



Short communication

A novel self-composite property-tunable LaTiNbO₆ microwave dielectric ceramic

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ABSTRACT

A novel self-composite LaTiNbO₆ microwave dielectric ceramic was fabricated via a solid-state reaction method together with an annealing process. A monoclinic LaTiNbO₆ after a conventional sintering was found to gradually transform into an orthorhombic counterpart with prolonging annealing time. Microwave dielectric properties of ceramics can be easily tailored by changing the relative content of two coexisting phases with complementary performances. A thermal-stable dielectric ceramic ($\epsilon_r = 30.2$, $Q \times f = \text{GHz}$) was yielded after annealing at 1100 °C for 1 h. The concept of the self composite might provide an innovative and simple way to develop property-tunable microwave dielectric ceramics.

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1. Introduction

High dielectric permittivity (ϵ_r), high quality factor ($Q \times f$) (low loss) and particularly near-zero temperature coefficient of resonant frequency (τ_f) are fundamental material parameters for dielectric ceramics applied for microwave dielectric resonators in modern communication systems. Unfortunately, high $Q \times f$ and near-zero τ_f are usually difficult to be satisfied simultaneously in a single undoped dielectric compound. Forming a solid solution or a two-phase composite using two compounds with an opposite-sign τ_f used to be an effective approach for achieving the goal of the temperature compensation [1–5]. However, undesired secondary phases and inhomogeneous microstructure might lead to the deterioration in electrical performances because of the chemical reaction of different compositions or phases [1–3].

ReTiNbO₆ (Re: rare-earth ions) ceramics have attracted a lot of attention due to their excellent microwave dielectric properties. Particularly, they exhibit interesting structural features probably as a result of the particularity of rare earth elements [6–8]. These compounds with Re = La–Eu adopt an aeschynite-type orthorhombic structure (*Pnma*) and ones with Re = Gd–Lu own a euxenite-type orthorhombic structure (*Pcan*). The former usually exhibits a positive τ_f and a high ϵ_r , whereas the latter presents a negative τ_f and a relatively low ϵ_r . However, the temperature stability of

resonance frequency can be easily adjusted by forming [Re_{1–x}Re'_x] TiNbO₆ (Re = Pr, Nd, Sm; Re' = Gd, Dy, Y) solid solutions, in which end-member compounds have opposite-sign τ_f values [7,8]. Among these ReTiNbO₆ compounds, LaTiNbO₆ belongs to a special one, and generally manifests a monoclinic (M) structure at room temperature with good microwave dielectric properties of $\epsilon_r = 22.3$, $Q \times f = 49,867 \text{ GHz}$, $\tau_f = -55 \text{ ppm/}^\circ\text{C}$ in the measuring frequency range of 3–10 GHz [9]. Moreover, an orthorhombic (O) to M polymorphic phase transition was reported in LaTiNbO₆ as temperature is over 1100 °C, which is far below its densification temperature ($\sim 1300^\circ\text{C}$) [10,11]. High-temperature M phase can be maintained stably after a conventional sintering. To the best of our knowledge, a pure O-phase LaTiNbO₆ ceramic and its microwave dielectric properties have been not yet reported so far.

In current work, a new technique approach to avoiding such problems was named 'self composite' by achieving the coexistence of two phases with different structures (essentially complementary performances) in a well-sintered LaTiNbO₆ ceramic matrix via a heat treatment. An O phase was induced thermally from the initial M phase through a prescribed annealing process. The stable coexistence of O and M phases in a dense ceramic becomes a structural fundament for property-tunable microwave dielectric ceramics. The relationship between structures and properties and the mechanism of the grain refinement as a result of the phase transition were explored and analyzed in depth.

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2. Experimental

LaTiNbO₆ ceramics were prepared by a conventional solid-state reaction process. High-purity (>99%) La₂O₃, Nb₂O₅ (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) and TiO₂ (Xilong Chemicals, Guangdong, China) powders were used as the starting materials. The raw powders of stoichiometric proportions were weighed and then ball milled using zirconia balls in ethanol medium for 4 h. The resultant slurry was then dried and calcined at 1250 °C for 4 h, followed by a second grinding process for 6 h. The reground powders were mixed with 5 wt% PVA binders, and then pressed into cylinders with 10 mm in diameter and 5–6 mm in thickness under a uniaxial pressure of 200 MPa. Sintering of these pellets was optimized in the temperatures range of 1300–1400 °C for 4 h. Subsequently, a batch of LaTiNbO₆ ceramics sintered at 1325 °C (abbreviated as A0) were used for the following annealing treatment at 1100 °C for 0.5–8 h at a cooling rate of 1 °C/min (abbreviated as A0.5–A8).

The phase structure of the sintered ceramics was identified by an X-ray diffractometer (XRD; D/Max2500V, Rigaku, Tokyo, Japan) using CuK α radiation. The structural parameters were obtained from the Rietveld refinement of the XRD data using the GSAS-EXPGUI program [12,13]. The theoretical density of different samples was carefully calculated using the above-refined parameters using the following equation: $D = (W_M + W_O) / (W_M/D_M + W_O/D_O)$, where W_M and W_O are the weight percentage of M and O phase with their respective theoretical densities D_M and D_O . Bulk

densities of the sintered ceramics were measured using the Archimedes method. The microstructure of the sintered samples was observed using a scanning electron microscope (SEM; JSM-6490LV, JEOL, Tokyo, Japan). The SEM photos were made directly on the natural surface of sample disks after sintering and then annealing in order to in-situ identify the evolution of grain morphology. No mechanical polishing was involved to exclude other possibilities for microcracks. Microwave dielectric properties were measured between 4 and 10 GHz by the Hakki-Coleman method and the TE_{01 δ} -shield cavity method with a network analyzer (N5230C; Agilent, Palo Alto, CA) [14]. The τ_f value of the samples was measured in the temperature range from 20 °C to 80 °C.

3. Results and discussion

As can be seen from the XRD patterns in Fig. 1(a), a well-sintered LaTiNbO₆ ceramic sample A0 crystallized in a single M phase with a space group of *C12/c1* and its diffraction peaks could be well indexed to the standard pattern (JCPDS# 15-0872). After the sample was annealed at 1100 °C for 0.5 h, the diffraction peaks corresponding to an O phase could also be observed besides the diffraction peaks of the initial M phase, indicating the transition of part of the M phase into the O phase during annealing. The diffraction peak intensity of the O phase was found to increase with prolonging annealing time until the peaks of the M phase faded away in A4. It can be seen that the diffraction pattern of the A4

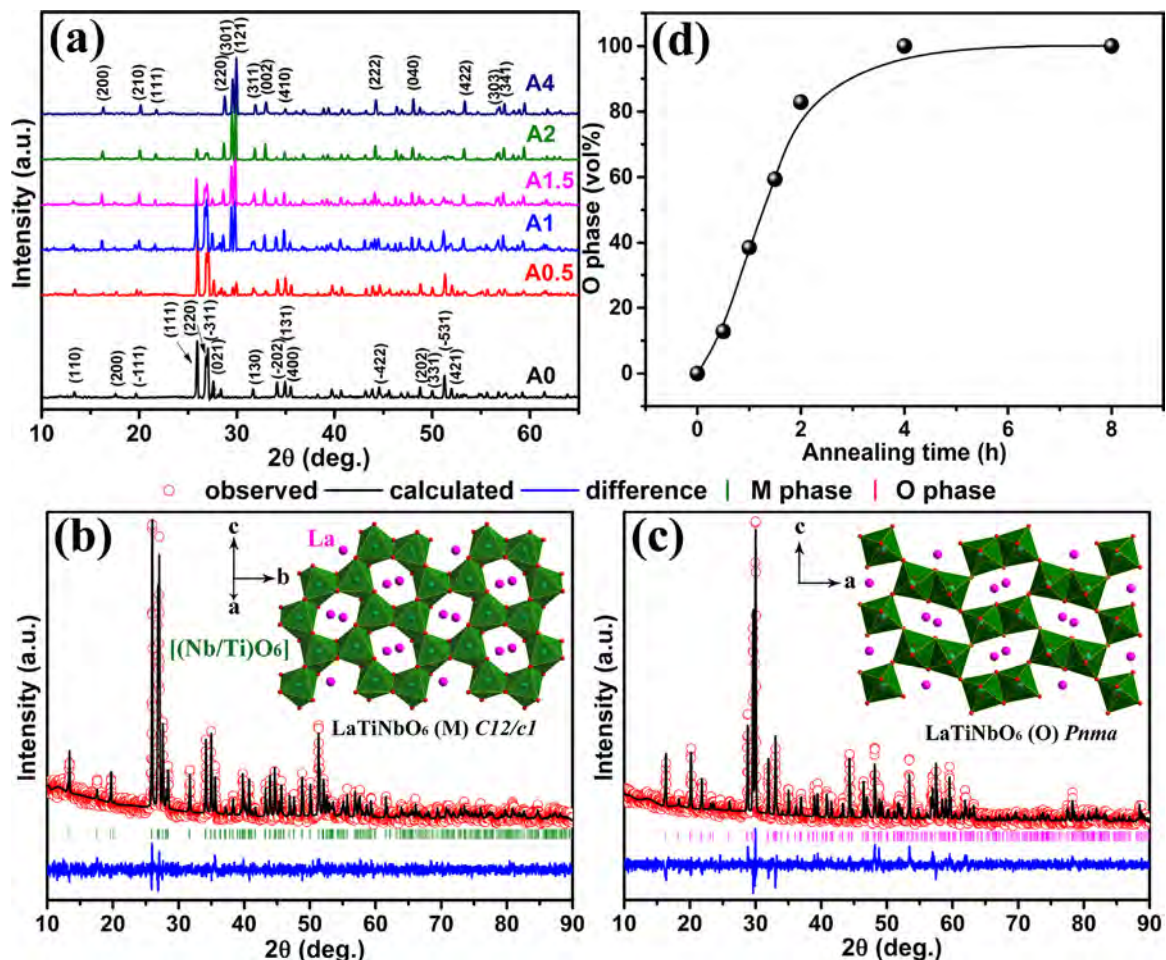


Fig. 1. (a) XRD patterns of different LaTiNbO₆ ceramic samples, (b, c) refinement plots of XRD patterns for A0 and A4 samples, respectively; insets show the crystal structural schematics of M and O phases in A0 and A4, respectively, (d) percentage of the O phase in LaTiNbO₆ ceramics as a function of annealing time.

Table 1

Refined structural parameters by using the Rietveld method for different LaTiNbO₆ ceramics.

Samples	A0	A1	A4	
Phases	M	M (61.5 vol.%) O (38.5 vol.%)	O	O
<i>a</i> (Å)	11.195(2)	11.1921(9)	10.9311(7)	10.9340(5)
<i>b</i> (Å)	8.842(2)	8.8394(7)	7.5788(4)	7.5794(3)
<i>c</i> (Å)	5.268(1)	5.2657(4)	5.4451(3)	5.4458(2)
$\alpha=\gamma$ (°)	90	90	90	90
β (°)	115.333(2)	115.339(4)	90	90
<i>V</i> (Å ³)	471.4(3)	470.83(8)	451.10(6)	451.32(4)
<i>D</i> (g/cm ³)	5.293	5.300	5.532	5.529
<i>D_m</i> (±0.02 g/cm ³)	4.94	4.93		4.98
<i>R_{wp}</i> (%)	9.71	9.69		10.66
<i>R_p</i> (%)	7.64	7.59		8.51
χ^2	1.498	1.527		1.802

V: unit cell volume; *D*: theoretical density; *D_m*: measured density; *R_{wp}*: the reliability factor of weighted patterns; *R_p*: the reliability factor of patterns; χ^2 : goodness-of-fit indicator = (*R_{wp}*/*R_{exp}*)².

sample matched well with that of JCPDS# 73-1059 (O phase with a space group *Pnma*). The relative content of two coexisting phases in all different samples was identified by means of the multiphase Rietveld refinement of their XRD data. M-phase (ICDD# 413439) [15] and O-phase (ICDD# 23509) [16] LaTiNbO₆ were chosen as their initial modes. As examples, Fig. 1(b) and (c) illustrate the refinement plots for the A0 and A4 samples, respectively. The refined lattice parameters and reliable factors of *R_{wp}*, *R_p*, and χ^2 for A0, A1 and A4 samples are listed Table 1. The *R_{wp}*, *R_p*, and χ^2 values were found to be in the range of 9–11%, 7–9%, and 1.4–1.8, respectively, indicating that the structural model is valid and the refinement result is reliable. It can be seen that the O phase has inherently smaller lattice parameters than the M phase. In addition, there is little difference in unit cell volume of the corresponding phase between A1 and A0 (A4), implying the

coexisting phase structure is stable after annealing. Moreover, the percentage of the O phase was plotted as a function of annealing time for all studied samples, as shown in Fig. 1(d). It can be seen that the O phase content increased with increasing annealing time. A single O phase was yielded when annealing time exceeded 4 h, which agreed well with the above XRD patterns. The insets of Fig. 1(b) and (c) show the structure illustrations of the M (A0) and O (A4), respectively. It is indicated that the structure of the M phase consists of the layers parallel to the (100) plane. The layers are formed by distorted Nb/TiO₆ octahedra sharing three edges. By comparison, the O-phase structure is built up of pairs of distorted Nb/TiO₆ octahedra with each pair sharing a common edge [15]. Therefore, when a pair of distorted Nb/TiO₆ octahedra is regarded as a structural unit, the M-O phase transition is essentially a change in the connection way of the structural units from sharing edges to sharing corners as a result of the ionic migration during annealing.

The grain morphology of typical LaTiNbO₆ ceramic samples A0, A1, and A4 is shown in Fig. 2. All samples presented dense microstructures with few pores. It seems that no changes in grain size were observed but the grain surface morphology became rougher with prolonging annealing time. The grain surface morphology of the pre-annealed A0 sample looks very smooth. The matte grains in post-annealed samples are actually made of smaller grains in the matrix grain (Fig. 2(b and c)), as clearly indicated by looking into locally magnified grains (marked in Fig. 2(c)) of the A4 sample in Fig. 2(d). This special microstructure evolution could be ascribed to the inner stress resulting from the volume shrinkage (~4.3%) of unit cells during the transition from the M (471.4 Å³) to O (451.32 Å³) phase. Possible large cracks were not observed in current study probably because the inner stress was minimized by using a controlled cooling rate after annealing. Moreover, there might be a more reasonable reason for the case in this study. The inner stress can be released by micro-cracking within a large grain into small parts, between which new grain

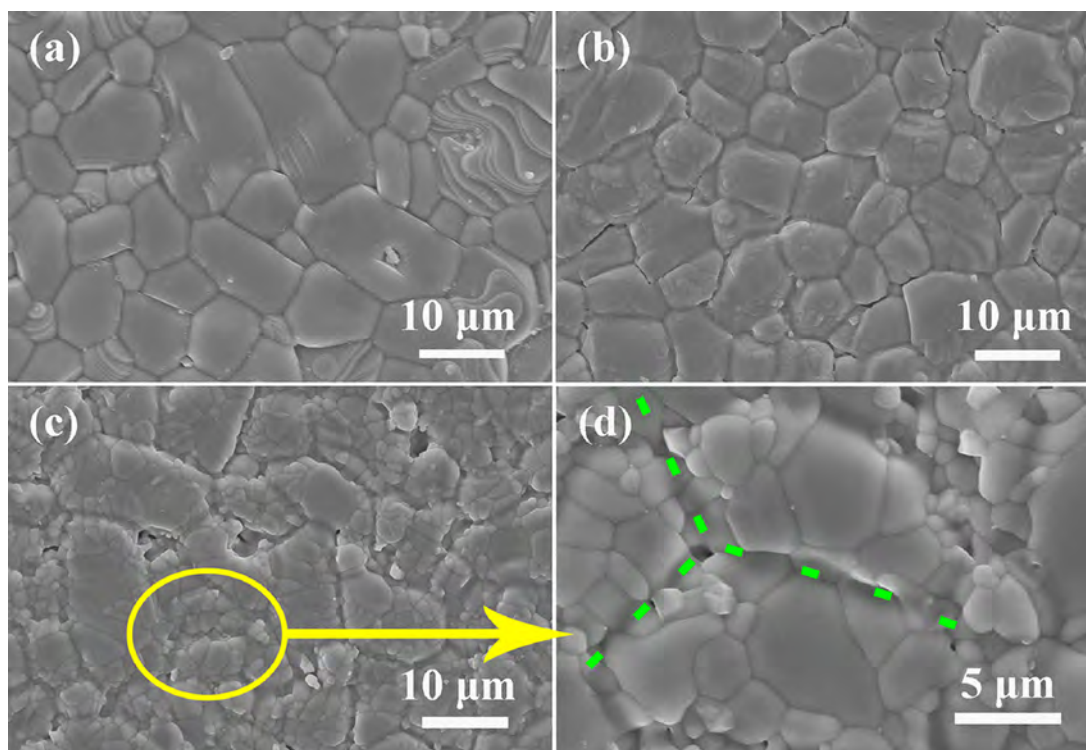


Fig. 2. Grain morphology on the natural surface of different LaTiNbO₆ ceramic samples: (a) A0, (b) A1, (c) A4, and (d) locally magnified graph in A4.

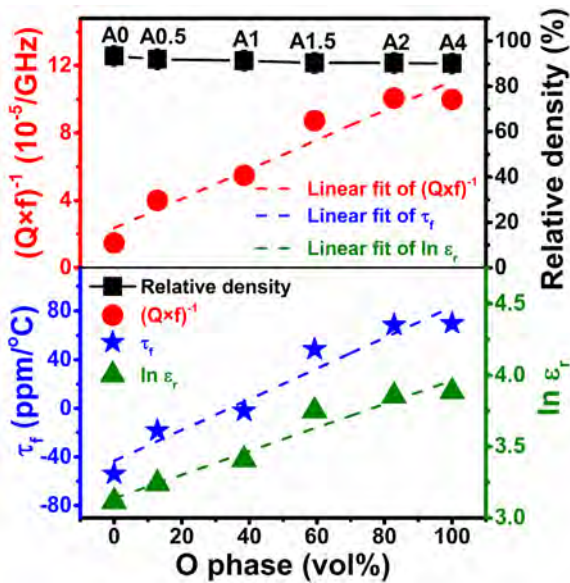


Fig. 3. The relative density and property parameters such as $(Q \times f)^{-1}$, ϵ_r and τ_f as a function of the O phase content for different LaTiNbO₆ samples.

boundaries were formed by a self-healing process (i.e., the formation of diffusion controlled sintering necks) at higher annealing temperatures. The absence of microcracks leading to the refinement of grains in the post-annealed LaTiNbO₆ samples can be further supported by good microwave dielectric properties infra because they will definitely deteriorate the final performance [17].

The relative density and microwave dielectric properties of LaTiNbO₆ ceramic samples annealed for different time are shown in Fig. 3. The relative density was found to slightly decrease from 93.4 to 90.1% with prolonging annealing time (with increasing the O phase content, as shown in Fig. 1(d)). It might be caused by the structure defects owing to the inner stress from the thermally-induced phase transition. Interestingly, τ_f was found to move from a negative value to a positive value with prolonging annealing time. Meanwhile, ϵ_r increased (i.e. $\ln \epsilon_r$ increased) and $Q \times f$ dropped quickly (i.e., $(Q \times f)^{-1}$ increased), primarily being attributed to the increased O phase content on the basis of the well-known empirical model of the composite as follows [18,19]:

$$\ln \epsilon_r = V_1 \ln \epsilon_{r1} + V_2 \ln \epsilon_{r2} \quad (1)$$

$$(Q \times f)^{-1} = V_1 (Q \times f)_1^{-1} + V_2 (Q \times f)_2^{-1} \quad (2)$$

$$\tau_f = V_1 \tau_{f1} + V_2 \tau_{f2} \quad (3)$$

where V_1 and V_2 stand for the volume fraction of each phase. Furthermore, it can be clearly shown that all three parameters $\ln \epsilon_r$, τ_f and $(Q \times f)^{-1}$ in current work have a nearly linear relationship with the volume percentage of the O phase, suggesting the annealed LaTiNbO₆ belongs to an M-O self composite. Moreover, we can see that the O-phase LaTiNbO₆ ceramic (A4) possessed a relatively high ϵ_r and a positive τ_f ($\epsilon_r = 48.7$, $\tau_f = 69.7 \text{ ppm}/^\circ\text{C}$), compared with the M-phase LaTiNbO₆ ceramic (A0) ($\epsilon_r = 22.5$, $\tau_f = -54 \text{ ppm}/^\circ\text{C}$). Temperature-stable microwave dielectric performances of $\epsilon_r = 30.2$, $Q \times f = 18,242 \text{ GHz}$ (@6.54 GHz) and $\tau_f = -2.1 \text{ ppm}/^\circ\text{C}$ can be obtained in A1. The big difference in performances of these two phases (M and O) might be closely related to the way of their octahedral connections, which is similar to the case in

titanates [20,21]. Nevertheless, the grain refinement and density improvement of the matrix ceramic after a conventional sintering need to be further pursued in future in order to advance microwave dielectric properties (for example, $Q \times f$ values) of self-composite ceramics.

4. Conclusions

An M to O phase structural transformation was thermally induced in a conventionally sintered M-phase LaTiNbO₆ ceramic. Through prolonging annealing time at 1100 °C, a pure O-phase LaTiNbO₆ ceramic with microwave properties of $\epsilon_r = 48.7$, $Q \times f = 10,018 \text{ GHz}$ (@5.21 GHz) and $\tau_f = 69.7 \text{ ppm}/^\circ\text{C}$ was successfully obtained. The relative content of two coexisting phases (M and O) can be conveniently adjusted by controlling annealing time. Most interestingly, a novel temperature-stable (near-zero τ_f) self-composite LaTiNbO₆ ceramic was thus yielded, exhibiting tunable microwave dielectric properties. The concept of the self-composite might provide a new and easy way to develop high-performance thermally-stable microwave dielectric ceramics.

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