

Dielectric properties and microstructure of $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$

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Abstract

The 1 MHz dielectric properties of $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ compounds were reported recently. Both compounds have a common characteristic dependence of the temperature coefficient of dielectric constant (TCK) and dielectric constant (ϵ_r) on sintering temperature. For both compounds a TCK < 5 ppm/deg can be achieved by selecting the right processing conditions. It was suggested that an order–disorder transition among the B-site ions in these perovskite-based compounds plays a major role in the determination of TCK. Since X-ray powder diffraction does not appear to be a good technique to detect the structural changes, transmission electron microscopy (TEM) was applied in this work. It was found that different types of ordering between (111) planes, namely 1:1, 1:2 and 1:3, as well as distortions by tilting of octahedra, are involved in the formation of a microstructural state at an ambient temperature. The compounds in the as-sintered conditions both have a microdomain structure but with a different type of ordering, 1:3 for $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ and 1:2 for $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$. Both compounds have a tilting phase transition from the distorted Pm3m to distorted Pnma (with the $a^-b^+a^-$ tilt of octahedra) structures at temperatures that coincide with the observed kinks at T_{A1} and T_{A2} in the TCK(T_S) and $K(T_S)$ curves. © 2001 Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

Complex perovskites (A,A')(B,B')O₃ are an important structural base for microwave dielectrics with important properties such as high dielectric permittivity K , low dielectric losses (high quality factor Q) and near-zero temperature coefficient of resonant frequencies TCK.¹ Among the best microwave dielectric materials are Ba- and Sr-based perovskites, e.g., $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ and $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$.² Recently, a few publications have reported a good combination of the aforementioned dielectric properties for Ca-based complex perovskites.^{3–6} In particular, Cava et al.⁵ reported a study of $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ compositions, shown by X-ray study to be a perovskite-based structure with an A-site occupied by Ca and a B-site having an average $\text{Ca}_{1/4}\text{Nb}_{1/2}\text{Ti}_{1/4}$ and $\text{Ca}_{1/4}\text{Ta}_{1/2}\text{Ti}_{1/4}$ occu-

pancy ($\text{Ca}(\text{Ca}_{1/4}\text{Nb}_{1/2}\text{Ti}_{1/4})\text{O}_3$ and $\text{Ca}(\text{Ca}_{1/4}\text{Ta}_{1/2}\text{Ti}_{1/4})\text{O}_3$ stoichiometries). Dielectric measurements in the MHz frequency range demonstrated reasonably high K , Q on the order of 5000 and TCK varying between negative and positive values. The study found a systematic effect of processing conditions on the dielectric properties, in particular on the dielectric constant K and its temperature dependence TCK. The dependencies on sintering temperature T_S are shown schematically in Fig. 1, where a change in the TCK(T_S) slope occurs around $T_{A1} = 1500$ °C for $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ and $T_{A2} = 1550$ °C for $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$. The drastic changes in TCK correlate with the anomalous changes in the dielectric constant $K(T_S)$. Cava et al. suggested that some order-disorder transition among the B-site ions should play an important role in the observed behavior. Here we report on the structural characterization of the $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ compounds sintered at temperatures ranging from 1600 to 1425 °C. The goal of the study is to verify and detail the suggested ordering, and to understand the observed correlation between processing temperature, local structure and dielectric properties.

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2. Experimental methods

The $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ specimens were synthesized from high purity CaCO_3 , Nb_2O_5 , Ta_2O_5 and TiO_2 powders. Batches were weighed out at the appropriate stoichiometric ratios and ground in an automatic agate mortar and pestle for 30 min. The mixed powders were fired in air at 1200°C for 16 h. The reacted powders were ball milled, pressed (without binder, to 4000 psi) and sintered. Pellets were sintered for 2 h on a dense alumina on powder of their own composition in air at temperatures between 1400 and 1600°C (with 25°C interval) and furnace cooled.

The TEM specimens were prepared from dense pellets by conventional polishing, dimpling and ion thinning. The specimens were examined using a Phillips 430 TEM¹ microscope operated at 200 kV. Structural imaging was performed with a Jeol 3010-UHR microscope operated at 300 kV.

3. Results

According to powder X-ray diffraction,⁵ all sintered $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ specimens appear to be a single-phase material. However, according to back-scattered SEM, slight compositional variations were also detected, especially for lower sintering temperatures. The sintered ceramics are quite porous, and the amount of porosity diminishes as the temperature of sintering increases.

3.1. $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ specimens

According to the TEM microstructural observations, specimens sintered at and above 1525°C consist of grains having a substructure of fine-scale twins (Fig. 2). The specimens sintered at and below 1500°C in general do not have the twin substructure. For both types of specimens, selected area electron diffraction (SAED) patterns have major reflections yielding the Pnma space group of CaTiO_3 ⁷ (Fig. 3). The observations suggest that there is a phase transition at a temperature of approximately 1500°C from the cubic $\text{Pm}\bar{3}\text{m}$ phase (disordered undistorted perovskite) to the orthorhombic Pnma phase (six twin-related variants of the disordered perovskite with $a^-b^+a^-$ -tilted octahedra⁷). Note that the twinning transition coincides with the temperature T_{A1} where the anomalous dielectric behavior occurs (Fig. 1).

Careful examination of the $[110]_c$ -type $[001]_O$ (c —cubic perovskite, a_p ; O —orthorhombic Pnma , $\cdot 2a_p \times 2a_p \times 2a_p$) SAED patterns (Fig. 3) reveals the following additional diffraction features: (a) diffuse scattering with a maxima

at $\mathbf{k} = 1/4(111)_c^* = 1/4(220)_O^*$ and streaking along $\langle 110 \rangle_O^*$, observed for *all* specimens; (b) 100_O and 110_O sharp reflections, observed only for the specimens sintered below 1500°C (Fig. 3b). The same diffraction features were observed for binary $\text{Ca}_4\text{Nb}_2\text{O}_9$ polymorphs studied by Levin et al.⁸ It is plausible to assume that $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ can be considered as a solid solution

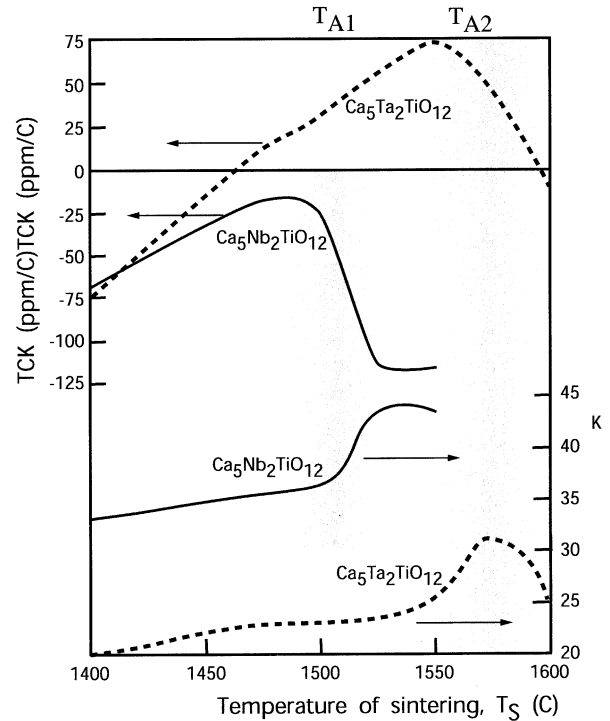


Fig. 1. A schematic diagram showing dependence of temperature coefficient of dielectric constant (TCK) and dielectric constant (K) on sintering temperature for $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ compounds. The diagram is based on the results published in Ref. [5]. The properties were measured with HP 4192A impedance meter at 1 MHz. TCK was measured at temperatures between 0 and 100°C .

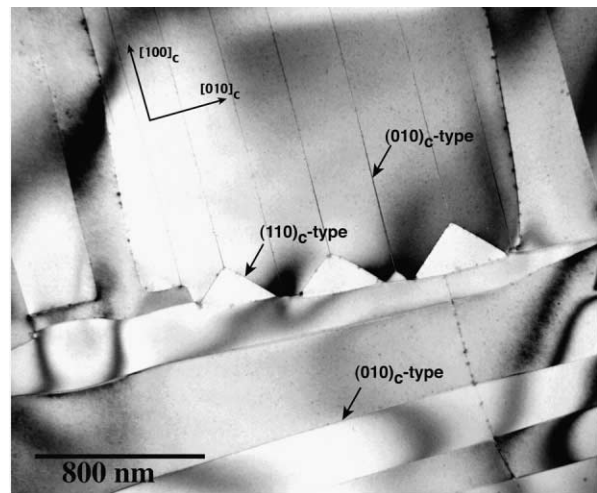


Fig. 2. Bright field TEM images of the $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ specimen sintered at 1525°C showing a microstructure of twin-related variants of the orthorhombic Pnma phase.

¹ The use of brand or trade names does not imply endorsement of the product by NIST.

extension of the binary phases, with incorporation of Ti on B-sites. Therefore, the 100_{O} and 110_{O} reflections suggest the presence of 1:1 ordering between B-site cations (FCC-type with $2a_{\text{p}} \times 2a_{\text{p}} \times 2a_{\text{p}}$ lattice). The 1:1 ordering in combination with the $a^{-}b^{+}a^{-}$ tilt of octahedra (Pnma) results in a monoclinic (pseudo-orthorhombic) $\text{P}12_1/\text{n}1$ ($2a_{\text{p}} \times 2a_{\text{p}} \times 2a_{\text{p}}$, $\beta \cong 90^\circ$ lattice) structure (labeled HTP_2 in⁸ and known in a literature as *elpasolite*).⁹ Hence, sintering of $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ at temperatures below 1500°C results in the formation of well-developed long-range 1:1 order, whereas post-sintering cooling from the $\text{Pm}\bar{3}\text{m}$ phase field results in a fast tilting transition, but only in a weakly developed 1:1 ordering.

$1/4\langle 111 \rangle_{\text{c}}^*$ diffuse scattering was interpreted as an evidence of the 1:3 ordering between $\{220\}_{\text{O}} = (111)_{\text{c}}$ -type planes of the pseudo-cubic structures, with the $(220)_{\text{O}}$ planes of B-sites (pseudo-hexagonal) different in occupancy but repeating every fifth layer (e.g. $\text{Ca}/(\text{Nb}_2\text{Ti})_{1/3}/(\text{Nb}_2\text{Ti})_{1/3}/(\text{Nb}_2\text{Ti})_{1/3}/\text{Ca}$ but not necessarily with an equivalent occupancy for the 2,3 and 4 planes). Such ordering, in combination with the tilting, will result in a triclinic structure (labeled in⁸ as $\text{LT}_{1/4}$ phase, with a $6a_{\text{p}} \times 2a_{\text{p}} \times 2 \cdot 2a_{\text{p}}$, $\beta \cong 90^\circ$ lattice). The diffuseness of the $\mathbf{k} = 1/4\langle 111 \rangle_{\text{c}}^*$ scattering suggests that the formation of fine 1:3 ordered domains occurred upon cooling. The domains are shown on a high-resolution image (Fig. 4). The image shows a high-density of sphere-like fine domains (5–10 nm in size). Two structural variants corresponding to two ordering \mathbf{k} -vectors, $1/4[111]_{\text{c}}^*$ and

$1/4[\bar{1}\bar{1}1]_{\text{c}}^*$, can be recognized by the intensity of fringes. It is difficult to see if there is a residual (matrix) phase between the domains, and therefore congruent ordering is possible.

In order to verify the stability of the 1:3 ordered phase, additional heat treatments were performed. Annealing at temperatures between 1300 and 1100°C did not produce a noticeable effect on the microdomain structure or state of ordering of $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$. However, a dramatic change occurred after annealing at 1000°C : the $1/4\langle 111 \rangle_{\text{c}}^*$ diffuse scattering of the as-sintered specimen was replaced by $1/3\langle 111 \rangle_{\text{c}}^*$ scattering (Fig. 5a), and a two-phase microstructure with lens-like precipitates was formed. Dark field imaging with $1/3\langle 111 \rangle_{\text{c}}^*$ reflections (Fig. 5b), demonstrates the formation of two intimately mixed variants of the $1/3\langle 111 \rangle_{\text{c}}^*$ -ordered precipitates. Both SAED patterns and dark field images suggest the presence of a small volume fraction of a matrix phase. The phase is coherent with the precipitates and apparently has the Pnma structure. The transformation demonstrates the metastability of the 1:3 ordered phase and the existence of a low temperature two-phase field.

The $1/3\langle 111 \rangle_{\text{c}}^*$ ordering reflections, the type of extinction, and the presence of a twin structure suggest a structure where 1:2-ordering is combined with the tilting of the Pnma structure. Such a phase has a monoclinic $\text{P}2_1/\text{c}$ symmetry ($6a_{\text{p}} \times 2a_{\text{p}} \times 3 \cdot 2a_{\text{p}}$, $\beta \cong 125^\circ$ lattice) and is similar to the low temperature polymorph ($\text{LT}_{1/6}$) of the

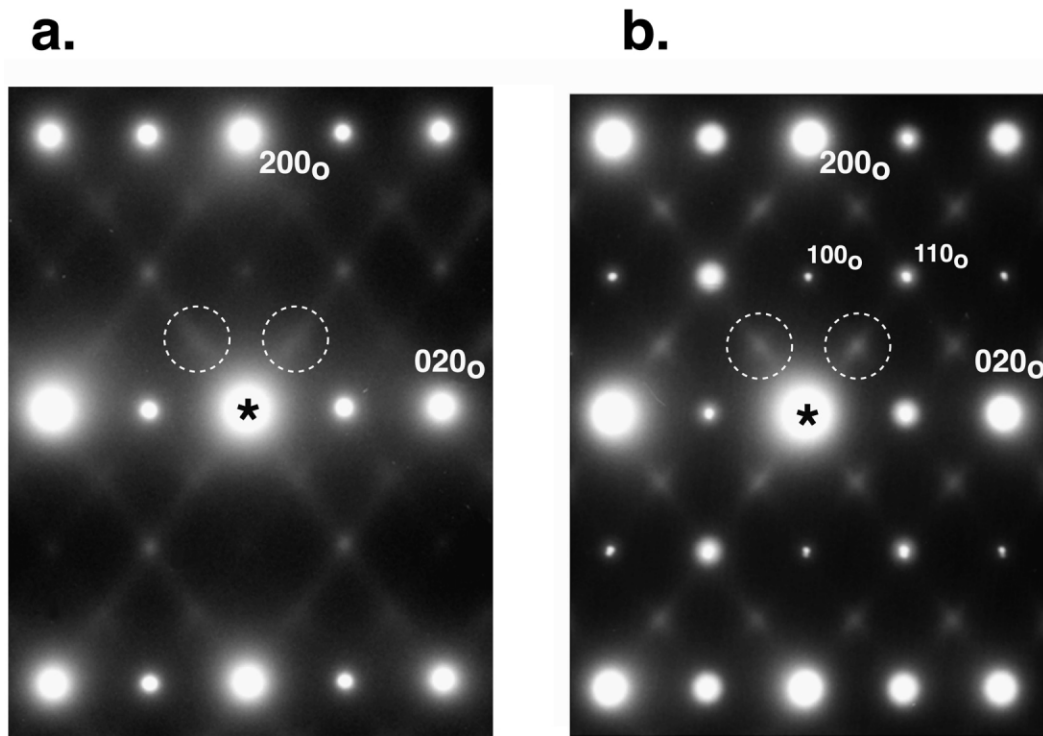


Fig. 3. $[110]_{\text{c}}$ -Type $[001]_{\text{O}}$ SAED patterns taken from the $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ specimens sintered at (a) 1525°C (a) and (b) 1475°C . Circles on the photographs indicate the locations of $1/4[111]_{\text{c}}^*$ diffuse scattering. 100_{O} and 110_{O} sharp reflections are observed only on (b).

binary $\text{Ca}_4\text{Nb}_2\text{O}_9 = \text{Ca}(\text{Ca}_{1/3}\text{Nb}_{1/3}\text{Nb}_{1/3})\text{O}_3$ phase.¹⁰ More detailed study on the phase equilibria in the $\text{Ca}_4\text{Nb}_2\text{O}_9$ – CaTiO_3 system is presented elsewhere.¹²

3.2. $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ specimens

Similar to $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$, there is a twinning transition from the disordered $\text{Pm}\bar{3}\text{m}$ perovskite to the orthor-

hombic Pnma structure in $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$. Observation of a twin-like structure (similar to that shown in Fig. 2) only for specimens sintered above 1550 °C identifies the transition temperature. The transition for $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ (around 1550 °C) coincides with T_{A2} where changes in slope of the $\text{TCK}(T_s)$ and $K(T_s)$ curves occurs (Fig. 1).

Fig. 6 shows a series of $[001]_O$ SAED patterns taken for specimens sintered at three different temperatures.

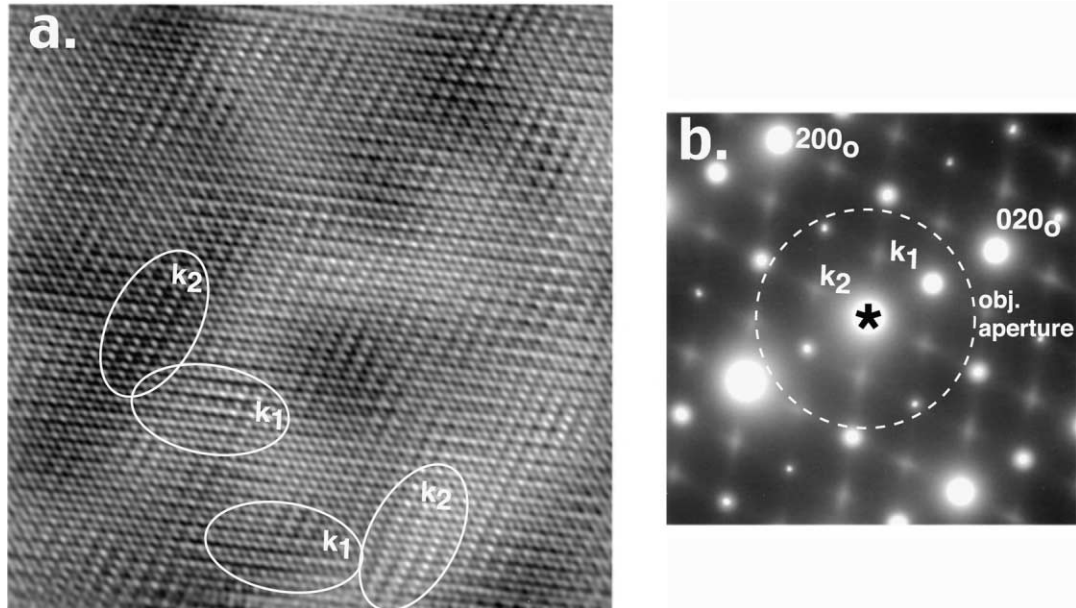


Fig. 4. $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ specimen sintered at 1500°C. (a) Two variants of the $1/4[111]^*$ ordered domains, as observed by high-resolution imaging. Selected nano-domains (two structural variants) of the 1:4 ordered phase are emphasized by encircling. (b) Corresponding $[001]_O$ SAD pattern.

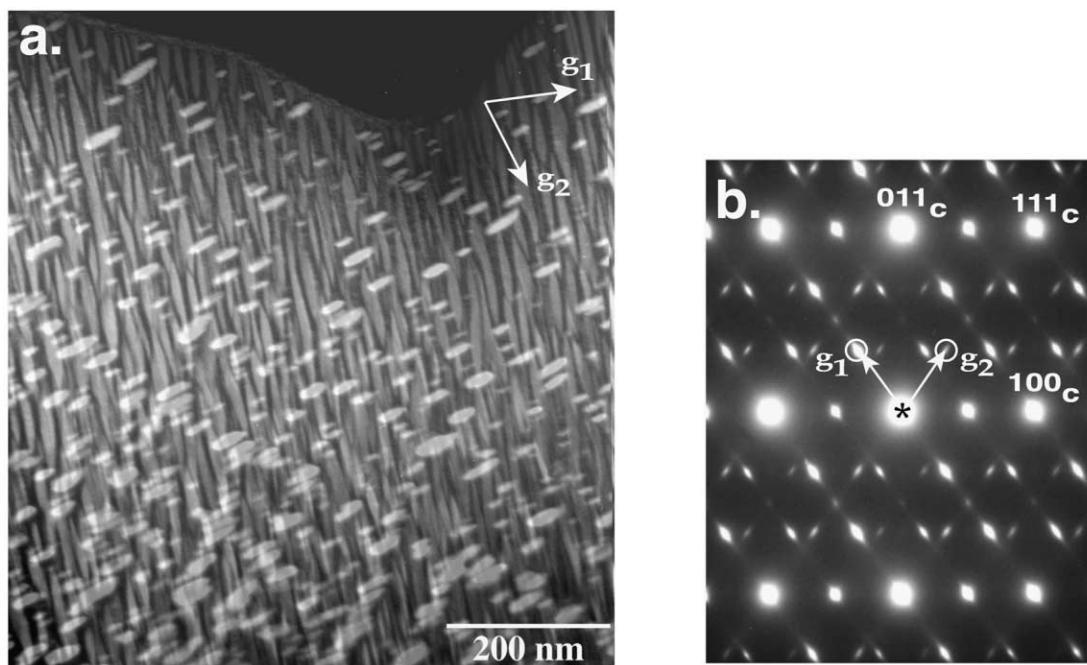


Fig. 5. (a) $[001]_O$ SAD pattern and (b) dark field image of lens-like precipitates obtained for the $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ specimen sintered at 1550 °C and subsequently annealed at 1000 °C for 100 h. Two variants of the precipitates were imaged separately, at a near-two-beam condition, using $1/3[111]^*_C$ and $1/3[-111]^*_C$ reflection. The dark field images were aligned and overlapped using Adobe® Photoshop technique of a layer transparency control.

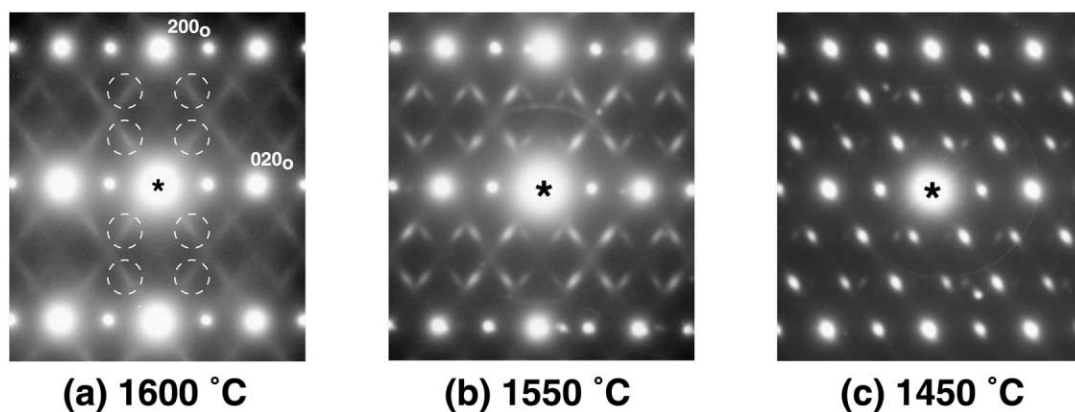


Fig. 6. A series of $[001]_O$ SAD patterns taken from the $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ specimens sintered (a) 1600 °C, (b) 1500 °C and (c) 1450 °C. In (a) the $1/3(220)^*_O$ positions are encircled.

In addition to the fundamental reflections of the Pnma structure, the following diffraction features are observed:

- (a) specimen sintered at 1600 °C: *diffuse streaking* along both $\langle 110 \rangle^*_O = \langle 111 \rangle^*_C$ reciprocal directions;
- (b) specimen sintered at 1500 °C: *diffuse reflections* at $\mathbf{k}_1 = 1/3[220]^*_O$ and $\mathbf{k}_2 = 1/3[2\bar{2}0]^*_O$, each elongated in the $\langle 110 \rangle^*_O$ direction;
- (c) specimen sintered at 1450 °C: *sharp reflections* at $\mathbf{k}_1 = 1/3[2\bar{2}0]^*_O$ (only one variant).

Dark field imaging using an objective aperture positioned at $1/3[220]^*_O$ showed that the ordered regions are extremely small for 1600 °C (few nm's), but develop into elongated domains at lower sintering temperatures. The dark field image in Fig. 7 shows such domains for the specimen sintered at 1450 °C (a single ordered variant). Dark layers between the domains suggest the presence of a coherent matrix, probably of the Pnma structure. Similar microstructure was obtained after post-sintering annealing (e.g. the 1550 °C sintered specimen annealed

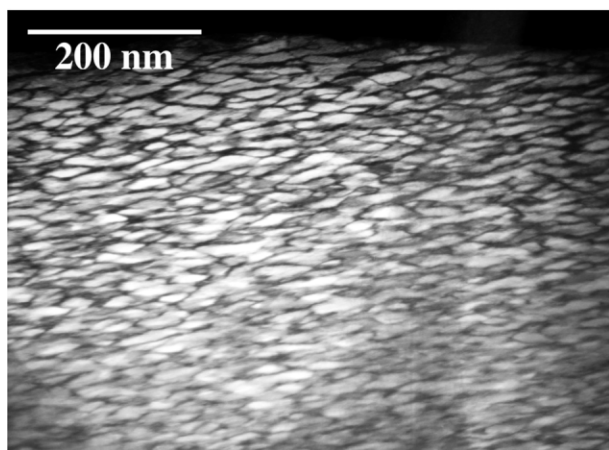


Fig. 7. A dark field image showing lens-like domains (a single variant) of the 1:2 ordered phase observed for the $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ specimen sintered at 1450 °C.

at 1300 °C for 5 h). These results demonstrate the existence of a two-phase field between the $1/3[220]^*_O$ -ordered phase and the Pnma structure at temperatures below 1300 °C (and possibly as high as 1450 °C). Diffraction analysis suggests that the $1/3[220]^*_O$ reflections are a result of the 1:2 ordering between $\{220\}_O = (111)_C$ -type planes of B-sites. Therefore, the ordered phase is similar to the monoclinic $\text{P}2_1/c$ ($\text{LT}_{1/6}$) variant of either $\text{Ca}_4\text{Nb}_2\text{O}_9$ or low-temperature $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$.

4. Discussion and conclusions

The results of our TEM study have shown that in spite of expected similarities between $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$, there are significant differences between the compounds in the as-sintered state. First, the similarities. Both compounds have a tilting phase transition from disordered $\text{Pm}\bar{3}m$ to distorted Pnma (with the $a^-b^+a^-$ tilt of octahedra) structures—at 1500 °C for $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ and 1550 °C for $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$. These temperatures coincide with the observed kinks at T_{A1} and T_{A2} in the $\text{TCK}(T_S)$ and $\text{K}(T_S)$ curves. Therefore, a framework of tilted octahedra (common for *all* as-sintered compounds) forms by two different processes: (a) a *martensitic-like transition* with the formation of domains during post-sintering cooling for the specimens sintered above T_{A1}/T_{A2} ; and (b) the *direct formation* of the structure by grain growth and recrystallization for sintering below T_{A1}/T_{A2} . Because the later process is expected to have a more equilibrated structure, the degree of octahedral distortions/tilt might be closer to equilibrium values for the specimens sintered below the tilting transition temperature. The equilibrium tilt increases with decreasing temperature for CaTiO_3 .⁷

The structures of $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ and $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ at temperatures below T_{A1}/T_{A2} are different—the disordered Pnma structure is found for $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$, and the 1:1 ordered Pnma (monoclinic $\text{P}2_1/c = \text{P}12_1/n1$)

structure is found for $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$. Because of kinetic reasons, the 1:1 ordering is only weakly developed during continuous cooling for $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ sintered at $T > 1500^\circ\text{C}$.

The final microstructural state of the as-sintered compounds is established during continuous cooling from the temperature of sintering by the low-temperature ordering transformation. Because of a limited time scale for diffusion, the ordering results in the formation of nano-domains. For $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$, the ordering forms a metastable 1:3 ordered triclinic structure. This structure, for kinetic/metastable equilibrium reasons not yet understood is preferable to the stable 1:2 ordered monoclinic phase. Formation of the phase is justified by the existence of a high-temperature binary Ca–Nb–O phase with apparently the same structure.¹¹ In the case of $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$, the low-temperature transition results in the formation of the 1:2 ordered monoclinic phase, apparently having the same structure as the $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ phase.

At this point we can only speculate about the effect of local structure on the dielectric properties. Detailed correlations between atomic structure and dielectric properties require precise information on the position of atoms, bond distances and atomic environments. Such information is not available from the TEM data. Moreover, considering the nano-domain nature of the sintered materials as a result of the described phase transitions in the course of cooling, it will probably be impossible to refine the as-sintered structures using standard neutron or X-ray powder diffraction techniques.

Nevertheless, we would like to make a few points concerning the effect of the observed structural variations on the measured dielectric properties. The gradual increase in $K(T_S)$ for both compounds sintered at temperatures between 1400 and 1500 °C is believed to be related to the decrease in porosity with increasing sintering temperature (according to the two-phase mixture model, pores being a secondary phase). In addition, the tilt of octahedra cannot reach the equilibrium value for the $T_S > T_{A1}/T_{A2}$ specimens, and therefore producing a lower density of polarization and lower K . The dramatic changes in dielectric properties for materials sintered at temperatures above 1500 °C are clearly associated with the formation of the twin structure for both materials.

Comparison of the dielectric properties of the two compounds and their type of ordering leads us to the conclusion that 1:2 ordering of $\text{Ca}_5\text{Ta}_2\text{TiO}_{12}$ results in higher TCK(T_S) and lower $K(T_S)$, as compared to the 1:1 + 1:3 ordering of $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$. Such an effect of ordering was recently demonstrated for the $\text{Ca}(\text{Ca}_{1/3}\text{Nb}_{2/3})\text{O}_3$ polymorphs (having similar to the studied here structures)¹⁴ and the $(\text{Sr}_{1-x}\text{Ba}_x)$

$(\text{Sr}_{1/3+y}\text{Ta}_{2/3-y})\text{O}_3$ system.^{13,15} For example, for the 1:2 ordered $\text{Ca}(\text{Ca}_{1/3}\text{Nb}_{2/3})\text{O}_3$ TCK is positive (+60 ppm/°C), while for the 1:1 and 1:3—negative (−4 and −7 60 ppm/°C, respectively). The effect was explained in¹⁴ by the more distorted coordination environment of Nb^{5+} for the 1:2 ordering.

The extreme chemical and microstructural complexity of the system, however, indicate that further analysis and characterization would be necessary to unambiguously associate the chemical and microstructural features with the dielectric properties, a correlation which has to date been made with very few members of this complex class of materials.

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