Materials Research Bulletin 83 (2016) 568–572

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Short communication

A novel self-composite property-tunable $LaTiNbO_6$ microwave dielectric ceramic

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ARTICLE INFO

Article history:
Received 16 May 2016
Received in revised form 30 June 2016
Accepted 3 July 2016
Available online 5 July 2016

Keywords:
A. Ceramics
B. Microstructure
B. Phase transitions
C. X-ray diffraction
D. Dielectric properties

ABSTRACT

A novel self-composite $LaTiNbO_6$ microwave dielectric ceramic was fabricated via a solid-state reaction method together with an annealing process. A monoclinic $LaTiNbO_6$ 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 (ε_r = 30.2, $Q \times f$ = 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.

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].

$ReTiNbO_6$ (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 $[Re_{1-x}Re'_x]TiNbO_6$ (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 $ReTiNbO_6$ compounds, $LaTiNbO_6$ belongs to a special one, and generally manifests a monoclinic (M) structure at room temperature with good microwave dielectric properties of ε_r = 22.3, $Q \times f$ = 49,867 GHz, τ_f = −55 ppm/°C in the measuring frequency range of 3–10 GHz [9]. Moreover, an orthorhombic (O) to M polymorphic phase transition was reported in $LaTiNbO_6$ as temperature is over 1100 °C, which is far below its densification temperature (~1300 °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 $LaTiNbO_6$ 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 $LaTiNbO_6$ 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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http://dx.doi.org/10.1016/j.materresbull.2016.07.004
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2. Experimental

$LaTiNbO_6$ ceramics were prepared by a conventional solid-state reaction process. High-purity (>99%) La_2O_3, Nb_2O_5 (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) and TiO_2 (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 $LaTiNbO_6$ 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 Cu$K\alpha$ 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 $TE_{01\delta}$-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 $LaTiNbO_6$ 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

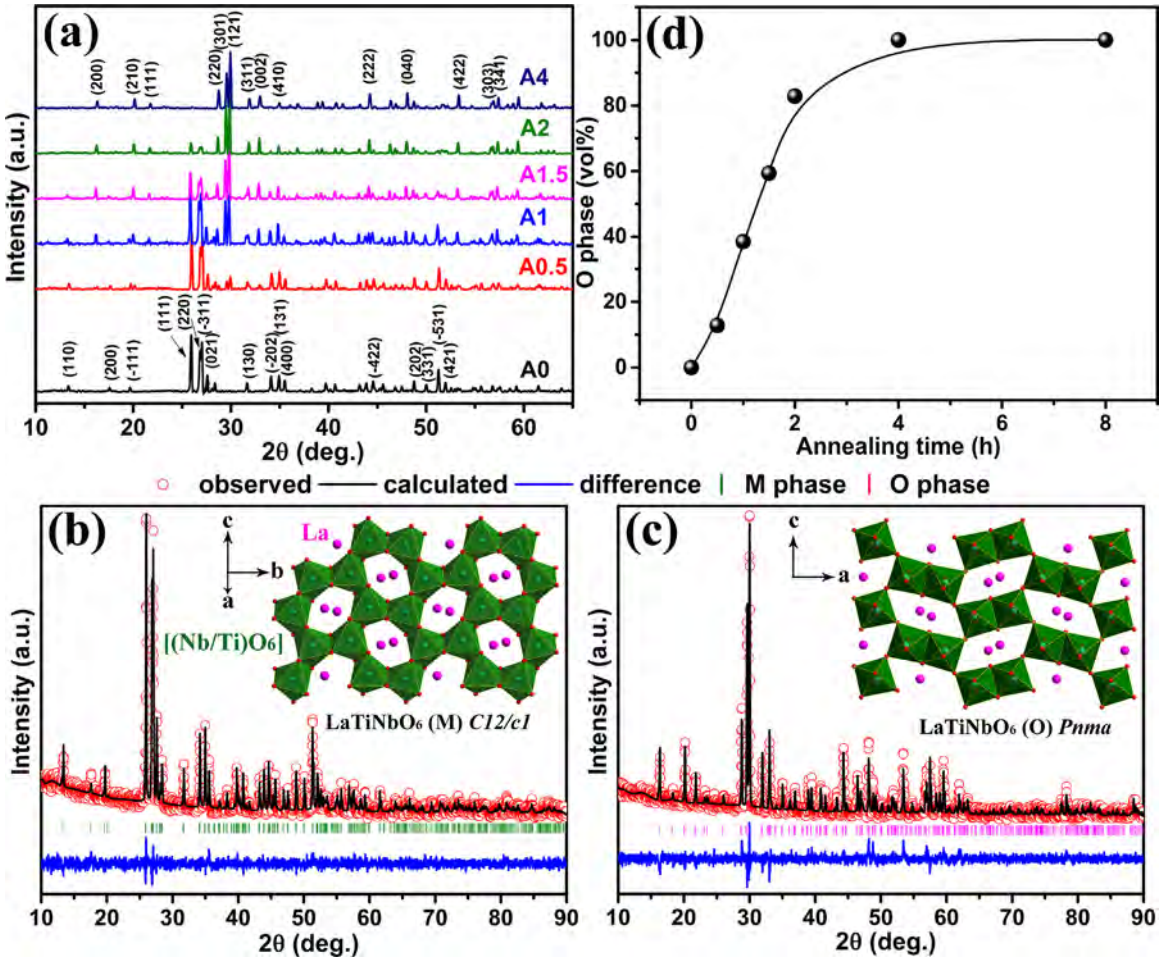

Fig. 1. (a) XRD patterns of different $LaTiNbO_6$ ceramic samples, (b, c) refinement plots of XRD patterns for A0 and A4 samples, respectively; insets show the crystal structural schematics of M and O phases in A0 and A4, respectively, (d) percentage of the O phase in $LaTiNbO_6$ ceramics as a function of annealing time.

Table 1
Refined structural parameters by using the Rietveld method for different $LaTiNbO_6$ ceramics.

Samples	A0	A1		A4
Phases	M	M (61.5 vol.%)	O (38.5 vol.%)	O
a (Å)	11.195(2)	11.1921(9)	10.9311(7)	10.9340(5)
b (Å)	8.842(2)	8.8394(7)	7.5788(4)	7.5794(3)
c (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
V (Å^3)	471.4(3)	470.83(8)	451.10(6)	451.32(4)
D (g/cm^3)	5.293	5.300	5.532	5.529
D_m (±0.02 g/cm^3)	4.94	4.93		4.98
R_{wp} (%)	9.71	9.69		10.66
R_p (%)	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] $LaTiNbO_6$ 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/TiO_6 octahedra sharing three edges. By comparison, the O-phase structure is built up of pairs of distorted Nb/TiO_6 octahedra with each pair sharing a common edge [15]. Therefore, when a pair of distorted Nb/TiO_6 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 $LaTiNbO_6$ 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 Å^3) to O (451.32 Å^3) 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

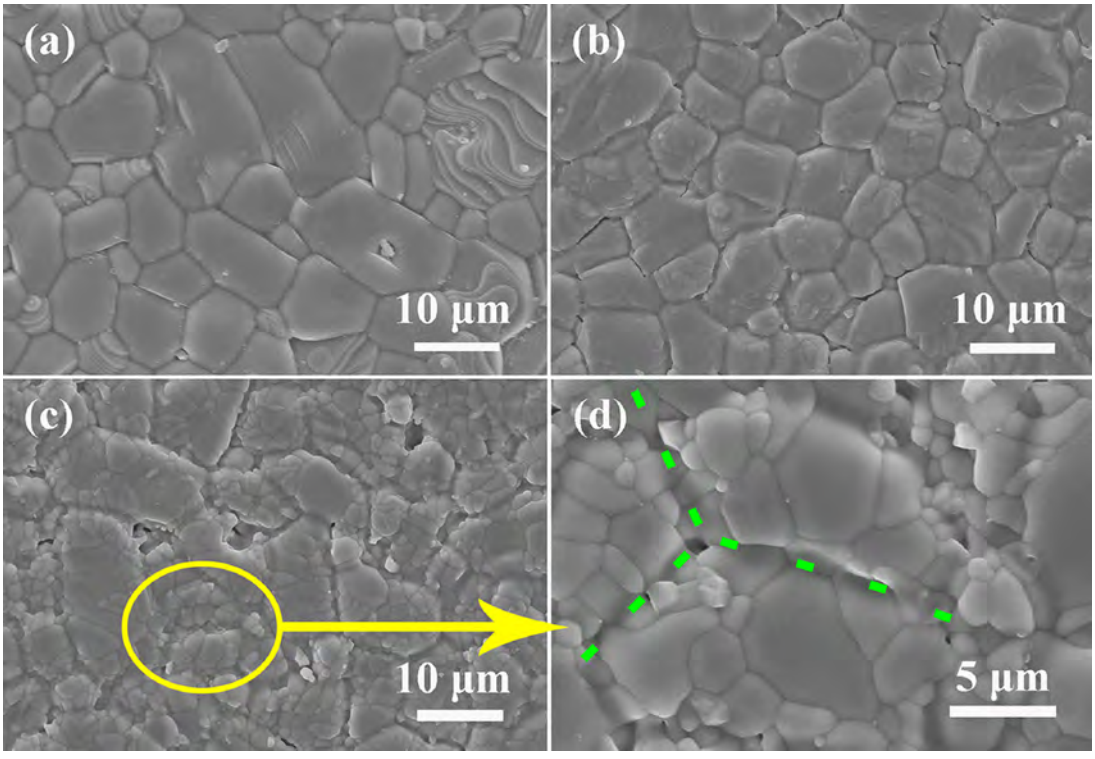

Fig. 2. Grain morphology on the natural surface of different $LaTiNbO_6$ ceramic samples: (a) A0, (b) A1, (c) A4, and (d) locally magnified graph in A4.

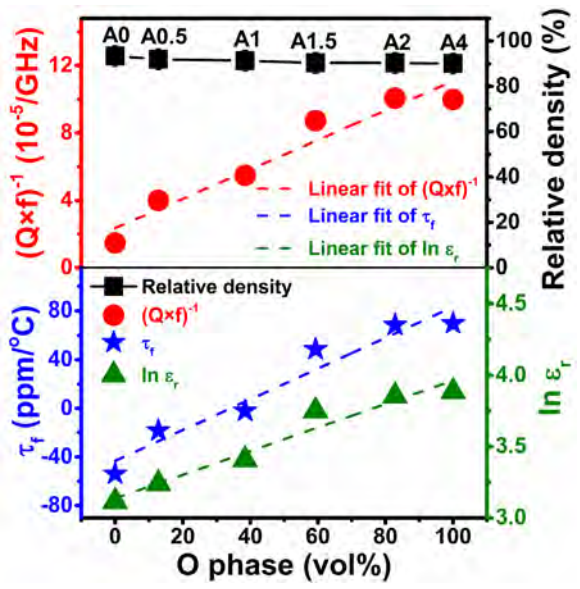

Fig. 3. The relative density and property parameters such as $(Q \times f)^{-1}$, ε_r and τ_f as a function of the O phase content for different $LaTiNbO_6$ samples.

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 $LaTiNbO_6$ 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 $LaTiNbO_6$ 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 ε_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]:

$$\ln\varepsilon_r = V_1 \ln\varepsilon_{r1} + V_2 \ln\varepsilon_{r2} \quad (1)$$

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

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

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 ε_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 $LaTiNbO_6$ belongs to an M-O self composite. Moreover, we can see that the O-phase $LaTiNbO_6$ ceramic (A4) possessed a relatively high ε_r and a positive τ_f (ε_r = 48.7, τ_f = 69.7 ppm/°C), compared with the M-phase $LaTiNbO_6$ ceramic (A0) (ε_r = 22.5, τ_f = −54 ppm/°C). Temperature-stable microwave dielectric performances of ε_r = 30.2, $Q \times f$ = 18,242 GHz (@6.54 GHz) and τ_f = −2.1 ppm/°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 $LaTiNbO_6$ ceramic. Through prolonging annealing time at 1100 °C, a pure O-phase $LaTiNbO_6$ ceramic with microwave properties of ε_r = 48.7, $Q \times f$ = 10,018 GHz (@5.21 GHz) and τ_f = 69.7 ppm/°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 $LaTiNbO_6$ 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.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 51272060) and the Natural Science Foundation of Anhui Province (Grant No. 1508085JGD04).

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