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Dielectric and mechanical characteristics of lanthanum aluminate ceramics with strontium niobate addition

X.Q. Liu, X.M. Chen*

Department of Materials Science & Engineering, Zhejiang University, Hangzhou 310027, PR China

Abstract

The microstructures, microwave dielectric properties and mechanical properties were investigated for $LaAlO_3$ ceramics with $Sr_2Nb_2O_7$ additive. The grain size decreased significantly when the additive was introduced, and the $Sr_2Nb_2O_7$ reacted with the $LaAlO_3$ ceramic matrix to form a $LaNbO_4$ secondary phase. The dielectric constant varied slightly, while the Qf value increased at first and then decreased when the additive content passed a critical value. The effects of the $Sr_2Nb_2O_7$ additive upon the temperature coefficient of resonant frequency were dependent on the sintering conditions. The fracture toughness was significantly improved by $Sr_2Nb_2O_7$ addition.

Keywords: Dielectic properties; $LaAlO_3$; Mechanical properties; $Sr_2Nb_2O_7$

1. Introduction

$LaAlO_3$ single crystals have been widely used as the substrates of high-temperature superconductor (HTSC) films due to their low dielectric loss and minor lattice parameter mismatch between the substrates and HTSC films.[1,2] $LaAlO_3$ ceramics are also potential microwave dielectric materials because of their high Qf value (68,000 GHz) and relative low temperature coefficient of resonant frequency τ_f (−44 ppm/°C),[3] and some investigations have been done for obtaining near-zero temperature coefficient of resonant frequency.[4–6]

On the other hand, the mechanical properties of $LaAlO_3$ ceramics have rarely been investigated, and it is a challenge issue to obtain the excellent microwave dielectric properties combined with enhanced mechanical properties, especially the enhanced fracture toughness in the present ceramics. Though the mechanical properties are not the primary requirements for microwave dielectric ceramics, the microwave dielectric ceramics with enhanced fracture toughness will efficiently reduce the processing flaws due to micro- or macrofractures and subsequently will enable us to design microwave devices with more complex structures with higher productivity.

In the previous work by the authors,[7] $Sr_2Nb_2O_7$ secondary was added to ZTA ceramics to enhance the fracture toughness. If the co-presence of $LaAlO_3$ ceramics with a secondary phase is possible, $Sr_2Nb_2O_7$ addition in $LaAlO_3$ ceramics may lead to the enhanced fracture toughness. Moreover, the presence of secondary phase in ceramics generally reduce the grain size which is beneficial for obtaining lower dielectric loss in oxide ceramics due to less oxygen vacancy.

In the present work, $LaAlO_3$ ceramics with $Sr_2Nb_2O_7$ addition are prepared and characterized, and the effects of such addition on microstructures are investigated together with the microwave dielectric and mechanical properties.

2. Experimental procedure

Reagent-grade $SrCO_3$ (99.5% purity) and Nb_2O_5 (99.99% purity) in 2:1 mole ratio were mixed by ball milling in ethanol using zirconia media for 24 h. The slurry was dried and then calcined at 1200 °C for 3 h to prepare $Sr_2Nb_2O_7$. And the $LaAlO_3$ powder was synthesized from reagent-grade La_2O_3 (99.99% purity) and Al_2O_3 (99.98% purity) by calcining them at 1200 °C for 3 h in air. Then, the $LaAlO_3$ powders with $x$mol% $Sr_2Nb_2O_7$ additive ($x = 0$, 5, 10, 15) were mixed by ball milling with zirconia media in ethanol for 24 h. After drying, such mixed powders were pressed into disc compacts of 12 mm in diameter and 1–4 mm in height, and

* Corresponding author. Tel./Fax: +86-571-8795-2112.
E-mail address: xmchen@cmsce.zju.edu.cn (X.M. Chen).

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these compacts were sintered at the temperature from 1575 to 1600 °C in air for different soaking time (1–6h).

The microstructures were evaluated by scanning electron microscopy (SEM, HITACHI S-570) companied with energy dispersive X-ray spectrometry (EDS), and the phases presented in the composite ceramics were characterized by X-ray diffraction (XRD, RIGAKU D/max-3B) analysis using CuK_α radiation after crushing and grinding.

The effective elastic modulus was evaluated using the method proposed by Marshall et al. where a diamond Knoop indenter was used combined with a diamond Vickers indenter.[8] The results were averaged over six indentations per specimen and the following formula was used in the calculations:[8]

$$b'/a' = b/a - \alpha H/E \quad (1)$$

where, b'/a' and b/a were the ratio of diagonal dimensions of Knoop indentation and that of Knoop indenter, respectively, α was a constant, H was Vickers hardness and E was effective elastic modulus. Here, $b/a = 1/7.11$ and $\alpha = 0.45$ were used during calculating.

The fracture toughness was evaluated by the modified indention method[9,10] at room temperature using a diamond Vickers indenter with a loading time of 15 s at a constant load of 100 N on polished surface. The results were averaged over six indentations per specimen and the following formula was used in the calculations:[9,10]

$$\left(K_{1C}\phi/Ha^{1/2}\right)(H/E\phi)^{2/5} = 0.035(l/a)^{-1/2} \quad (2)$$

where K_{1C} was the toughness of the composite ceramic, H was the Vickers hardness, E was the effective elastic modulus, ϕ was the constraint factor (≈3), l was the length of the crack, and a was the half diagonal length of an indentation.

On the other hand, the microwave dielectric properties were evaluated at about 10 GHz by Hakki and Coleman's resonator method,[11] and the temperature coefficient of resonant frequency was calculated from the equation

$$\tau_f = -\frac{\tau_\varepsilon}{2} - \alpha \quad (3)$$

where, α is the linear expansion coefficient (~10 ppm/°C),[12] τ_ϵ is the temperature coefficient of dielectric constant evaluated at 1 MHz by an LCR meter (HP4284A) equipped with a thermostat, in the range from room temperature to 85 °C.

3. Results and discussion

Dense $LaAlO_3$ ceramics contented $x$mol% $Sr_2Nb_2O_7$ additive could be obtained by sintering at temperatures above 1575 °C, and the relative densities higher than 0.95 were observed. The grain size of $LaAlO_3$ ceramics sharply decreased with incorporating $Sr_2Nb_2O_7$ additive, and the porosity increased with increasing additive content (Figs. 1 and 2; Tables 1 and 2). The very fine-grained structures are obtained in the situation with 5 and 10 mol% $Sr_2Nb_2O_7$ additive, and the grain size turns to increase for 15 mol% $Sr_2Nb_2O_7$ added $LaAlO_3$ ceramics but it is still much finer than that for $LaAlO_3$ ceramics without additives. EDS analysis identified the elements of La, Nb in phase B, while phase A was consisted of La, Al and Sr elements. As shown in Fig. 3, $Sr_2Nb_2O_7$ was not detected by XRD, but some alternative secondary phases were observed in the $Sr_2Nb_2O_7$ added $LaAlO_3$ ceramics. The $LaNbO_4$ (JCPD card No. 86-0909) secondary phases was observed together with $LaAlO_3$ matrix for compositions of $x = 10$ and 15 mol%, and a minor amount of $LaAl_{11}O_{18}$ phase (JCPD card No. 34-0467) and $LaNbO_4$ were observed as the secondary phases for the composition with $x = 5$ mol%. We could discuss the question where had Sr^{2+} ion gone. The radius of Sr^{2+} was larger than that of La^{3+} when the coordinate number was the same,[13] and the calculated cell volume of $LaAlO_3$ increased with $Sr_2Nb_2O_7$ content (Fig. 4), so the following reaction should occur during sintering:

$$2LaAlO_3 + xSr_2Nb_2O_7 \rightarrow 2(La_{1-x}Sr_x)AlO_{3-\frac{x}{2}} + 2xLaNbO_4 \quad (4)$$

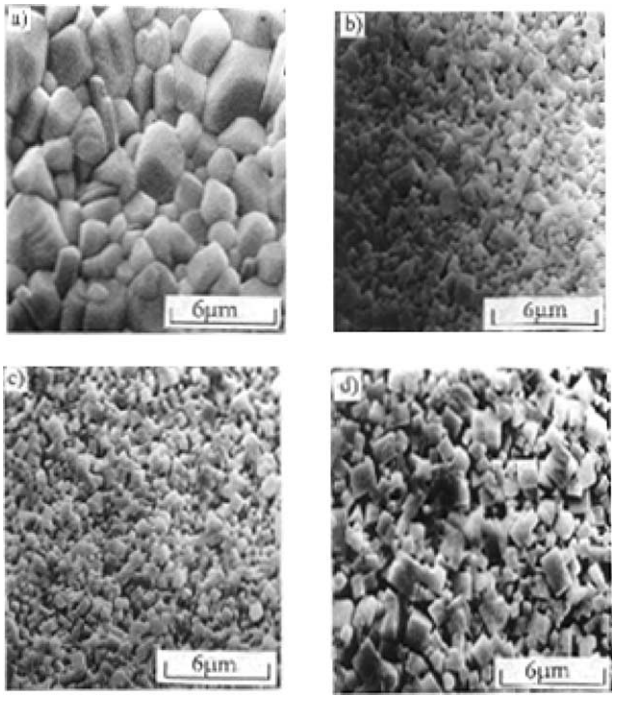

Fig. 1. SEM micrographs of the $LaAlO_3$ ceramics contented $x$mol% $Sr_2Nb_2O_7$ additive sintered at 1600 °C for 3 h: (a) $x = 0$ mol%; (b) $x = 5$ mol%; (c) $x = 10$ mol%; (d) $x = 15$ mol%.

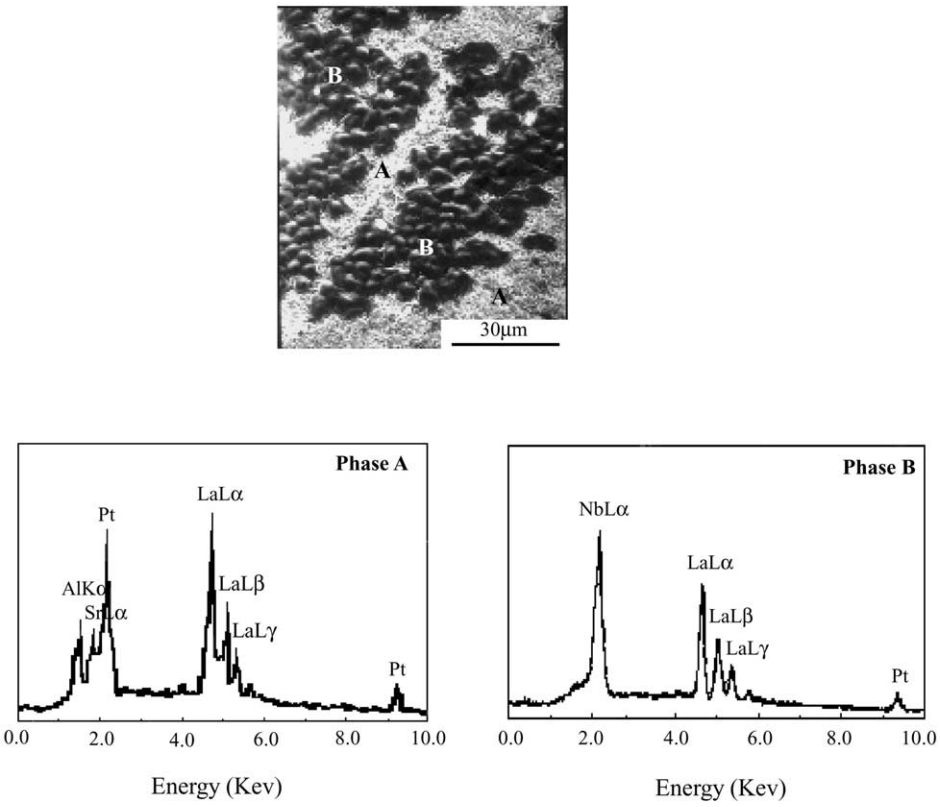

Fig. 2. SEM micrograph and EDS analysis results of the $LaAlO_3$ ceramics contented 5 mol% $Sr_2Nb_2O_7$ additive sintered at 1600 °C for 3 h.

Table 1
Microwave dielectric properties of the $LaAlO_3$ ceramics contented $x$mol% $Sr_2Nb_2O_7$ additive sintered under different conditions

x (mol%)	Sintering condition	f_0 (GHz)	ε	Tanδ	Q×f (GHz)	τ_f (ppm/°C)
0	1575 °C/3 h	8.13	23.0	0.00051	15 940	−56
5	1575 °C/3 h	10.81	23.4	0.00052	20 790	−25
10	1575 °C/3 h	7.63	22.8	0.00041	18 610	46
15	1575 °C/3 h	7.99	23.0	0.00140	5710	−36
0	1600 °C/1 h	7.85	23.2	0.00051	15 390	−36
5	1600 °C/1 h	10.89	23.1	0.00053	20 550	4.5
10	1600 °C/1 h	8.34	22.6	0.00044	18 950	98
0	1600 °C/3 h	7.74	23.2	0.00049	15 800	−44
5	1600 °C/3 h	11.05	23.1	0.00056	19 730	31
10	1600 °C/3 h	7.62	22.8	0.00054	14 110	−7.5
15	1600 °C/3 h	8.06	23.4	0.00200	4030	156
0	1600 °C/6 h	7.55	23.2	0.00047	16 060	−19
5	1600 °C/6 h	11.43	23.3	0.00065	17 580	−25
10	1600 °C/6 h	7.75	23.8	0.00160	4840	−129

Table 2
Mechanical properties of the $LaAlO_3$ ceramics contented $x$mol% $Sr_2Nb_2O_7$ additive sintered under different conditions

x (mol%)	Sintering condition	Grain size (μm)	E (GPa)	Hv (GPa)	K_{1C} (MPa $m^{1/2}$)
0	1575 °C/3 h	2.18	–	–	–
5	1575 °C/3 h	0.78	206±17	10.7±0.2	4.1±0.4
10	1575 °C/3 h	0.98	187±15	10.3±0.3	3.9±0.5
15	1575 °C/3 h	1.10	135±37	9.0±0.3	3.9±0.5
0	1600 °C/1 h	–	–	–	–
5	1600 °C/1 h	–	182±9	11.4±0.2	3.6±0.2
10	1600 °C/1 h	–	155±7	10.4±0.3	3.6±0.5
15	1600 °C/1 h	–	166±15	10.4±0.1	4.1±0.3
0	1600 °C/3 h	1.78	181±30	11.5±0.1	3.1±0.1
5	1600 °C/3 h	0.78	181±23	11.1±0.2	4.3±0.6
10	1600 °C/3 h	0.85	156±18	10.2±0.4	4.3±0.4
15	1600 °C/3 h	1.15	142±17	8.9±0.2	4.3±0.8
0	1600 °C/6 h	–	181±31	11.1±0.1	3.2±0.1
5	1600 °C/6 h	–	165±12	11.0±0.1	4.1±0.5
10	1600 °C/6 h	–	186±14	10.5±0.1	4.6±0.4
15	1600 °C/6 h	–	140±14	8.4±0.4	4.5±0.6

and the defect reaction equation could be written as

$$2Sr^{2+} + 2O^{2-} \xrightarrow{2LaAlO_3} 2Sr'_{La} + V_O^{\cdot\cdot} + 2O_O \quad (5)$$

where, oxygen vacancies appeared after Sr^{2+} had replace La^{3+}, and its concentration should be in proportion to Sr^{2+} content which in turn was relative to content of $Sr_2Nb_2O_7$.

Dielectric constant of $Sr_2Nb_2O_7$ added $LaAlO_3$ ceramics varied slightly for all compositions and sintering conditions investigated here (Fig. 5). While the Qf value increased with increasing $Sr_2Nb_2O_7$ addition at first and then decreased when $x > 5$ mol% (Fig. 6). The highest Qf value was 20,790 GHz for $LaAlO_3$ contented 5 mol% $Sr_2Nb_2O_7$ additive sintered at 1575 °C for 3 h.

There were two factors affecting the Qf value, i.e. secondary phase and oxygen vacancies. Noted that the dielectric loss of the $LaNbO_4$ secondary phase was high,[14] and this would decrease the Qf value of ceramics. On the other hand, the appearance of secondary phase decreased the grain size, which was of benefit to the decease of oxygen vacancies and in turn increasing Qf values for the composite ceramics. Also, the content of oxygen vacancies would be effected by many factors. During cooling after sintering, re-oxidation would occur to compensate oxygen vacancies generated during soaking, and the concentration of oxygen vacancy was in proportion to the grain size since the re-oxidation process would be more difficult to penetrate the coarse grains. On the other hand, the concentration of oxygen vacancy would increase with $Sr_2Nb_2O_7$ content for Sr^{2+} substituting La^{3+}. Different factor would be dominant for different composition. The grain size effect was dominant for composition of $x=5$ mol%, where $Sr_2Nb_2O_7$ addition effectively suppressed the grain growth and subsequently led to the less oxygen vacancy and this combined with low content high dielectric loss secondary phase improved Qf value. On the contrary, the additive content effect was dominant for composition of $x=15$ mol%, where large number of oxygen vacancies generated and high content of high-loss secondary phase then resulted in the reduced Qf value. The variation tendency of temperature coefficient of

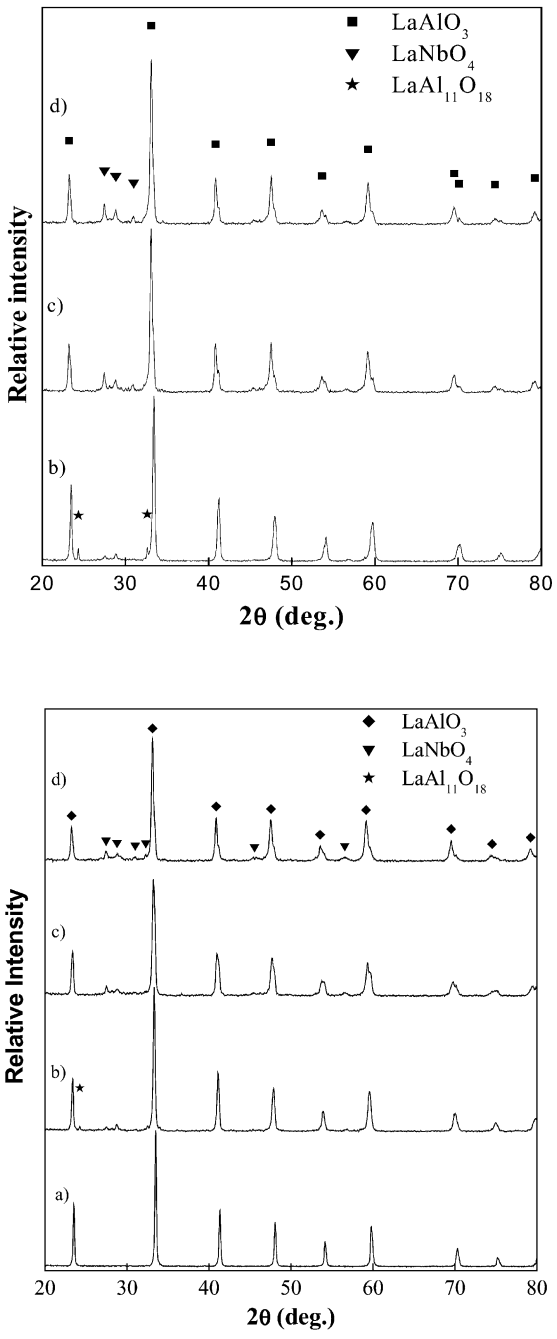

Fig. 3. XRD patterns of the $LaAlO_3$ ceramics contented $x$mol% $Sr_2Nb_2O_7$ additive sintered at 1600 °C: (a) $x=0$ mol%; (b) $x=5$ mol%; (c) $x=10$ mol%; (d) $x=15$ mol% for 1 h (upper) and 3 h (lower).

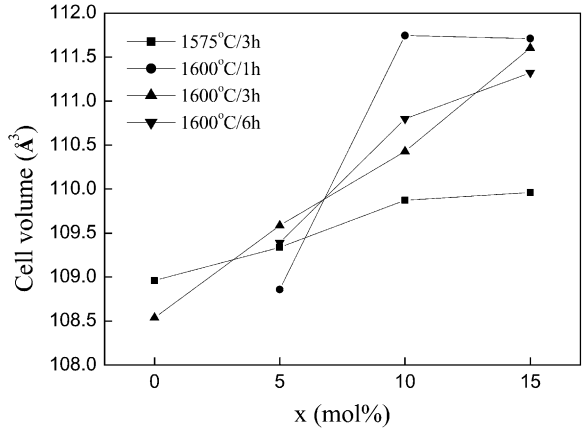

Fig. 4. Cell volume of $LaAlO_3$ matrix in the present ceramics sintered under various conditions as function of $Sr_2Nb_2O_7$ addition content.

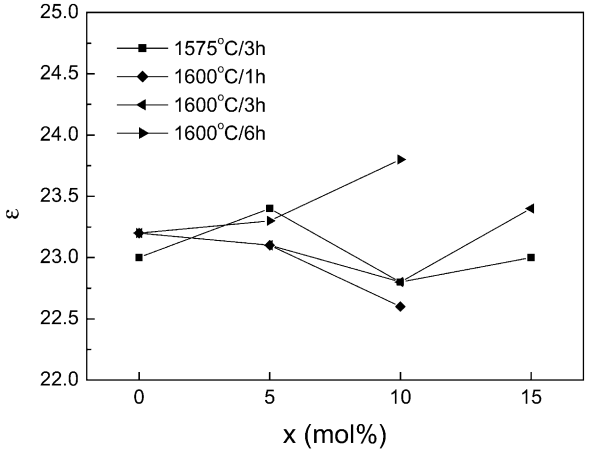

Fig. 5. Effects of sintering conditions on dielectric constant of the $LaAlO_3$ ceramics contented $x$mol% $Sr_2Nb_2O_7$ additive.

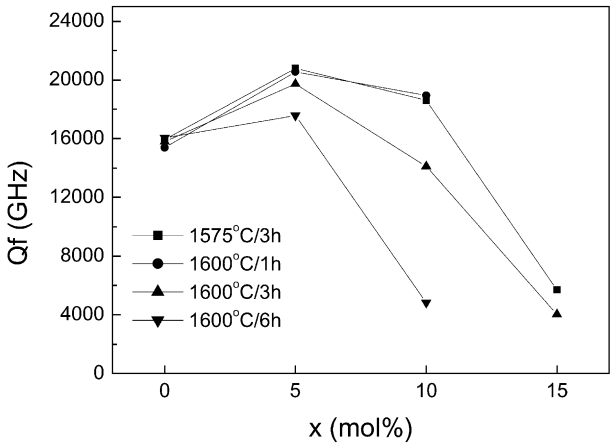

Fig. 6. Effects of sintering conditions on Qf value of the $LaAlO_3$ ceramics contented $x$mol% $Sr_2Nb_2O_7$ additive.

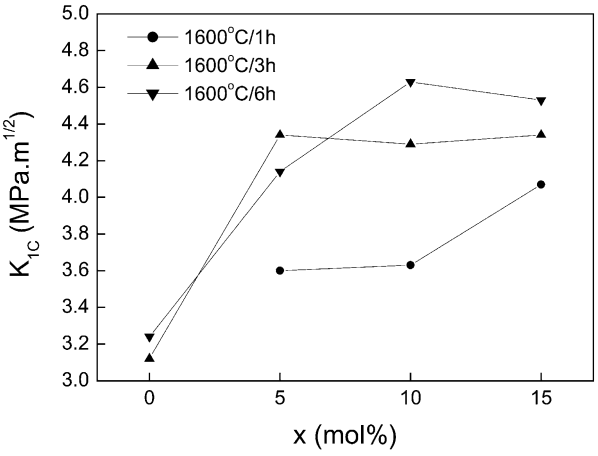

Fig. 8. Fracture toughness of the $LaAlO_3$ ceramics contented $x$mol% $Sr_2Nb_2O_7$ additive sintered at 1600 °C in air for different soaking time.

resonant frequency τ_f with×depended on the sintering conditions (Fig. 7). τ_f increased with $Sr_2Nb_2O_7$ content from negative to positive value for those sintered at 1600 °C for 1 h, while τ_f decreased with additive content to departure zero for those sintered at 1600 °C for 6 h. As the result of the combination of the above opposite tendencies, the curve of τ_f vs x was vibratory for the present ceramics sintered at 1575 and 1600 °C for 3 h. These phenomena were linked with the reaction process of $Sr_2Nb_2O_7$ with $LaAlO_3$ and the final phase constitution, which depended on the sintering conditions.

The Vickers hardness of $LaAlO_3$ ceramics contented $x$mol% $Sr_2Nb_2O_7$ additive decreased with x for all compositions and sintering conditions investigated here due to the lower hardness value of secondary phase, while the elastic modulus for the present ceramics varied with sintering temperature. For the ceramics sintered at 1575 °C, the elastic modulus of composites decreased with the additive content; while for ceramics sintered at 1600 °C, the variation tendency of elastic modulus was not clear. On the other hand, incorporation of $Sr_2Nb_2O_7$ significantly improved the fracture toughness of $LaAlO_3$ ceramics (Fig. 8), and the maximum K_{1C} value reached 4.63 MPa $m^{1/2}$ for $x=10$ mol% sintered at 1600 °C for 6 h, while that of $LaAlO_3$ end-member was only 3.24 MPa $m^{1/2}$. For the present ceramics sintered at 1600 °C, the fracture toughness almost increased with content of $Sr_2Nb_2O_7$.

$Sr_2Nb_2O_7$ unexpectedly reacted with $LaAlO_3$ ceramic matrix, and new secondary phase $LaNbO_4$ belonged to 2/m appeared. Noted that second phase was exist in the present ceramics, the difference of thermal expanding coefficient and/or Young's modulus of two phase could conduct residual stress field which led to crack deflecting or crack pinning, and the residual stress field also could conduct microcrack.

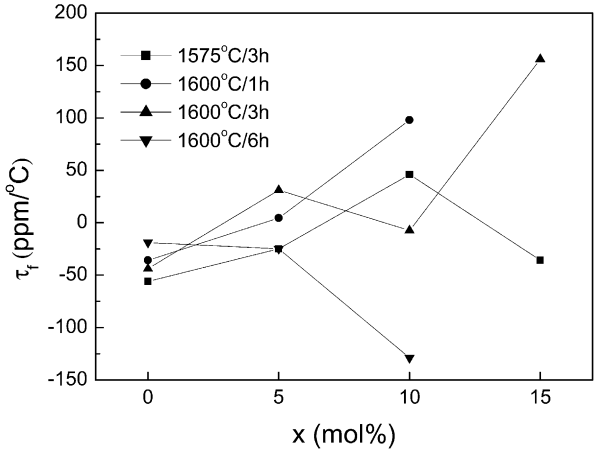

Fig. 7. Effects of sintering conditions on temperature coefficient of resonant frequency of the $LaAlO_3$ ceramics contented $x$mol% $Sr_2Nb_2O_7$ additive.

4. Conclusions

Introducing $Sr_2Nb_2O_7$ additive led to the significant decrease in grain size of $LaAlO_3$ ceramics, where $Sr_2Nb_2O_7$ additive reacted with $LaAlO_3$ ceramic matrix to form $LaNbO_4$ secondary phase. Dielectric constant of $Sr_2Nb_2O_7$ added $LaAlO_3$ ceramics varied slightly with additive content, while Qf value increased at first and then decreased when additive content was beyond 5 mol%. The relationship between temperature coefficient of resonant frequency and $Sr_2Nb_2O_7$ content varied with the sintering condition. The fracture toughness was significantly improved by introducing $Sr_2Nb_2O_7$ into $LaAlO_3$ ceramics due to crack deflecting toughening, while the Vickers hardness of $LaAlO_3$ ceramics decreased, and the variation tendency of Young's modulus was not very clear.

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