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Short communication

Low temperature sintering and microwave dielectric properties of Li_2TiO_3–Li_2WO_4 composite ceramics

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Abstract

$(1-x)Li_2TiO_3$–xLi_2WO_4 composite ceramics could be densified at low temperature (950 °C) by liquid-phase sintering. The phase assemblage, microstructure and chemical compatibility with Ag were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). Microwave dielectric properties were measured with a network analyzer. It was found that Li_2TiO_3 and Li_2WO_4 coexisted after sintering at 950 °C/2 h. Both ε_r and τ_f of the composite ceramics decreased linearly with the increase of Li_2WO_4 phase. The optimized Qf value increased with increasing Li_2WO_4 content and reached a maximum value of about 80,000 GHz at $x=0.1$–0.15. Further increase in x remarkably decreased the Qf value. The 0.15 composition sintered at 950 °C possesses excellent combined microwave properties with $\varepsilon_r=18.1$, $Qf=81{,}099$ GHz and $\tau_f=2.2$ ppm/°C. It indicates that Ag diffused into the Li_2WO_4 phase and formed $(Li,Ag)_2WO_4$ solid solution at 900 °C/2 h, although isolated Ag still existed in the cofired specimen.

Keywords: Composite ceramics; LTCC; Microwave dielectric properties

1. Introduction

Li_2TiO_3 with monoclinic rock salt structure was reported to have microwave dielectric properties of ε_r~22, Qf~63,500 GHz (8.6 GHz), and τ_f~20.3 ppm/°C after sintering at 1300 °C/2 h. The Qf value is considerably improved to about 100,000 GHz and the τ_f value can be tuned to near zero simultaneously by a small amount of MgO or ZnO doping [1,2]. Extensive solid solutions can occur between Li_2TiO_3 and Mg(Zn)O or Li_3NbO_4 [1–3]. Both of the ordering degree and the temperature of the order–disorder transition decrease with the increase of MgO or Li_3NbO_4 content [1,3]. However high porosity remains in the pure or doped Li_2TiO_3 ceramic in our previous studies [1–3], which is detrimental to its practical applications. Doping with appropriate amount of LiF coupled with lithium excess could lead to the remarkable reduction of sintering temperature (~900 °C/2 h) and porosity. Optimized microwave dielectric properties with ε_r of ~22.8, Qf of ~63,000 GHz and τ_f of ~1.0 ppm/°C could be obtained for the sample sintered at 900 °C/2 h [4]. The improvement of sinterability could be attributed to the synergetic effect from the weakening of bond strength by the LiF doping and liquid phase sintering originated from the transient presence of Li_2CO_3. The ceramic was compatible with Ag powders after sintering at 900 °C/2 h. Thus, it can be used as a promising glass-free microwave dielectric material for LTCC applications.

Addition of another phase with opposite τ_f value and low sintering temperature to form composite ceramic is another effective way to compensate the τ_f value and reduce the sintering temperature simultaneously. The chemical compatibility between two phases is desired to achieve the τ_f value compensation. Two phases with different crystal structure are usually chosen to restrict the formation of solid solution. Li_2WO_4 with the phenacite structure was reported to have ε_r~5.5, Qf~62,000 GHz, and τ_f~−146 ppm/°C after sintering at 640 °C [5]. One can expect that a dielectric composite material with a near-zero τ_f value and low sintering temperature could be obtained by combining Li_2TiO_3 with Li_2WO_4.

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Therefore, the chemical compatibility between two phases, sintering behavior and microwave dielectric properties of Li_2TiO_3–Li_2WO_4 composite ceramic have been investigated in this paper.

2. Experimental procedure

Starting materials including Li_2CO_3 (99.9%), TiO_2 (99.7%) and WO_3 (99.6%) were used. Phase pure Li_2TiO_3 and Li_2WO_4 were separately synthesized using the solid-state reaction process by firing at 800 °C/2 h and 500 °C/2 h, respectively. The $(1-x)Li_2TiO_3$–xLi_2WO_4 mixtures were then prepared from pure Li_2TiO_3 and Li_2WO_4 with different mole ratios ($x=0.05$–0.2). The mixtures were ball milled in ethanol with zirconia milling media for 24 h. The slurries were dried, then mixed with 7 wt%–10 wt% PVA as binder and granulated. The granulated powders were uni-axially pressed into compacts 10 mm in diameter and 4.5–5.5 mm in height under the pressure of 100 Mpa. The pellets were sintered at 850 °C to 1000 °C for 2 h. The sintering temperature was optimized by the maximum bulk density and Qf value. In order to prevent lithium evaporation during the sintering, the compacts were covered with sacrificial powder of the same composition. The chemical compatibility with silver was investigated by cofiring the mixed powders with pure silver powders (30 wt% Ag) in ambient atmosphere at temperatures of 900 °C for 2 h.

The phase compositions of the sintered specimens were identified by X-ray powder diffraction with Ni-filtered Cu Kα radiation (Rigaku D/max2200, Tokyo, Japan). The bulk densities of the sintered samples were measured by the Archimedes' method. The relative densities of specimens were obtained from the bulk densities and the theoretical densities. The theoretical density was calculated by the following equation:

$$\rho=\frac{\omega_1+\omega_2}{\omega_1/\rho_1+\omega_2/\rho_2} \tag{1}$$

where ρ_1 and ρ_2 are the theoretical densities of Li_2TiO_3 and Li_2WO_4 (3.43 g/cm^3 for Li_2TiO_3 phase and 4.56 g/cm^3 for Li_2WO_4), respectively; ω_1 and ω_1 are mass fractions of Li_2TiO_3 and Li_2WO_4, respectively.

The microstructures of the sintered samples were observed by scanning electron microscopy (TESCAN VEGA 3 LMU) equipped with an energy dispersive spectrometer (EDS). All the samples were polished without thermally etched. Microwave dielectric properties of the sintered specimens were measured at about 7–11 GHz using a network analyzer (model N5230A, Agilent, Palo Alto, CA). The quality factor was measured by the transmission cavity method. The relative dielectric constant was measured according to the Hakki–Coleman method with the TE_{011} resonant mode, and the temperature coefficient of the resonator frequency were measured using invar cavity at the temperature range from 20 °C to 80 °C.

3. Results and discussion

Fig. 1 shows the powder XRD patterns of $(1-x)Li_2TiO_3$–xLi_2WO_4 composite ceramics sintered at 950 °C for 2 h. All the main peaks could be indexed in terms of Li_2TiO_3 (JCPDS #33-0831) and Li_2WO_4 (JCPDS #12-0760), and no trace of the impurity phase existed. This suggests that no chemical reaction between Li_2TiO_3 and Li_2WO_4 has occurred. The crystal structure of Li_2TiO_3 is monoclinic C2/c, and Li_2WO_4 is rhombohedra R-3, respectively [6,7]. The big difference in crystal structure and good stability of both phases limited the reaction between Li_2TiO_3 and Li_2WO_4.

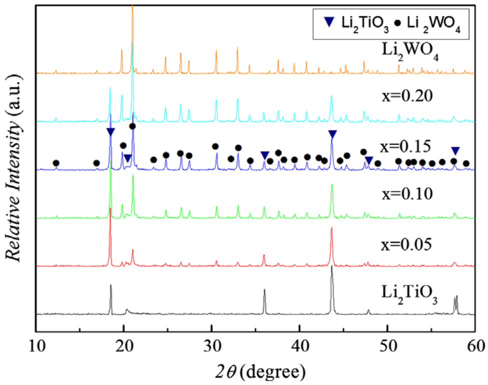

Fig. 1. XRD powder patterns of $(1-x)Li_2TiO_3$–xLi_2WO_4 ($0.05\leq x\leq 0.2$) ceramics sintered at 950 °C for 2 h.

Fig. 2(a) shows the backscattered scanning electron images of $(1-x)Li_2TiO_3$–xLi_2WO_4 ceramics sintered at 950 °C for 2 h. Note that all specimens exhibited two distinct phase grains. The EDS analysis (Fig. 2(b)) shows that the dark ones are Li_2TiO_3 (marked 1 in Fig. 2(a)) and the light-colored grains are Li_2WO_4 (marked 2 in Fig. 2(a)), which is in well agreement with the XRD result. Lithium could not be detected by EDS due to its light atomic mass. No interdiffusions of the cations were observed from the EDS analysis. The plate like grains of the Li_2TiO_3 phase is caused by preferred oriented grain growth due to its layer-ordered crystal structure. It is reported that Li_2WO_4 congruently melts at 742 °C [8]. The sintering temperature in this case is above the melting point of Li_2WO_4. So, liquid phase sintering is supposed to be occurred during the sintering process of $(1-x)Li_2TiO_3$–xLi_2WO_4 composites. It is well known that extensive densification could occur if the solid solubility in liquid is high, but the reverse solubility of the liquid in the solid is low. This ensures that the liquid is not transient. In the case of $(1-x)Li_2TiO_3$–xLi_2WO_4 system the mass transport of lithium in Li_2TiO_3 goes through the liquid phase of Li_2WO_4 by a solution-precipitation method, and thus promotes the sintering. The Li_2WO_4 liquid phase crystallized again during the cooling process. Note also that the grain size of Li_2TiO_3 phase and density of the composite increased with the increase of Li_2WO_4 phase content. Grains of Li_2TiO_3 phase which has a much higher sintering temperature did not develop very well for the $x=0.05$ composition at the sintering temperature of 950 °C/2 h due to the low amount of liquid phase and inhomogeneity. The increase of Li_2WO_4 liquid phase amount accelerated the grain growth and sintering process. However larger amount of liquid phase caused abnormal grain growth (Fig. 2(a), image D). Fig. 3 shows the variation of relative density with x. The relative density

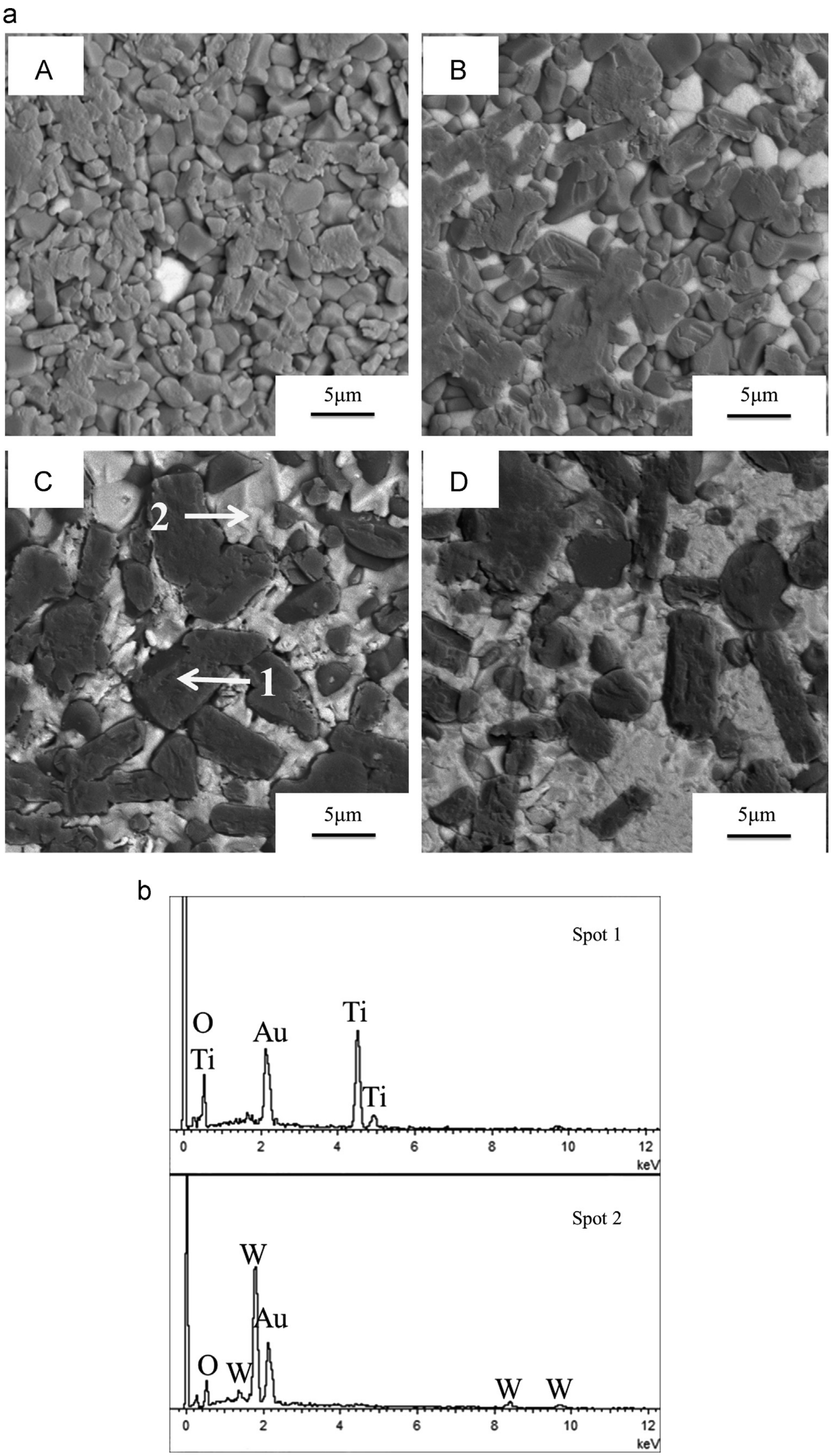

Fig. 2. (a) Backscattered electron images of $(1-x)Li_2TiO_3$–xLi_2WO_4 ($0.05 \leq x \leq 0.2$) ceramics sintered at 950 °C for 2 h: (A) $x=0.05$, (B) $x=0.10$, (C) $x=0.15$, and (D) $x=0.20$ and (b) EDS analysis of $x=0.15$ composition.

increased with the increase of Li_2WO_4 content up to $x=0.1$ and then slightly decreased with the further increase of x. At low liquid contents of Li_2WO_4 ($x=0.05$) the solid skeleton inhibited the densification, which resulted in the lower density of $x=0.05$ composition. With the increase in liquid content of Li_2WO_4, high density could be achieved via rearrangement of grains upon liquid formation. On the other hand, higher content of liquid phase caused abnormal grain growth as shown in (image D), which resulted in the decrease in density.

Variations of dielectric permittivities of $(1-x)Li_2TiO_3$–xLi_2WO_4 with x are shown in Fig. 4. It can be seen that ε_r decreased linearly with the increase of Li_2WO_4 phase which has much lower dielectric permittivity (ε_r~5.5) compared with that of Li_2TiO_3 (ε_r~22). The variation of dielectric permittivity in this case is obviously controlled by the mechanical mixture law. Fig. 5 shows the variation of Qf value with x. The Qf value depends on sintering temperature for the fixed composition. The optimized Qf value increased with increasing Li_2WO_4 content and reached a maximum value of about 80,000 GHz at $x=0.1$–0.15. Further increase in x remarkably decreased the Qf value. Note that the maximum Qf values of the composite at $x=0.1$–0.15 are higher than those of end members ($Qf=63{,}500$ GHz for Li_2TiO_3 and 62,000 GHz for Li_2WO_4). The improvement of Qf values for the $x=0.1$–0.15 compositions can be ascribed to the increase of density and improvement of microstructure as shown in Figs. 2(a) and 3. Higher sintering temperature and/or larger amount of Li_2WO_4 liquid phase accelerated the sintering process as described above, which is expected to increase the density and thus improve the Qf value. On the other hand, however, the increase in sintering temperature and/or amount of Li_2WO_4 liquid phase led to the increase in evaporation of lithium and degradation of microstructure due to the abnormal grain growth, which deteriorated the Qf value. The total Qf value was affected by the above two competing factors. The change of τ_f value of $(1-x)Li_2TiO_3$–xLi_2WO_4 ceramic sintered at 950 °C/2 h is shown in Fig. 6. The τ_f value changed from positive into negative with the increase of Li_2WO_4 phase content and a near-zero τ_f value of 2.2 ppm/°C could be obtained at $x=0.15$ composition.

The chemical compatibility with silver was investigated by co-firing the mixed powders with pure silver powders (30 wt% Ag) in ambient atmosphere at temperatures of 900 °C for 2 h. The XRD pattern of the $x=0.15$ composition co-fired with Ag at 900 °C/2 h is shown in Fig. 7. For comparison, the XRD patterns of $x=0.15$ composition and the mixtures between Ag and the end members cofired at 900 °C/2 h are also appended here. The strong reflections from silver, Li_2WO_4 and Li_2TiO_3 phases could be identified easily. No Ag_2WO_4 or $Ag_2W_2O_7$

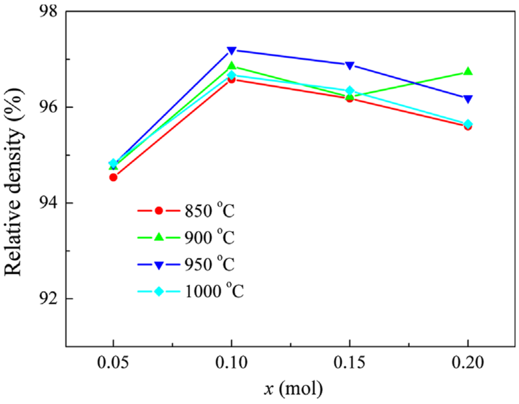

Fig. 3. Change of relative densities of $(1-x)Li_2TiO_3$–xLi_2WO_4 ($0.05\leq x\leq0.2$) ceramics sintered at different temperatures with x.

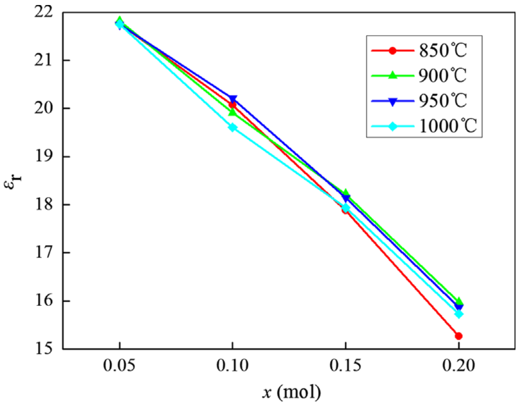

Fig. 4. Variation of dielectric permittivities of $(1-x)Li_2TiO_3$–xLi_2WO_4 ($0.05\leq x\leq0.2$) ceramics with x.

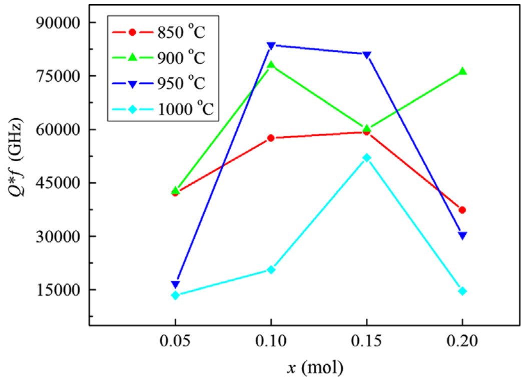

Fig. 5. Variation of Qf value of $(1-x)Li_2TiO_3$–xLi_2WO_4 ($0.05\leq x\leq0.2$) ceramics with x.

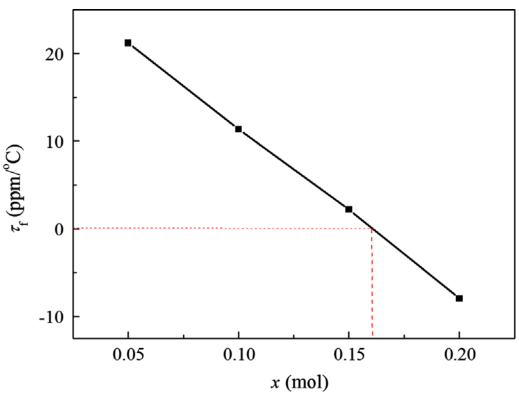

Fig. 6. Variation of τ_f value of $(1-x)Li_2TiO_3$–xLi_2WO_4 ($0.05\leq x\leq0.2$) ceramics with x sintered at 950 °C for 2 h.

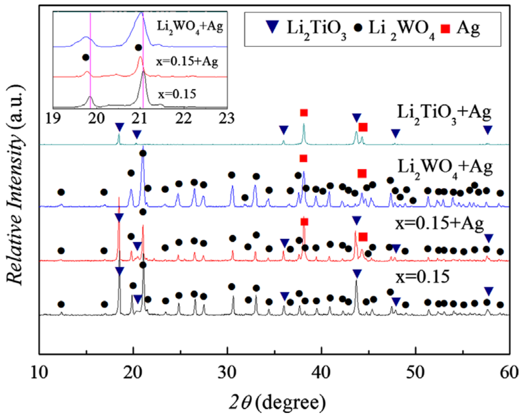

Fig. 7. XRD patterns of the $x=0.15$ composition co-fired with Ag at 900 °C/2 h. (For comparison, the XRD patterns of $x=0.15$ composition and the mixtures between Ag and the end members cofired at 900 °C/2 h are also appended here.)

phase was detected within the experimental limitation, which seems to show that no chemical reaction has taken place between the matrix phase and Ag. The XRD patterns of the mixtures between Ag and the end members cofired at 900 °C/2 h also revealed no impurity phase. However, the reflections from Li_2WO_4 shifted to low angle for the mixture with Ag cofired at 900 °C/2 h compared with that without Ag (Fig. 7 inset). It seems to imply the substitution of Ag for Li, which caused the little expansion of the lattice cell volume due to the comparatively larger size of Ag^+ than that of Li^+ (($R(Li^+)=0.92$ Å, $R(Ag^+)=1.28$ Å) [9]. Fig. 8 shows the backscattered SEM image and corresponding EDS analysis of the $x=0.15$ composition co-fired with Ag at 900 °C/2 h. Isolated Ag was detected, which is consistent with the XRD result in Fig. 7. However, trace amount of Ag, coupled with the matrix element, were detected in the matrix. It implies that some Ag entered the matrix structure. Since no chemical reaction was detected between Ag and Li_2TiO_3 phase after co-firing at 900 °C/2 h as indicated by XRD shown in Fig. 7. The diffusion of Ag into the Li_2TiO_3 phase could be excluded. Although the chemical compatibility between Ag and Li_2WO_4 phase after cofiring at 640 °C was confirmed [5], higher cofiring temperature would increase the possibility of chemical reaction between Ag and Li_2WO_4 phase. Therefore Ag diffused into the Li_2WO_4 phase and formed solid solution at the cofiring temperature of 900 °C/2 h, which is consistent with the XRD analysis in Fig. 7.

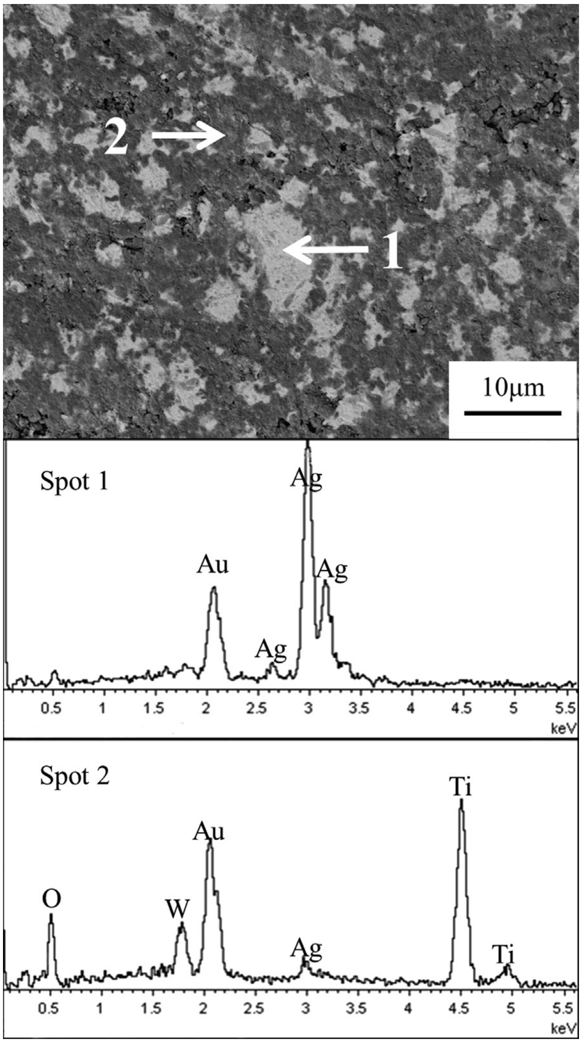

Fig. 8. Backscattered SEM image and corresponding EDS analysis of $0.85Li_2TiO_3$–$0.15Li_2WO_4$ composition co-fired with Ag at 900 °C/2 h.

4. Conclusions

Li_2TiO_3 could be successfully densified after sintering at 950 °C by adding Li_2WO_4 phase. A composite ceramic with mixture phases of Li_2TiO_3 and Li_2WO_4 could be obtained. The dielectric permittivity decreased and the τ_f value changed from positive into negative with increasing Li_2WO_4 phase content. The $x=0.15$ composition sintered at 950 °C exhibited excellent combined microwave dielectric properties with near-zero τ_f value of 2.2 ppm/°C, high Qf value of 81,099 GHz and ε_r value of 18.1. The chemical compatibility of the $x=0.15$ composition with silver (Ag) powders was also investigated. Some Ag would diffuse into the Li_2WO_4 phase and formed solid solution at 900 °C/2 h, although isolated Ag still existed in the cofired specimen.

Acknowledgments

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