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Short communication

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

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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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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

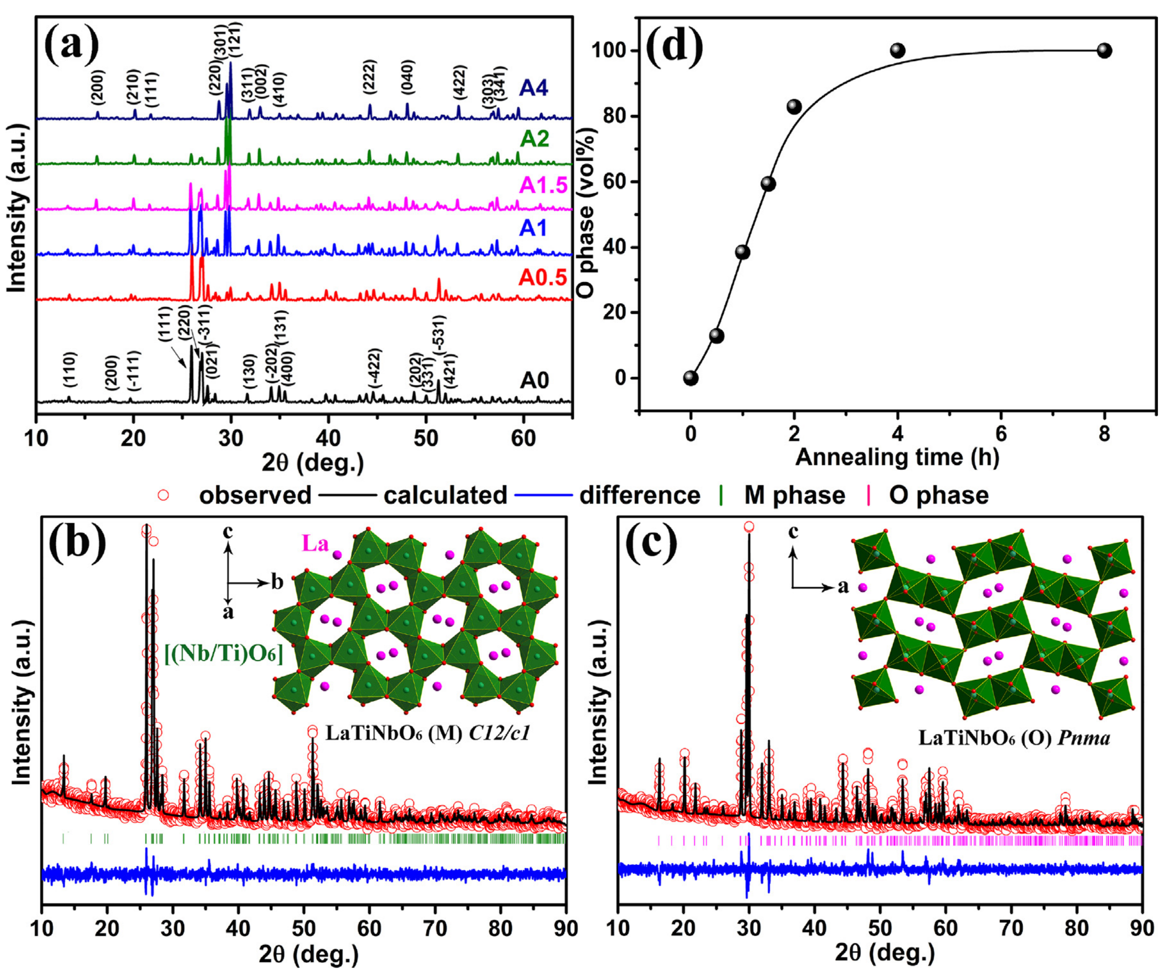

Fig. 1. (a) XRD patterns of different $LaTiNbO_6$ ceramic samples, (b, c) refinement plots of XRD patterns for A0 and A4 samples, respectively; insets show the crystal structural schematics of M and O phases in A0 and A4, respectively, (d) percentage of the O phase in $LaTiNbO_6$ ceramics as a function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