we will report on our investigations of these phenomena. We compare pure $KTaO_3$ with isovalently and aliovalently doped $KTaO_3$, in which point defect such as substitutional ions, off-centering and vacancies are present. Low-temperature dielectric measurements that were performed on these samples gave us a tool to associate these point defects to appearance of polarons and polar nano-domains. These were further correlated to the observed changes in the relaxation processes.

2. Experimental

Starting powders of K_2CO_3 (99.9% BDH AnalaR), Ta_2O_5 (99.995% Pi-Kem Ltd.) MnO_2 and Na_2CO_3 (both Alfa Aesar 99.9%) were carefully dried prior to stoichiometric mixing. The mixture was homogenised by dry ball milling using yttria-stabilized zirconia balls, pressed into pellets (13 mm stainless steel die, 100 MPa) and fired in a muffle furnace in an air atmosphere. The progress of the reaction was monitored by X-ray diffractometry (Philips X'pert Pro) Cu K_α radiation and high throughput detector (X'Celerator, Philips Analytical) equipped with diffracted beam monochromator. The fraction of the phases formed during the reaction was estimated from peak integrals on normalized X-ray scans. The processes occurring during heat treatment were evaluated with thermo-gravimetry (TG), differential thermal analysis (DTA) and evolved gas analysis (EGA) (Netzsch STA 449C) system coupled to a quadrupole mass spectrometer. The microstructures were examined using scanning electron microscope (JEOL 840A) and INCA 4.07 (Oxford Instruments) software.

The characteristics of sintering were examined using a dilatometer (Netzsch 402C). The pellets were then placed in a dilatometer and heated to a temperature of 1360 °C at a heating rate of 5 °C/min. Based on the obtained sintering curves the optimum sintering conditions were selected. Density was evaluated by measuring dimensions and mass of the sintered samples.

Microwave measurements were carried out on a Vector Network Analyser (Agilent HP8720C) with 1 Hz resolution using a silver coated high-purity copper cavity. The $TE_{01\delta}$ fundamental mode was used for measurement in transmission mode. This resonance mode was used due to its high electric energy filling factor. The measurements were performed on sintered pucks with approximately 10.7 mm in diameter and 2.5–3.5 mm in height. The corresponding resonant frequency at room temperature was always between 2.5 and 3.5 GHz and varied as a consequence of the temperature dependence of the relative permittivity. To reduce conduction losses the samples were placed on a low-loss small diameter quartz post. The cavity assembly was placed on a cold-head of a two-stage Gifford-McMahon cryo-cooler (Cryophysics, Abingdon, U.K.), which operates over a temperature range 10–320 K. All measurements started with initial 30 min temperature stabilization at 15 K, followed by a ramp up of 1 K/min. Resonant frequency, insertion loss and loaded Q were measured at small temperature intervals. In-house written software[c] was used for an accurate evaluation of unloaded Q and relative permittivity based on radial mode matching technique.[11]

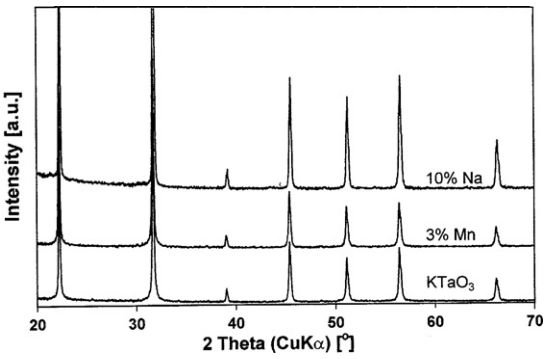

Fig. 1. XRD patterns of $KTaO_3$, $K_{0.94}Mn_{0.03}TaO_3$ and $K_{0.90}Na_{0.10}TaO_3$ powders calcined at 950 °C for 5 h.

Raman spectra from the sintered optical polished pucks were recorded using a MicroRaman Spectrometer (Renishaw System 2000) with a 514 nm line of an Ar^+ laser as exciting radiation with nominally <4 mW power incident on the sample surface. The laser line was focused onto the sample by a cylindrical microscope lens of 50× magnification with a spot diameter of 2 ± 1 μm.

3. Results

Three different $KTaO_3$-based materials were synthesized for this study: pure $KTaO_3$, Na- and Mn-substituted $KTaO_3$. *K* ions were isovalently substituted by *Na* ions according to the formula $(K_{1-x}Na_x)TaO_3$ or aliovalently by *Mn* ions according to $(K_{1-2x}Mn_x\square_x)TaO_3$, where □ represents vacancies on A-site of the perovskites. The incorporation of Mn^{2+} has been a subject of many detailed investigation. Although early investigations suggested on partial Mn^{2+} incorporation onto B-site and creation of Mn^{2+}–V_O centers[12] the new results have confirmed the substitution of potassium without formation of Mn^{2+}–V_O centers, i.e. the stoichiometry that we adopted in this paper. It has been established that electronic/orbital interactions in Mn-doped $KTaO_3$ cause the dopant Mn^{2+} ions to off-center along the [1 0 0] direction from the potassium Vykoff *1b* position for as much as 0.9 Å.[13–15] This means that the Mn^{2+} ion occupies a position somewhat in the middle of the adjacent oxygen planes and can be regarded as a sort of Frenkel defect.[7]

We studied the sample with 10% Na-substitution, for which the synthesis yielded a single-phase reaction product (Fig. 1). In the case of *Mn* we could not used the sample with 10% substitution because the substitution limit is low, ∼4%. We performed the studies on $(K_{0.98}Mn_{0.01})TaO_3$ and $(K_{0.94}Mn_{0.03})TaO_3$, for which a single-phase material was obtained after calcination at 950 °C/5 h. For a direct comparison of the dielectric relaxation

[c] The software was written by Jonathan Breeze, Department of Materials, Imperial College London.