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Sintering behavior and microwave dielectric properties of $Ca_{1-x}Bi_xW_{1-x}V_xO_4$ ceramics

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Abstract

Structure, sintering behavior and microwave dielectric properties of ceramics have been investigated by x-ray powder diffraction (XRD) and scanning electron microscopy (SEM) in this paper. The microwave dielectric properties of the ceramics were studied with a network analyzer at the frequency of about 6–11 GHz. The sintering temperature and microwave dielectric properties could be successfully tuned in a wide window simultaneously by adjusting the A–O bond characteristics. The sintering temperature of $CaWO_4$ was successfully reduced from 1100 °C to about 950 °C by $BiVO_4$ addition. Approximately 95%–96% theoretical density could be obtained after sintering at 950 °C for 2 h. All samples exhibit single Scheelite structure ($I4_1/a$) phase. The dielectric constant increased, whereas the $Q \times f$ value decreased, with the increase of x. The τ_f value changed from negative to positive with the increases of x. Combined excellent microwave dielectric properties with $\varepsilon_r = 22.1$, $Q \times f = 16{,}730$ GHz and $\tau_f = 2.39$ ppm/°C could be obtained after sintered at the 950 °C for 2 h for $x = 0.3$ compositions.

Keywords: C. Dielectric properties; Ceramics

1. Introduction

The Low temperature co-fired ceramic (LTCC) technology has played an important role in the fabrication to meet the requirement of miniaturization and integration for wireless communication. It requires the microwave dielectric ceramics to have a lower sintering temperature than the melting point of inner electrode materials, such as Ag, Cu [1]. Reducing the sintering temperature without affecting the properties is a challenging problem in LTCC material research. Addition of low melting glass either leads to poor microwave dielectric properties or significantly increases the possibility of chemical interaction with the metal electrode due to the presence of complicated phases in the LTCC system. So, a glass-free LTCC material with appropriate microwave dielectric properties are strongly desired for the multilayer structure applications.

In search for new materials with low sintering temperature we look to open crystal structure in which rapid mass diffusions can occur. Scheelite structures appear especially attractive because of their open structures. AWO_4 (A = Ca, Sr, Ba) ceramics with Scheelite structure were found to have excellent microwave dielectric properties ($Q \times f$ value from 30,000 to 100,000 GHz) and relatively low sintering temperature [2–4]. Among them $SrWO_4$ could be sintered below 900 °C. However it was found to be very hygroscopic and properties gradually deteriorated when the ceramics were exposed to humid air [4]. $CaWO_4$ ceramic showed no such degradation of the properties in humid air, but little higher sintering temperature (>1000 °C). Also the temperature coefficient of resonant frequency (τ_f) of $CaWO_4$ ceramic is still too large negative for practical applications. Recently, designing guidelines for glass-free LTCC materials were proposed from the view point of crystal chemistry [5]. The sintering temperature is expected to be reduced by decreasing lattice packing fraction and/or the bond strength or increasing bond covalency. One of the authors successfully reduced the sintering temperatures of $CaWO_4$ to 850 °C by decreasing the bond polarity through the small amount of substitution of Te^{6+} for W^{6+} (10 mol%) without affecting the microwave dielectric

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properties greatly [6]. Both of the sintering temperature and microwave dielectric properties, especially the temperature coefficient of resonant frequency (τ_f), could be tuned in a wide range by substituting $(Nd_{0.5}Li_{0.5})^{2+}$ for Ca^{2+}. Combined excellent microwave dielectric properties with $\varepsilon_r=11.7$, $Q\times f=36700$ GHz and $\tau_f=5.36$ ppm/°C could be obtained for the $x=0.2$ composition after sintering at 825 °C/2 h. And no chemical reaction has been found between the matrix phase and Ag after sintering at 850 °C for 2 h [5].

Since $BiVO_4$ has the similar scheelite structure (Pnca) as $CaWO_4$ which exhibits excellent dielectric properties ($\varepsilon_r=68$, $Q\times f=6\ 500$ GHz @ $f_o=5$ GHz, and $\tau_f=-260$ ppm/°C), and low sintering temperature (below 900 °C) [7]. Yao et al. studied the structure and photocatalyst properties of $Ca_{1-x}Bi_xMo_{1-x}V_xO_4$ ($0\le x\le 1$) [8], and it was found that $CaMoO_4$ and $BiVO_4$ can fully form solid solution in the compositional range. In this paper, therefore, we investigated the structure and microwave dielectric properties of $Ca_{1-x}Bi_xW_{1-x}V_xO_4$ ($0.10\le x\le 0.50$) ceramics. The objective of this paper is to tune the sintering temperature and microwave dielectric properties of $CaWO_4$ in a wide range simultaneously through the substitution of Bi^{3+} for Ca^{2+} and V^{5+} for W^{6+}, respectively. The relationship between the structure and microwave dielectric property of ceramics were also discussed in this paper.

2. Experimental procedure

Powders of $Ca_{1-x}Bi_xW_{1-x}V_xO_4$ with $x=0.10$, 0.20, 0.30, 0.40 and 0.50 were prepared by a solid-state reaction process, from the starting materials including $CaCO_3$ (99.5%), Bi_2O_3 (99.0%), WO_3 (99.0%) and V_2O_5 (99.0%). Stoichiometric mixtures of the starting materials were mixed with ZrO_2 balls in ethanol for 24 h, dried and calcined at 650°C for 2 h. The calcined powders were pulverized again by ball milling. After drying, mixed with 7–10 wt% PVA and sieving, the granulated powders were uniaxially pressed into compacts with 10 mm diameter and 4.5–5.5 mm thickness under a pressure of 100–150 MPa. The compacts were sintered at the temperature ranging from 850 °C to 950 °C for 2 h.

The densities of the ceramics were measured using the Archimedes' method. The phase compositions of the sintered specimens were identified using X-ray powder diffraction (XRD) with Ni-filtered Cu K_α: radiation (Rigaku D/max 2550, Tokyo, Japan). For Rietveld refinement of the x-ray patterns, the powder diffraction data were collected at room temperature with a step size $\Delta 2\theta=0.02°$ over the angular range $5\le 2\theta(°)\le 135$ using monochromatic Cu K_α: radiation (40 kV, 250 mA). The obtained data were refined by the Rietveld method using the WINSCD program [9]. The microstructure of sintered sample was characterized by scanning electron microscopy (SEM, JSM-6700F, Japan). All samples were polished and thermal electron at a temperature that was 100 °C lower than its sintering temperature. Microwave dielectric properties of the sintered specimens were measured at about 6–11 GHz using a network analyzer (Model N5230A, Agilent, Palo Alto, CA). The quality factor was measured using the transmission cavity method. The relative dielectric constant (ε_r) was measured according to the Hakki-Coleman method with the TE_{011} resonant mode, and the temperature coefficient of the resonator frequency (τ_f) was measured using an invar cavity in the temperature range from 20 °C to 80 °C.

3. Results and discussions

Fig. 1 shows the XRD patterns of $Ca_{1-x}Bi_xW_{1-x}V_xO_4$ ($0.10\le x\le 0.50$) ceramics sintered at 900 °C for 2 h. All specimens exhibit single phase with a tetragonal scheelite structure. It is noteworthy that the (004) and (200) diffraction peak monotonically shift to low and high 2θ angle, respectively, with the increase of $BiVO_4$ content,

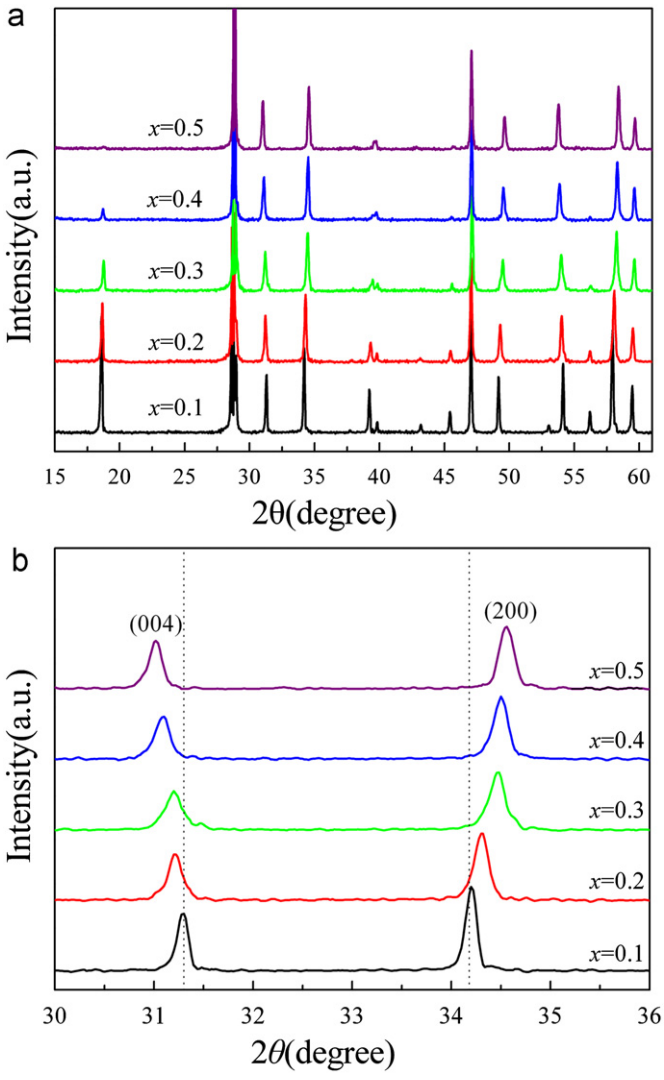

Fig. 1. (a) Powder XRD patterns of $Ca_{1-x}Bi_xW_{1-x}V_xO_4$ ($0.10\le x\le 0.50$) ceramics sintered at 900°C for 2 h; (b) the enlarged part of the $Ca_{1-x}Bi_xW_{1-x}V_xO_4$ XRD patterns ranging from $2\theta=30$–36°.

which is good agreement with that observed by Yao et al [8]. The observed shift of (004) and (200) reflections corresponds to the enlargement of c axis and contraction of a axis, respectively, due to the different effective ionic size ($R_{Ca}2+$(1.12 Å), $R_{Bi}3+$(1.17 Å), R_W6+(0.42 Å) and R_V5+(0.335 Å)) [10] in the solid solutions. In order to clarify the variation of structural evolution, the tetragonal structures of $Ca_{1-x}Bi_xW_{1-x}V_xO_4$ ($x=0.1$, 0.3 and 0.5) ceramics were further verified by the Rietveld refinement of the observed powder XRD profiles. $I4_1/a$ (s) space group was proposed for all compositions. Polynomial function with six-refinable coefficients was used to fit the background. The profiles were described using a Pseudo-Voigt function. The fractional occupancies for all cations were fixed to the stoichiometric composition. The observed, calculated and different profiles for the $x=0.1$, $x=0.3$ and $x=0.5$ compositions are plotted in Fig. 2. Refined crystallographic results and main interatomic distances are given in Table 1 and Table 2, respectively. The unit cell volume decreases slightly, although the length of c axis increases and a axis decreases with the increase of x. The atomic coordinates of oxygen vary with the doping amount of $BiVO_4$ due to the expansion of the Ca/BiO_8 polyhedra and contraction of W/VO_4 tetrahedra caused by the substitution of larger Bi^{3+} for Ca^{2+} and smaller V^{5+} for W^{6+}, respectively. And these oxygen displacements coupled with the presence of lone pair electrons (6s) of Bi^{3+} are responsible for the distortion of Ca/BiO_8 polyhedra in which four shorter and four longer Ca/Bi–O bond distances with respect to the mean values are observed. Noted that the average of Ca/Bi–O bond length (2.415 Å) for the $x=0.1$ composition is smaller than the Shanon ionic radii sum (2.485 Å) [10], whereas those for the $x=0.3$ and $x=0.5$ compositions are larger compared with their corresponding Shanon ionic radii sums. Opposite trend can be observed for the variation of W/V–O interatomic distance with x. It seems to indicate that the Ca/Bi cations in the Ca/BiO_8 polyhedra changed from the compressed state into rattling state, and vice versa for the W/V cations in the tetrahedra, with the increase of x.

The relative densities of $Ca_{1-x}Bi_xW_{1-x}V_xO_4$ ($0.10 \le x \le 0.50$) ceramics sintered at different temperature are shown in Fig. 3. The sintering temperature of $CaWO_4$ could be reduced to 900–950 °C with the addition of $BiVO_4$. Maximum relative density of about 96% could be obtained after sintering at 950 °C for 2 h. Also note that the sinterabilities of the $x=0.2-0.4$ compositions are poorer than those of the $x=0.1$ and $x=0.5$ compositions. As we reported earlier [5], the bond characteristics (bond strength and bond covalency) and crystal packing fraction would affect the sintering temperature and microwave dielectric properties simultaneously. The weaker or more covalent bond or lower packing fraction, the lower is the sintering temperature. The packing fraction increases with the increase of x as shown in Fig. 4, which would increase the sintering temperature. However the bond strength of Ca/Bi–O bond decreases and its bond covalency increases manifested by the variation of bond length and electronegativity with the increase of x ($EN_{Bi}=1.9$, $EN_{Ca}=1.0$), which leads to the decrease of sintering temperature. Therefore, the variation of sintering behavior in this case might result from the combined effect of all of the above factors. It mainly depends on the dominative factor. The comparative poorer sinterabilities of $x=0.2-0.4$ compositions may be mainly associated with the increase in packing fraction in the crystal structure, regardless of the decrease in bond strength and an increase in bond covalency of Ca/Bi–O bond. SEM images of the samples sintered at 900 °C for 2 h are illustrated in Fig. 5. The higher porosity and smaller rain size could be observed for the $x=0.2$–0.4 compositions compared with those of $x=0.1$ and 0.5, which is agreement with the density data shown in Fig. 3. Variation of dielectric permittivity with x is shown in Fig. 6. The calculated dielectric permittivities by C–M equation ($\varepsilon_r = 3V+8\pi\alpha/3V-4\pi\alpha$) are also shown in the figure. The calculated dielectric permittivity increases slightly with increasing x due to the increase of ionic polarizability coupled with the contraction of cell volume according to the C–M equation [11]. However, it is much lower than that measured, and the discrepancy increased considerably with increasing x, which could be ascribed to the rattling effect of Ca/Bi cations in the Ca/BiO_8 polyhedra as discussed above. A similar phenomenon was also found in the case of $(Ca_{1-x}(Nd_{0.5}Li_{0.5})_x)WO_4$ and $(La_{0.5}Na_{0.5})_{1-x}(Nd_{0.5}Li_{0.5})_xWO_4$ system [5,12]. The change of $Q\times f$ value with x is shown in Fig. 7. The

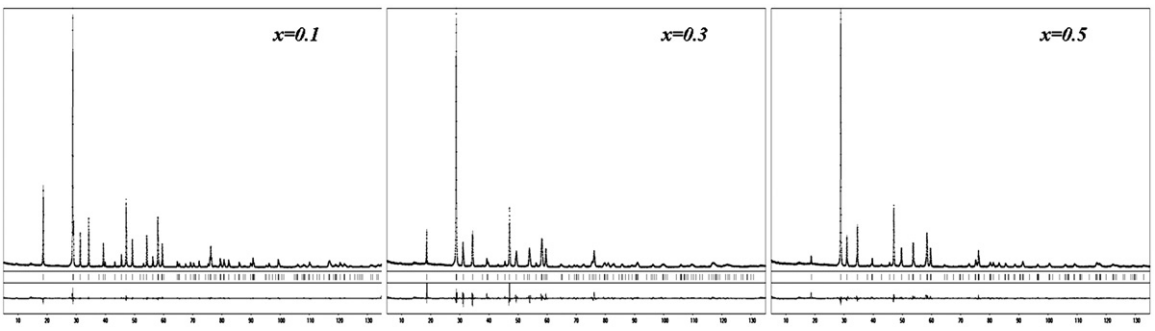

Fig. 2. Observed, calculated and different profiles for the $x=0.1$, $x=0.3$ and $x=0.5$ compositions, respectively.

Table 1
Atomic coordinates and thermal displacement parameters for $Ca_{1-x}Bi_xW_{1-x}V_xO_4$.

Composition	Atom	Site	x/a	y/b	z/c	B (Å^2)	S.O.F
x=0.1	Ca	4b	0.5000	0.0000	0.2500	1.31(10)	0.9
	Bi	4b	0.5000	0.0000	0.2500	1.31(10)	0.1
	W	4a	0.5000	0.0000	0.7500	0.74(2)	0.9
	V	4a	0.5000	0.0000	0.7500	0.74(2)	0.1
	O	16f	0.2591(4)	0.3456(5)	0.1659(2)	0.283(7)	1.0
x=0.3	Ca	4b	0.5000	0.0000	0.2500	2.33(5)	0.7
	Bi	4b	0.5000	0.0000	0.2500	2.33(5)	0.3
	W	4a	0.5000	0.0000	0.7500	0.26(2)	0.7
	V	4a	0.5000	0.0000	0.7500	0.26(2)	0.3
	O	16f	0.2792(11)	0.1368(11)	0.6594(5)	1.8(2)	1.0
x=0.5	Ca	4b	0.5000	0.0000	0.2500	0.50(3)	0.5
	Bi	4b	0.5000	0.0000	0.2500	0.50(3)	0.5
	W	4a	0.5000	0.0000	0.7500	1.16(5)	0.5
	V	4a	0.5000	0.0000	0.7500	1.16(5)	0.5
	O	16f	0.3008(12)	0.0.1449(12)	0.6696(4)	1.72(14)	1.0

Table 2
Rietveld refinement results and bond distances from the X-ray powder diffraction data of $Ca_{1-x}Bi_xW_{1-x}V_xO_4$.

Composition	x=0.1	x=0.3	x=0.5
Volume(Å^3)	312.66(1)	312.64(6)	310.65(3)
a(Å)	5.23407(6)	5.2160(3)	5.1680(2)
c(Å)	11.4128(2)	11.4913(9)	11.5507(5)
Rwp(%)	9.42	20.81	15.63
Rp(%)	6.59	18.40	12.63
Rexp(%)	4.97	5.91	6.19
$d_{Ca/Bi-O}$(Å) × 4	2.41	2.44	2.59
$d_{Ca/Bi-O}$(Å) × 4	2.42	2.61	2.62
$d_{Ca/Bi-O}$(av) (Å)	2.415	2.525	2.605
$R_{Ca/Bi-O}$(Å)	2.485	2.495	2.505
$d_{W/V-O}$(Å) × 4	1.85	1.71	1.58
$R_{W/V-O}$(Å)	1.7735	1.7605	1.7475

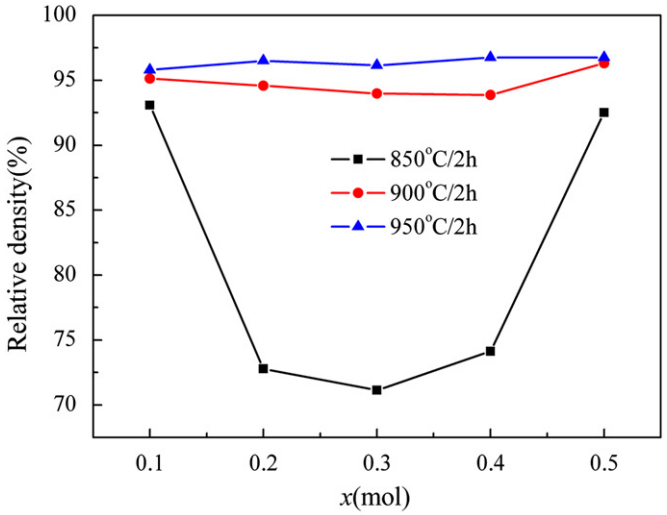

Fig. 3. Variation of relative density as a function of $BiVO_4$ content for the samples sintered at different temperature.

$Q \times f$ value decreases with increasing x at fixed sintering temperature. It is assumed that the intrinsic dielectric loss is mainly dominated by low frequency modes corresponding to Ca/Bi–W/VO_4 vibrations. So the decrease in $Q \times f$ value could be attributed to the decrease in bond strength of Ca/Bi–O bond with the increase of x. Variation of temperature coefficient of resonant frequency (τ_f) as a function of x is shown in Fig. 8. The τ_f value changes from negative to positive with the increase of x. Near-zero τ_f value (2.39 ppm/°C) could be obtained at $x=0.3$ compositions. The variation of τ_f value for ceramics with the tetragonal scheelite structure is found to be related to the variation of their cell volume. The τ_f value increases as the unit cell decreases in the same tetragonal scheelite structure $Ca_{1-x}Bi_xW_{1-x}V_xO_4$, which is similar to that observed by Choi et al. [13].

4. Conclusions

$Ca_{1-x}Bi_xW_{1-x}V_xO_4$ ($0.10 \le x \le 0.50$) ceramics were prepared by the solid-state reaction method. The sintering temperature of $CaWO_4$ has been successfully reduced from 1100 °C to about 950 °C by $BiVO_4$ addition as expected. Approximately 96% theoretical density could be obtained after sintering at 950 °C for 2 h. The variation of sintering behavior with the addition of $BiVO_4$ might result from the combined effect of increase in packing fraction and decrease in bond strength of Ca/Bi–O bond coupled with the increase of its bond covalency. The comparative poorer sinterabilities of $x=0.2$–0.4 compositions can be mainly ascribed to the increase in packing fraction, regardless of the decrease in

bond strength and increase in bond covalency of Ca/Bi–O bond. All samples exhibit single Scheelite structure ($I4_1/a$) phase. The dielectric constant increased, whereas the $Q \times f$ value decreased with the increase of x, which could mainly be ascribed to the rattling effect of Ca/Bi cations in Ca/BiO_8 polyhedra caused by the weakening of Ca/Bi–O bond. The τ_f value changed from negative to positive with the increases of x, and near-zero value of 2.39 ppm/°C could be obtained at

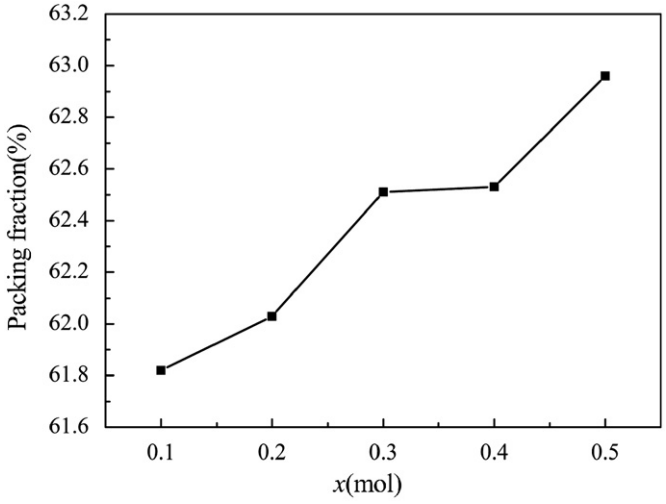

Fig. 4. Change of packing fraction with x.

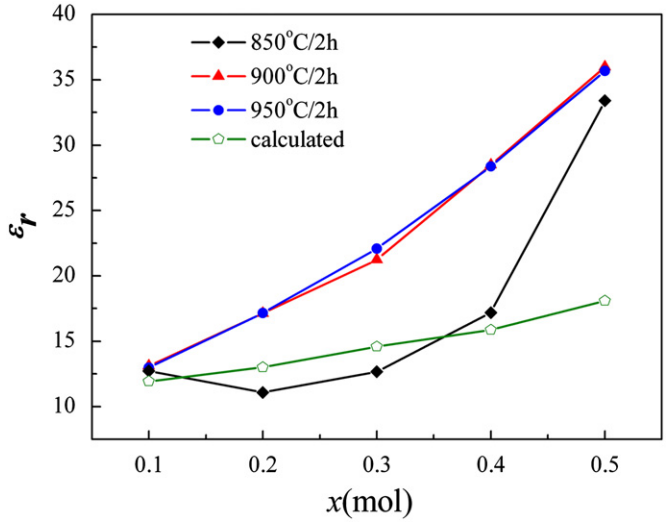

Fig. 6. Variation of dielectric constants as a function of x.

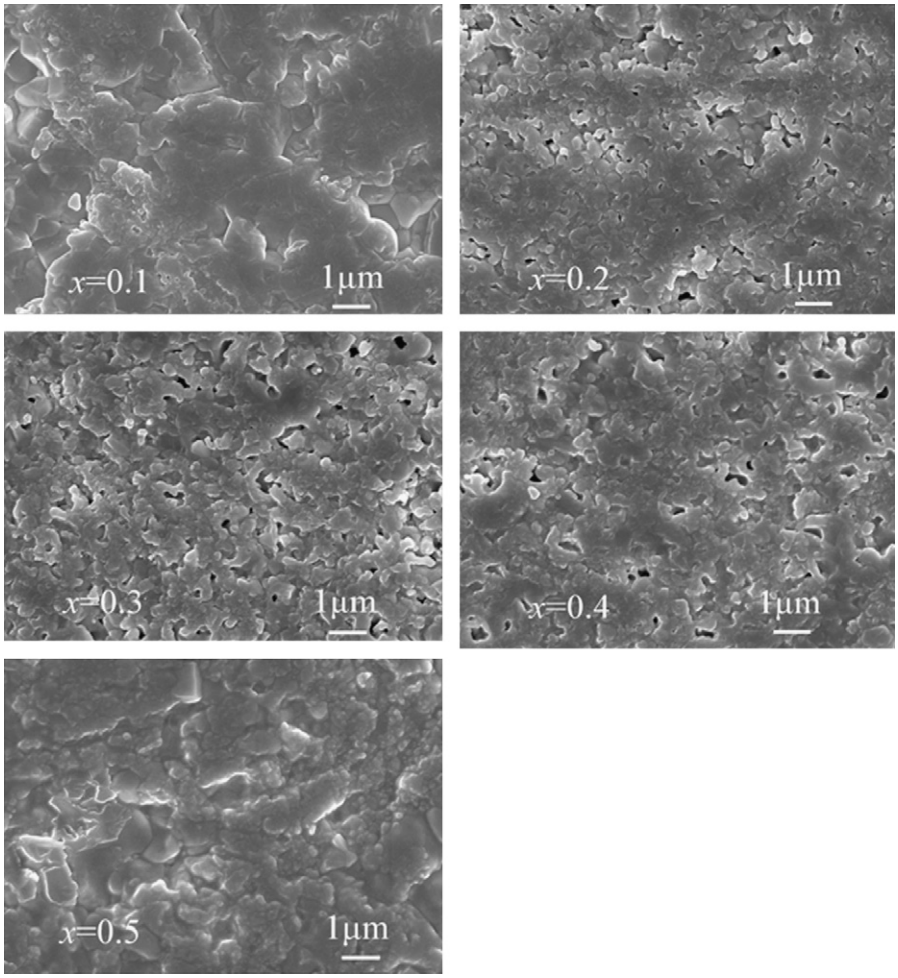

Fig. 5. SEM images of the samples with $x=0.1$–0.5 sintered at 900 °C for 2 h.

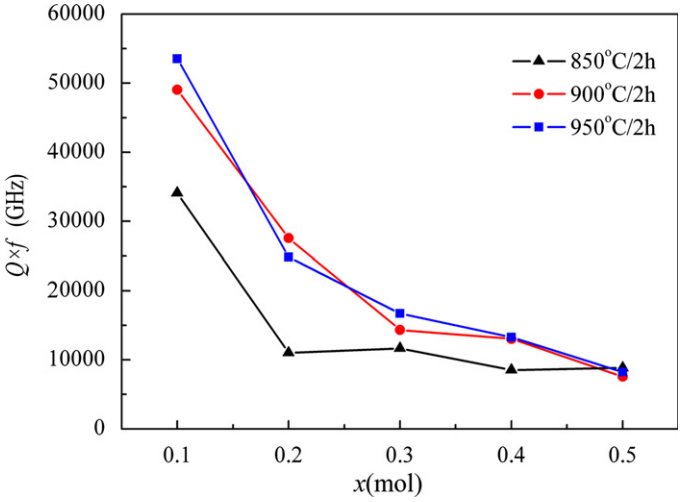

Fig. 7. Variation of $Q \times f$ value as a function of x.

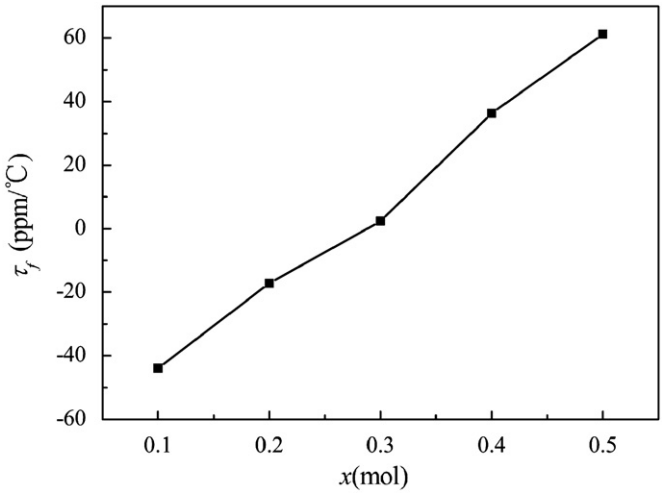

Fig. 8. Variation of τ_f value with x.

$x=0.3$ compositions. Combined excellent microwave dielectric properties with $\varepsilon_r=22.1$, $Q \times f=16{,}730$ GHz ($f_0=8.08$ GHz) and $\tau_f=2.39$ ppm/°C could be obtained after sintered at 950 °C for 2 h.

Acknowledgments

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