

Stability and microwave dielectric characteristics of $(\text{Ca}_{1-x}\text{Sr}_x)\text{LaAlO}_4$ ceramics

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Abstract The stability of K_2NiF_4 structure in MRAIO_4 ($M=\text{Sr}$ and Ca ; $R=\text{La}$, Nd , Sm , and Y) ceramics was discussed via calculating the relative difference between the tolerance factors for ABCO_4 and ABO_3 structure, and the K_2NiF_4 structure became unstable when the above difference was greater than 4.3%. Among the above ceramics, CaLaAlO_4 and SrYAlO_4 were not stable. To improve the stability of K_2NiF_4 structure in CaLaAlO_4 , the effects of Sr substitution for Ca were investigated. The stability of K_2NiF_4 structure in $(\text{Ca}_{1-x}\text{Sr}_x)\text{LaAlO}_4$ ceramics increased with increasing x , and it became stable when $x>0.9$. Good microwave dielectric properties were achieved in $(\text{Ca}_{0.05}\text{Sr}_{0.95})\text{LaAlO}_4$ ceramics: $\varepsilon=16.7$, $Qf=28,171$ GHz, $\tau_f=-52.4$ ppm/°C.

Keywords K_2NiF_4 structure · Microwave dielectric properties · Microstructure

1 Introduction

The revolution in wireless communication and information access requires materials with high relative dielectric constant, ultra-low dielectric loss, and near zero temperature coefficient of resonant frequency [1–3]. A large variety of materials have been developed in this area such as $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ [4], $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ [5], and LaAlO_3 [6] ceramics. Materials with the formula of ABCO_4 and K_2NiF_4 structure may also be promising candidates

considering their ultra-low dielectric loss in microwave frequency. Until now, much research work has been performed on single crystals with the formula of ABCO_4 and K_2NiF_4 structure [7–15], which is of two-dimensional structure and consists of alternating layers of KNiF_3 perovskite layers and KF rock-salt layers. The stability of this structure has attracted much attention, and the existence of K_2NiF_4 type structure is associated with the crystal chemical constraints originating in the 1:1 intergrowth of the rock-salt layer and perovskite layer. These constraints are mainly assumed to depend on steric and chemical effects related to the simultaneous presence of A^{3+} , B^{3+} and C^{2+} cations in the KF layers [8, 16, 17]. As reported previously by Smirnov et al [19], CaLaAlO_4 crystal is of metastability and will decompose into LaAlO_3 -like phase at 1,200°C.

In this article, the stability of some formerly investigated MRAIO_4 ($M=\text{Sr}$ and Ca ; $R=\text{Nd}$, Sm , and Y) ceramics with K_2NiF_4 structure is discussed [20–22], and $(\text{Ca}_{1-x}\text{Sr}_x)\text{LaAlO}_4$ ceramics are prepared along with the determination of microwave dielectric properties and microstructure, as well as the effects of Sr substitution for Ca on the stability of K_2NiF_4 structure.

2 Experimental procedure

$(\text{Ca}_{1-x}\text{Sr}_x)\text{LaAlO}_4$ ceramics were prepared by a solid-state reaction process, using reagent-grade CaCO_3 (99.0%), SrCO_3 (99.95%), La_2O_3 (99.99%), and Al_2O_3 (99.98%) powders as the raw materials. The weighed raw materials were mixed by ball milling with zirconia media in distilled water for 24 h, then were dried and heated at 1,250°C in air for 3 h. The calcined powders, with 6–10 wt% of PVA added, were pressed into disks measuring 12 mm in diameter

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Table 1 Tolerance factor of $ABCO_4$ and ABO_3 structures.

t	CaLaAlO ₄	CaNdAlO ₄	CaSmAlO ₄	CaYAlO ₄	SrLaAlO ₄	SrNdAlO ₄	SrSmAlO ₄	SrYAlO ₄
t_{ABCO_4}	0.949	0.940	0.934	0.924	0.973	0.963	0.958	0.947
t_{ABO_3}	1.0086	0.9757	0.965	0.906	1.0086	0.9757	0.965	0.906
Δt	0.0596	0.0357	0.031	0.018	0.0356	0.0127	0.007	0.041
$\Delta t\%$	6.3%	3.8%	3.3%	1.9%	3.7%	1.3%	0.73%	4.3%

and 2–6 mm high and then sintered at 1,375–1475°C in air for 3 h. After cooling from sintering temperature to 1,100°C at a rate of 2°C/min, the ceramics were cooled inside the furnace. The bulk density was evaluated by measuring the mass and dimensions. The calcined and sintered samples were characterized by x-ray diffraction (XRD) using Cu-K α radiation for phase identification. Ground and thermal-etched surfaces of sintered samples and the fractured surfaces were observed by electron back-scattering. The microwave dielectric constant ϵ , and the quality factor Q (the inverse of the dielectric loss, $\tan \delta$) were evaluated at about 10 GHz, using the Hakki–Coleman method [23]. Because the Q -factor generally varies inversely with frequency (f) in the microwave region, the product Qf , rather than Q alone, was used to evaluate dielectric loss.

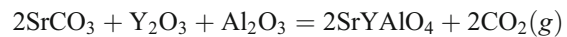
3 Results and discussion

The stability of K_2NiF_4 structure in compounds with formula $ABCO_4$ is usually discussed in terms of the Goldschmidt tolerance factor t defined as

$$t = d_{A/B-O} / \sqrt{2d_{C-O}}$$

Here, $d_{A/B-O}$ and d_{C-O} represent the mean equilibrium bond lengths between metal and oxygen atoms [16]. The tetragonal K_2NiF_4 structure is assumed to be stable, whereas t changes between the range of 1.02 and 0.85, and t values of $MRAIO_4$ (M =Sr and Ca; R =Nd, Sm, and Y) and the relevant ABO_3 compounds are listed in Table 1. In this table, Δt represents the difference of tolerance factor between $ABCO_4$ and the relevant ABO_3 structures. $\Delta t\%$ is defined as the ratio of Δt and t_{ABCO_4} . Larger $\Delta t\%$ value means that the perovskite layer in the K_2NiF_4 structure is unstable, which also represents the material's instability. As shown in the table, all the tolerance factors of $ABCO_4$ structure are within the stability limits, whereas $\Delta t\%$ values for CaLaAlO₄ and SrYAlO₄ are larger than other CaRAIO₄ and SrRAIO₄ (R =Nd, Sm, Y, and La) compounds. So it suggests the metastability of these two compounds. In our previous work, the stability of CaR'AlO₄ (R' =Nd, Sm, and Y) and SrR''AlO₄ (R'' =La, Nd, and Sm) ceramics has been proved [20–22]. Smirnov et al have pointed out the metastability of CaLaAlO₄ [16–19], which is in accordance

with our tolerance factor analysis. Moreover, our work also proves the poor stability of SrYAlO₄ compound. On the hypothesis that SrYAlO₄ phase is stable, it should be synthesized through the following reaction:



In our experiment, stoichiometric mixed SrCO₃, Y₂O₃ and Al₂O₃ powders are calcined at 1,200 and 1250°C in air for 3 h, respectively. Multi-phase composition of Y₂O₃, SrAl₂O₄, SrY₂O₄, YSrAl₃O₇, and Sr₃Al₂O₆ is found, whereas no K_2NiF_4 phase is recognized (Fig. 1). So the $\Delta t\%$ value could be regarded as the stability criteria for K_2NiF_4 structure. The structure is unstable when $\Delta t\%$ value is larger than 4.3%.

On the other hand, SrLaAlO₄ is a promising low-loss microwave dielectric material for its stability and the excellent microwave dielectric properties [7, 9]. To further invest the stability of CaLaAlO₄ ceramics, we prepare the (Ca_{1-x}Sr_x)LaAlO₄ ceramics. The powders are calcined at 1,250°C in air for 3 h, and their XRD patterns are shown in Fig. 2. For all compositions of $0.1 \leq x \leq 0.9$, (Sr,Ca)LaAlO₄ solid solution, LaAlO₃, and Ca₃Al₂O₆ are observed, whereas (Ca_{1-x}Sr_x)LaAlO₄ solid solution is observed as a major phase from $x=0.3$. With increasing x , the amount of LaAlO₃ and Ca₃Al₂O₆ phases decreases. When x increases

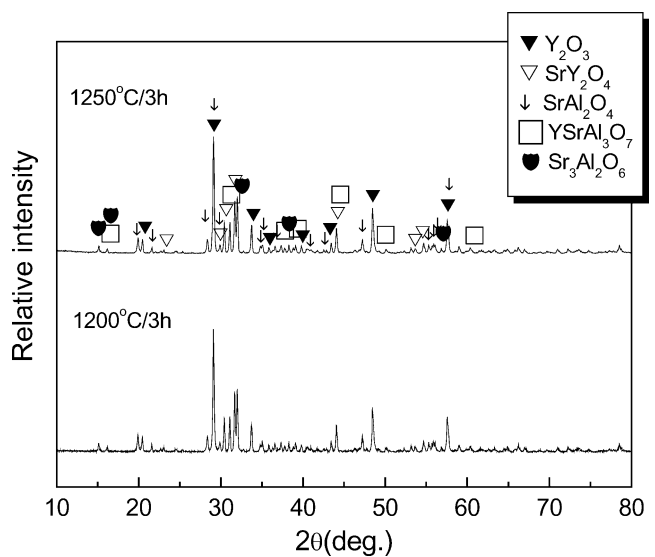
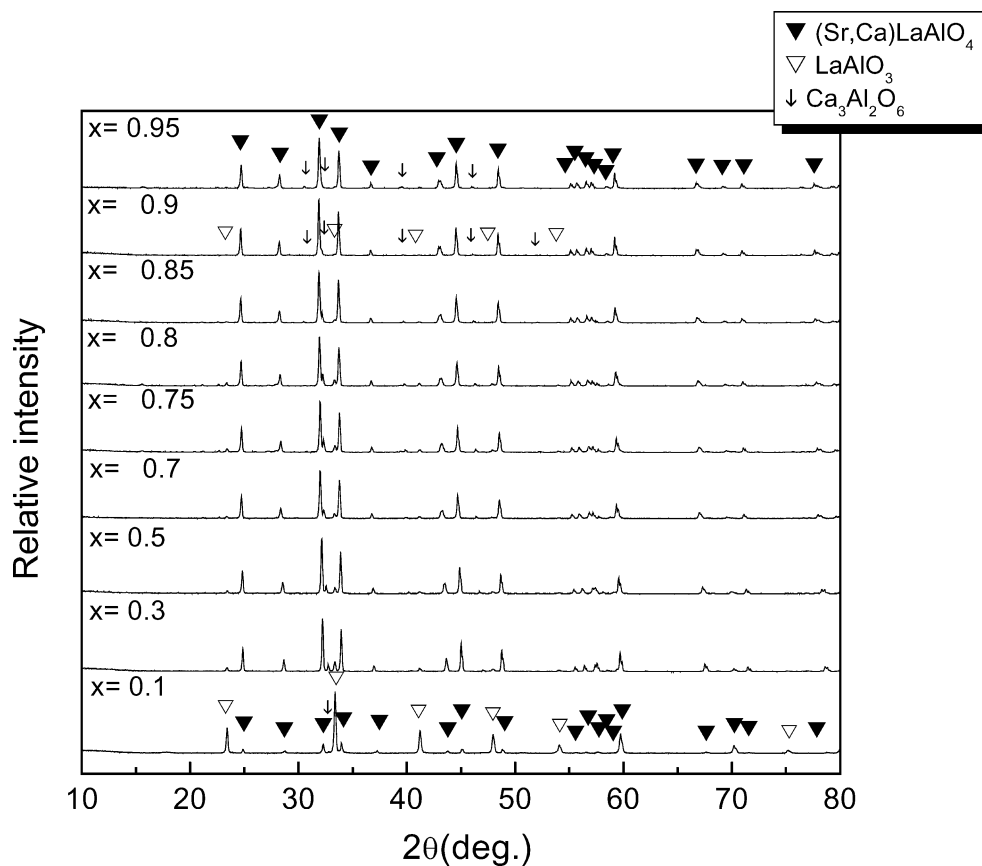
**Fig. 1** XRD patterns of calcined SrYAlO₄ powders

Fig. 2 XRD patterns of $(\text{Ca}_{1-x}\text{Sr}_x)\text{LaAlO}_4$ powders calcined at 1,250°C in air for 3 h



to 0.95, only small amount of $\text{Ca}_3\text{Al}_2\text{O}_6$ phase is recognized and LaAlO_3 phase disappears. The maximum bulk densities of sintered samples are obtained at the sintering temperature ranged from 1,425 to 1,450°C. The phase constitutions of the sintered ceramics are similar to those of the calcined powders. For all compositions, K_2NiF_4 phase can be recognized while for $x=0.95$, single phase of $(\text{Sr,Ca})\text{LaAlO}_4$ solid solution with K_2NiF_4 structure is obtained. Figure 3 shows the XRD patterns of single-phased $(\text{Ca}_{0.05}\text{Sr}_{0.95})\text{LaAlO}_4$ ceramics sintered at 1,450°C in air for 3 h. All the peaks can be assigned to K_2NiF_4 structure. Comparing to the standard JCPD card, the peaks of $\text{Ca}_3\text{Al}_2\text{O}_6$ in calcined and sintered powders all shift slightly to lower angles, which suggests some Sr substitution for Ca in these compositions.

The electron back-scattering is used to confirm the phase constitution. The fractured surfaces are examined by electron back-scattering (Fig. 4). For all compositions from $x=0.75$ to $x=0.95$, the multi-phase constitution is observed. Figure 5 shows the EDS analysis results for the composition $x=0.75$. The large area of gray matrix (spectrum 2) is recognized as $(\text{Ca}_{1-x}\text{Sr}_x)\text{LaAlO}_4$ solid solution with 5.79 mol% Ca^{2+} substitution. The dark areas (spectrum 1) should be characterized as $\text{Ca}_3\text{Al}_2\text{O}_6$ according to XRD analysis (Fig. 2), and 16.95 mol% Sr^{2+} and 4.66 mol% La^{3+} are also detected. There might be some Sr substitution for

Ca in $\text{Ca}_3\text{Al}_2\text{O}_6$, which is in accordance with the peak shift in XRD results. On the other hand, the diffraction scale of the spectrum is around 10 μm [Fig. 5(b)], which might not be small enough to detect the second-phase area because of the nearby Sr and La. The small amount of light spot areas

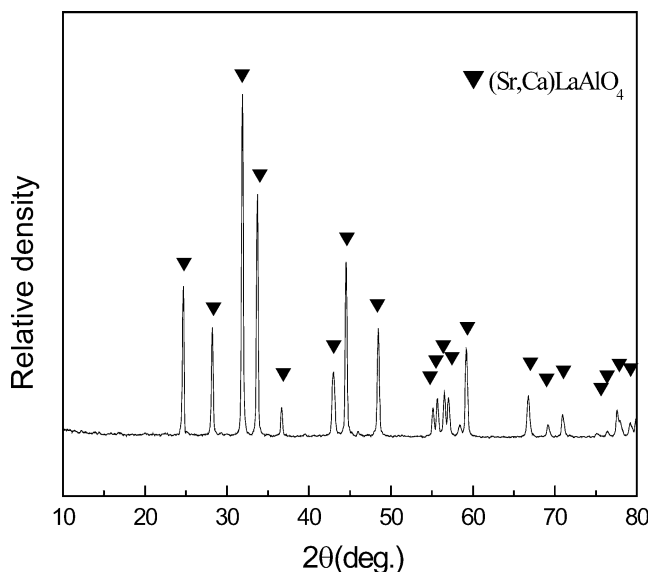
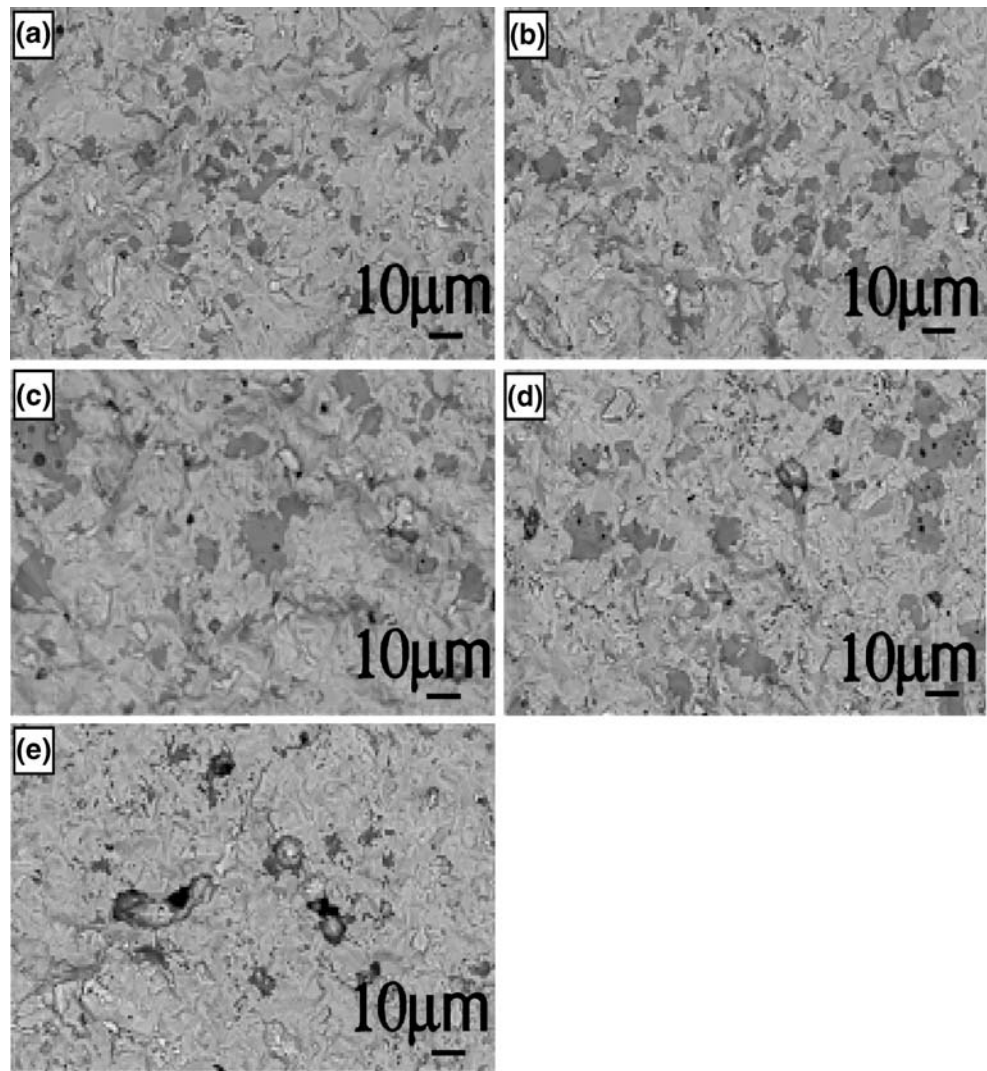


Fig. 3 XRD patterns of $(\text{Ca}_{0.05}\text{Sr}_{0.95})\text{LaAlO}_4$ ceramics sintered at 1,450°C in air for 3 h

Fig. 4 Electron back scattering micrographs of fractured surfaces of $(\text{Ca}_{1-x}\text{Sr}_x)\text{LaAlO}_4$ ceramics sintered at 1,450°C in air for 3 h: (a) $x=0.75$; (b) $x=0.8$; (c) $x=0.85$; (d) $x=0.9$; (e) $x=0.95$



in Fig. 5(a) represents LaAlO_3 phase (spectrum 3). Some Sr and Ca are also observed for the same reasons above. With increasing x , the amount of $\text{Ca}_3\text{Al}_2\text{O}_6$ and LaAlO_3 decreases. When x equals 0.95, only very little $\text{Ca}_3\text{Al}_2\text{O}_6$ is detected [Fig. 4(e)], which is too little for XRD to recognize in Fig. 3. According to the previous tolerance factor analysis, CaLaAlO_4 phase is unstable. However, its stability can be improved by substituting Sr^{2+} for Ca^{2+} . With increasing x , both XRD and electron back-scattering results show the amount of $(\text{Ca}_{1-x}\text{Sr}_x)\text{LaAlO}_4$ solid solution with K_2NiF_4 structure increases, whereas the amount of secondary phases decreases, which represents the improvement of the stability with K_2NiF_4 structure in CaLaAlO_4 .

The microwave dielectric properties of $(\text{Ca}_{1-x}\text{Sr}_x)\text{LaAlO}_4$ ceramics are shown in Figs. 6 and 7. With increasing x , the dielectric constant decreases from 18.4 ($x=0.1$) to 16.7 ($x=0.95$), then increases to 17.1 ($x=1.0$). For these compositions, the multi-phase constitution is observed. The dielectric constants for LaAlO_3 and SrLaAlO_4 are 23.4 and 16.7, respectively [4, 7, 9], whereas the dielectric

constants of CaO and Al_2O_3 are both around 10, which means the dielectric constant of $\text{Ca}_3\text{Al}_2\text{O}_6(3\text{CaO}\cdot 2\text{Al}_2\text{O}_3)$ is much smaller than that of SrLaAlO_4 . So the decline of the curve for $x \leq 0.95$ may attribute to the decrease of LaAlO_3 phase, which is of larger dielectric constant comparing with SrLaAlO_4 . At the same time, when x equals 1.0, the rise of dielectric constant values might be caused by the elimination of $\text{Ca}_3\text{Al}_2\text{O}_6$ phase. The Qf values of $(\text{Ca}_{1-x}\text{Sr}_x)\text{LaAlO}_4$ ceramics are also shown in Fig. 6. Significant increase of Qf values is observed for compositions $0.75 \leq x \leq 1.0$ when the amount of secondary phases decreases. While for $x=0.1$ to $x=0.3$, the major phase changes from LaAlO_3 and $\text{Ca}_3\text{Al}_2\text{O}_6$ mixture to $(\text{Sr}, \text{Ca})\text{LaAlO}_4$ solid solution according to XRD results, which accounts for the Qf increase. However, the slight decrease of Qf values for compositions $0.3 \leq x \leq 0.75$ is still unknown. Interesting change of τ_f is also obtained, which is presented in Fig. 7. From the XRD result, the proportion of LaAlO_3 and $\text{Ca}_3\text{Al}_2\text{O}_6$ secondary phases in the compositions of $0.3 \leq x \leq 1.0$ is very small, which means they contribute

Fig. 5 EDS results for the composition $x=0.75$ of $(\text{Ca}_{1-x}\text{Sr}_x)\text{LaAlO}_4$ ceramics sintered at $1,450^\circ\text{C}/3\text{ h}$

Spectrum 1		
Element	Weight%	Atomic%
O K	24.29	56.27
Al K	11.89	16.32
Ca K	6.27	5.79
Sr L	40.09	16.95
La L	17.46	4.66
Totals	100.00	

Spectrum 2		
Element	Weight%	Atomic%
O K	21.66	59.15
Al K	7.58	12.27
Ca K	3.23	3.52
Sr L	20.72	10.33
La L	46.82	14.73
Totals	100.00	

Spectrum 3		
Element	Weight%	Atomic%
O K	24.71	63.13
Al K	7.63	11.56
Ca K	3.18	3.24
Sr L	17.92	8.36
La L	46.57	13.71
Totals	100.00	

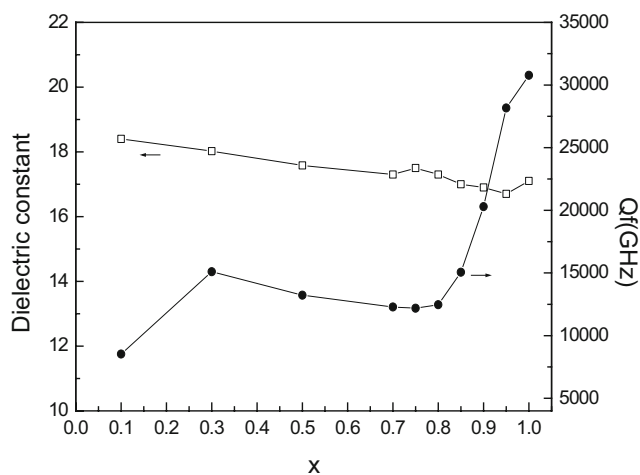
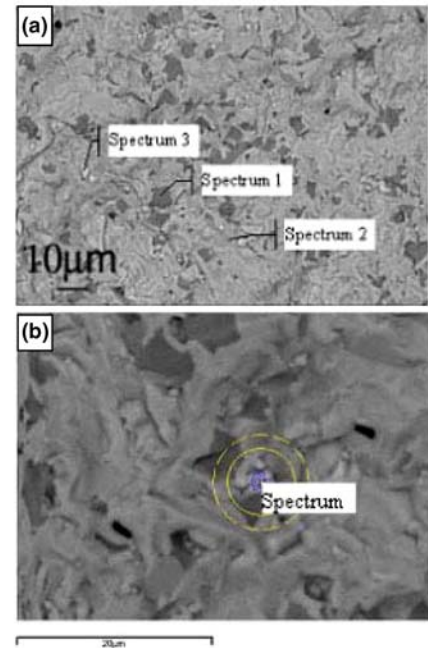


Fig. 6 Microwave dielectric properties of $(\text{Ca}_{1-x}\text{Sr}_x)\text{LaAlO}_4$ ceramics sintered at $1,450^\circ\text{C}$ in air for 3 h

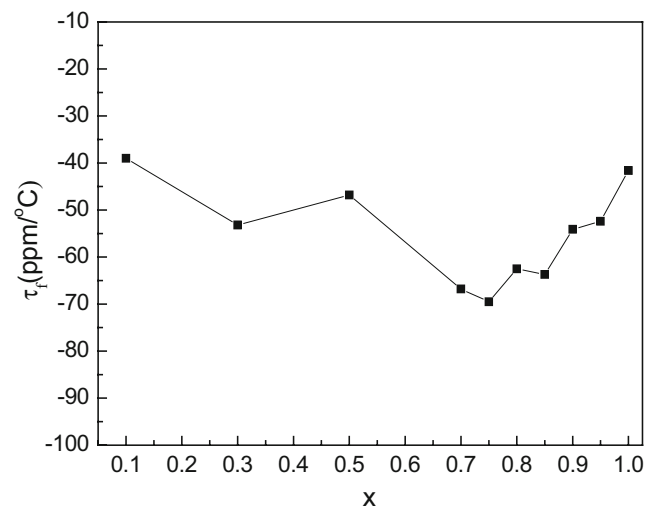


Fig. 7 τ_r of $(\text{Ca}_{1-x}\text{Sr}_x)\text{LaAlO}_4$ ceramics sintered at $1,450^\circ\text{C}$ in air for 3 h

little to τ_f because this value is a combined effect of all the compositions. So the τ_f for $0.3 \leq x \leq 1.0$ is mainly determined by the major phase of (Sr,Ca)LaAlO₄. As for ABCO₄ structure, the τ_f value is mainly decided by the vibration of C site ion that is located at the center of the oxygen octahedra. With increasing x value, the average ionic radius of A/B site also increases, and it can induce larger cell parameters and a larger vibration space for C site ion. When $x=0.75$, the largest C site vibration space may appear, which accounts for the largest τ_f value at this point.

4 Conclusion

The stability of K₂NiF₄ structure in MRAIO₄ (M =Sr and Ca; R =Nd, Sm, and Y) ceramics was discussed, and it was closely related to the $\Delta t\%$ value. Poor stability was found for MRAIO₄ compositions with $\Delta t\% > 4.3\%$, such as CaLaAlO₄ and SrYAlO₄. Solid solution of (Ca_{1-x}Sr_x)LaAlO₄ ceramics were prepared by a solid-state reaction approach to further investigate the stability of CaLaAlO₄. For all compositions, (Ca_{1-x}Sr_x)LaAlO₄ solid solution with K₂NiF₄ structures and LaAlO₃ and Ca₃Al₂O₆ phases were detected. With increasing x values, the amount of K₂NiF₄ structure composition increased, whereas the content of LaAlO₃ and Ca₃Al₂O₆ secondary phases decreased. For (Ca_{0.05}Sr_{0.95})LaAlO₄, only very little second phase of Ca₃Al₂O₆ was detected. In other words, with more Sr substitution, the K₂NiF₄ structure became more stable in CaLaAlO₄. The microwave dielectric characteristics were greatly influenced by the phase constitution. With larger x value and fewer secondary phases, better dielectric properties could be achieved. Good microwave dielectric properties were obtained in (Ca_{0.05}Sr_{0.95})LaAlO₄: $\epsilon=16.7$, $Q_f=28,171$ GHz, $\tau_f=-52.4$ ppm/°C

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