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Microwave dielectric properties in the $Li_{4+x}Ti_5O_{12}$ ($0 \le x \le 1.2$) ceramics

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Abstract

Microwave dielectric ceramics, with a $Li_{4+x}Ti_5O_{12}$ ($0 \le x \le 1.2$) formula, were prepared using a conventional solid-state reaction method. The effects of doping amount on the phase stability, microstructure and microwave dielectric properties were investigated. The XRD analysis showed that at $x = 0$, pure $Li_4Ti_5O_{12}$ could not be obtained but with trace amount of TiO_2 as a secondary phase, while single phase of the $Li_4Ti_5O_{12}$ solid solution was formed in x range of 0.2 to 0.4. The $Li_4Ti_5O_{12}$ and Li_2TiO_3 coexisted in the compositions with $0.6 \le x \le 1.2$ and the amount of Li_2TiO_3 phase increased with increasing doping concentration. The microwave dielectric properties were strongly dependent on the sintering temperature and composition. A near-zero τ_f of +2.7 ppm/°C along with a $Q\times f$ of 36,000 GHz and a ε_r of 25.1 was obtained in $x = 1.2$ sample sintered at 1000 °C. Moreover, promising low temperature co-fired ceramic (LTCC) materials with thermal stability and chemical compatibility with silver can be obtained in the $x = 1.2$ sample with 0.5 wt% B_2O_3 addition sintered

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at 940 °C. This material has good microwave dielectric properties with ε_r of 28.0, $Q \times f$ of 32,000GHz and τ_f of -7.8 ppm/°C.

Keywords: Microwave dielectric properties; Cubic spinel structure; LTCC

1. Introduction

In recent years, the increasing demands for miniaturization and portability of electronic devices have revolutionized wireless communication [1-3]. The LTCC technology has become an irreplaceable approach in the development of various modules and substrates due to its ability to integrate the various passive components to a three-dimensional modules with embedded silver or copper electrodes [4,5]. To qualify as a commercially viable candidate as microwave ceramic, the crucial requirements are: a lower sintering temperature than the melting point of the inner metal electrode (< 960 °C for silver); a suitable relative permittivity; a high quality factor to improve the transmission quality; a near-zero temperature coefficient of resonant frequency ($\tau_f \sim 0$ ppm/°C) for temperature stability [6]. Besides, chemical compatibility, compactness, light weight, and low cost are also important figure of merits from practical application point of view.

Li-contained oxides have attracted wide attention as LTCCs due to their low sintering temperatures and high dielectric performance. For example, the rock-salt structured Li_2TiO_3 ceramics sintered in temperature range of 1100-1300 °C had ε_r = 20-24, $Q \times f$ = 20,000-70,000 GHz, and τ_f = +20-+40 ppm/°C [7-10]. And its positive τ_f value was successfully used to adjust the thermal stability of several dielectric ceramics with negative τ_f values [11,12]. More recently, some Li-based spinel microwave dielectric ceramics, such as $Li_4Ti_5O_{12}$, $Li_2Zn_3Ti_4O_{12}$ and $Li_2ZnTi_3O_8$ have been reported [13-15]. Among them, the $Li_4Ti_5O_{12}$ ceramic has been extensively investigated for LTCC application because of its relatively low sintering temperature (~ 930 ^oC) and encouraging microwave dielectric properties (ε_r = 18.5-30.1, $Q\times f$ = 9,200-29,530 GHz and τ_f = -10.4--15 ppm/^{o}C [13,16].

It is reported that the vaporization of Li in Li-containing ceramics at elevated sintering temperatures is inevitable and harmful to the microwave dielectric properties [17]. For example, owing to the volatilization of Li, pure $Li_4Ti_5O_{12}$ was difficult to obtain through the stoichiometric mixture of Li_2O and TiO_2 [18]. Zuo [16] *et.al* reported that by adjusting the molar ratio of Li:Ti to 4.08:5 through reducing the concentration of TiO_2, single phase $Li_4Ti_5O_{12}$ could be obtained. In this work, the $Q\times f$ values of the Li-excess samples (67,926 GHz for $Li_{4.08}Ti_5O_{12}$) were significantly enhanced compared to the stoichiometric $Li_4Ti_5O_{12}$ sample with $Q\times f$ = 9,200 GHz. On the other hand, in the binary phase diagram of Li_2O-TiO_2, by increasing the molar ratio of Li, the Li_2TiO_3 phase appeared and co-exist with $Li_4Ti_5O_{12}$ within 4.3:5 to 9.6:5 of Li:Ti ratio range [19]. Considering the opposite sign of their τ_f values, it is expected that near zero τ_f value can be achieved by the formation of Li_2TiO_3 in $Li_4Ti_5O_{12}$ through excess of Li_2O addition. In present work, the $Li_{4+x}Ti_5O_{12}$ ($0 \leq x \leq 1.2$) ceramics were prepared and B_2O_3 is used as sintering aid to lower the sintering temperature. Chemical compatibility between the $Li_{4+x}Ti_5O_{12}$ ($0 \leq x \leq 1.2$) ceramics and silver was also studied.

2. Experimental procedure

The $Li_{4+x}Ti_5O_{12}$ ($0 \leq x \leq 1.2$) and Li_2TiO_3 were prepared by conventional solid-state reaction technique using high-purity starting reagents of Li_2CO_3 and TiO_2 (99.99%). The mixed oxides were ball-milled for 4 h in nylon jars with zirconia balls using alcohol as a medium. The wet mixture were rapidly dried and calcined at 900 ^oC for 4 h and then ball-milled again for 4 h. The calcined sample $x = 1.2$ was reground with 0.5 wt% B_2O_3. These resulting slurries were dried and reground with PVA as binder. The granulated powders were pressed into 10 mm-diameter disks at a uniaxial pressure of 200 MPa. The samples were first heated at 550 ^oC for 4 h for debinding and then sintered at various temperatures in ambient atmosphere. The sample $x = 1.2$ with 0.5 wt% B_2O_3 sintered at 940 ^oC for 4 h was crushed and then reground with 15 wt% Ag. The mixed powder was pressed into small disks and then sintered at 940 ^oC for 2 h.

The phase composition of the sintered ceramics was confirmed by an X-ray diffractometer (XRD; Model X'Pert PRO, PANalytical, Almelo, the Netherlands) and a Raman spectrometer (DXR; Thermo Fisher Scientific, American). The bulk densities of the specimen were measured with the Archimede's method. To observe grain morphology, the polished and thermal etched surfaces of as-fired ceramics (fired 25 ^oC below the optimized sintering temperature) were examined by scanning electron microscopy (SEM; JSM6380-LV, JEOL, Tokyo, Japan). Microwave dielectric properties of the sintered ceramics were measured using a network analyzer (N5230A, Agilent Co., Palo Alto, California) and a temperature chamber (Delta 9039; Delta

Design, San Diego, California). The τ_f values were calculated with the following formula:

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

where, f_1 and f_2 represent resonant frequencies at temperatures T_1 and T_2, respectively.

3. Results and discussion

Fig. 1 shows the room-temperature XRD patterns recorded on the sintered $Li_{4+x}Ti_5O_{12}$ ceramics at their relative optimum temperatures. The nominal sample (x = 0) exhibited the cubic $Li_4Ti_5O_{12}$ phase and trace amount of rutile TiO_2 phase (marked as solid heart-shaped symbol) with no other phases containing Li or Ti detected. It is believed that the existence of TiO_2 was attributed to the volatilization of Li, resulting in the deviation of the molar ratio of Li:Ti from 4:5. This is similar to the earlier reports [16,19]. When x increased to 0.4, the peaks belonging to TiO_2 disappeared and only the diffraction peaks of the $Li_4Ti_5O_{12}$ could be observed within the limitation of XRD. It is expected that the addition of Li successfully compensated the Li volatilization, leading to the formation of the single phase $Li_4Ti_5O_{12}$. However, beyond x = 0.4, another phase with a main peak around 44^o (as shown in the enlarged profile) appeared and detected as monoclinic β-Li_2TiO_3 with a C2/c space group. The formation of Li_2TiO_3 is because of the excess of Li after compensation and can be expressed by the following reaction: $Li_4Ti_5O_{12} + 3Li_2O = 5Li_2TiO_3$ [20]. Besides, the intensity of diffraction peaks of the Li_2TiO_3 phase increased with increasing x, indicating that the Li_2TiO_3 content increased. Herein, Rietveld refinement was employed to calculate the content ratio of the Li_2TiO_3 phase and the results is listed on

Table 1. The content ratio of the Li_2TiO_3 increased from 10.1 mol % at x = 0.6 to 25.3 mol % at x = 1.2.

To further confirm the phase composition, the Raman spectroscopy was utilized. Fig. 2 shows the Raman spectra of the $Li_{4+x}Ti_5O_{12}$ ceramics in the wavenumber range of 100-1000 cm^{-1}. The samples with $x \leq 0.4$ exhibited main Raman bands at 224, 275, 347, 419, and 665 cm^{-1}, which are the characteristic modes of the pure spinel $Li_4Ti_5O_{12}$ ceramic [21]. The peak at 665 cm^{-1} (A_{1g} mode) is assigned to the vibration of TiO_6 octahedral. The peak at 419 cm^{-1} (E_g mode) is involving stretching bending vibration of LiO_4 tetrahedral. It is reported that two main Raman peaks at 609 and 406 cm^{-1} are assigned as A_{1g} and E_g modes for the TiO_2 rutile, respectively [18]. For the x = 0 sample, characteristic Raman peaks from TiO_2 were invisible, possibly because of the modes broadening and overlapping. With further increasing x from 0.6 to 1.2, two additional bands around 284 and 392 cm^{-1} were observed, which were reported to be the characteristic bands from the Li_2TiO_3 phase [17]. This result further indicates the formation the Li_2TiO_3 phase.

The SEM micrographs of the polished and thermal etched surfaces of the $Li_{4+x}Ti_5O_{12}$ ceramics sintered at their optimum temperature are illustrated in Fig. 3. For all compositions, dense microstructures with few pores can be observed, suggesting the high densification when sintered at optimum temperatures. Moreover, with increasing Li addition, the amount of porosity gradually decreased. Obviously, for the x = 0.2 and 0.4 sample, only one grain morphology with plate-like shape was observed. However, the microstructure of the x = 0.6 ceramic is characterized by a bimodal grain morphology consisting of small columnar grains (spot 2) embedded in a matrix of large plate-like grains (spot 1). The EDS analysis (shown in the inset of Fig. 3) verified that the Ti:O ratio of spot 1 and spot 2 was different, which was closed to that of the $Li_4Ti_5O_{12}$ and Li_2TiO_3, respectively. Similar grain morphology and distribution were reported for some spinel-rock salt composites [11,12,22]. Further, the grain size and the amount of the second phase increased as x increased. Those results conform to the XRD and Raman analysis.

Fig. 4 depicts the bulk density and microwave dielectric properties of the $Li_{4+x}Ti_5O_{12}$ ceramics at their optimum temperature as function of x. The bulk density first increased to a maximum value (3.26 g/cm^3) at x = 0.4 and then decreased. The increase of bulk density was the result from the formation of the pure-phase $Li_4Ti_5O_{12}$ as suitable excess of Li not only compensated for the volatilization of Li but greatly promoted the sintering behavior. Due to the smaller density of the Li_2TiO_3 (3.14 g/cm^3) than $Li_4Ti_5O_{12}$, the bulk density almost linearly decreased from 3.23 g/cm^3 to 3.18 g/cm^3 as x increased from 0.6 to 1.2. It is obvious that microwave dielectric performances were affected by compositions, which was primarily ascribed to density and impurity. As $0 \leq x \leq 0.4$, the permittivity and $Q\times f$ value were enhaced because of the improved density, and the τ_f value decreased owing to the disappearance of impurity TiO_2, which has a large positive τ_f value about +465 ppm/^{o}C [16].

It is well known that many factors affect the microwave dielectric properties which can be classified into two aspects, the intrinsic factors (lattice vibration) and extrinsic ones (e.g. second phases, densification, and grain size, etc) [23]. Especially, the second phases exert a vital role in adjusting the relative permittivity and thermal stability of resonance frequency. Several models have been proposed to predict the effective permittivity of a bi-phase system, such as Maxwell-Garnett rule, Bruggeman rule and Lichtenecker logarithmic rule [24-26]. Among them, the Lichtenecker formula is usually applied to calculate the microwave permittivity of composite ceramics. Thus, in the present work, in the range of $0.6 \leq x \leq 1.2$ with Li_2TiO_3 as a second phase, the Lichtenecker empirical logarithmic rule were used to calculate the permittivity of the $Li_4Ti_5O_{12}$-Li_2TiO_3 composite [27]:

$$\log \varepsilon = X_1 \log \varepsilon_1 + X_2 \log \varepsilon_2 \qquad (2)$$

where X_1 and X_2 are the volume fractions ($X_1 + X_2 = 1$); ε_1 and ε_2 are the relative permittivity of the pure $Li_4Ti_5O_{12}$ and Li_2TiO_3 ceramics. The results are given on Table 2. As expected, as x increased from 0.6 to 1.2 the calculated permittivity of the $Li_4Ti_5O_{12}$-Li_2TiO_3 composites decreased monotonously from 26 to 25.2 due to the smaller permittivity of Li_2TiO_3 (ε_r = 21.9), which agrees well with the measured values.

The theoretical τ_f values of the two-phase composite ceramics are calculated by the empirical linear rule [28]:

$$\tau_f = X_1 \tau_{f1} + X_2 \tau_{f2} \qquad (3)$$

where X_1 and X_2 are the volume fractions; τ_{f1} and τ_{f2} are the τ_f value of the pure $Li_4Ti_5O_{12}$ and Li_2TiO_3 phase, respectively. The $Li_4Ti_5O_{12}$ has a negative τ_f of -15.6 ppm/^{o}C, while the Li_2TiO_3 has a large positive of τ_f of +39.6 ppm/^{o}C. As expected, the calculated τ_f value of the composite ceramics gradually increased from -10 ppm/^{o}C at

x = 0.6 to -1.6 ppm/°C at x = 1.2. The variation tendency is consistent with that of the measured value and a near-zero τ_f of 2.7 ppm/°C is obtained at x = 1.2.

The $Q\times f$ value is sensitive to many factors, especially the extrinsic ones, such as porosity, defects, second phases, densification, and grain size and distribution, etc. As observed, in the whole addition range, the $Q\times f$ value increased remarkably from 9,000 GHz at x = 0 to 36,000 GHz at x = 1.2. It is anticipated that Li compensation depressed defects and improved densification, resulting in the enhancement in the $Q\times f$ value. In addition, due to the high sintering temperature of pure Li_2TiO_3, the sintering temperature of the $Li_4Ti_5O_{12}$-Li_2TiO_3 increases as the x value rises. The higher sintering temperature is also favorable for densification. For samples with x > 0.4, the increase in the $Q\times f$ value might partly related to the higher $Q\times f$ value of the pure Li_2TiO_3 (42,000 GHz) than that of the $Li_4Ti_5O_{12}$ (30,000 GHz).

Although the ceramic x = 1.2 sintered at 1000 °C has excellent microwave dielectric properties, the high sintering temperature restricts its cofiring with silver electrodes for LTCC application. A small amount of B_2O_3 addition (0.5 wt%) could effectively lower the sintering temperature to 940 °C. The B_2O_3 addition did not affect the phase composition of the ceramic x = 1.2 and no other phase can be identified from the XRD patterns (seen in Fig. 5 (b)). Compared with the counterpart without B_2O_3 addition, the ε_r value increased from 25.1 to 28 probably because of the improved density, and the τ_f value shifted towards the negative direction, decreasing from 2.7 ppm/°C to -7.8 ppm/°C. Considering the small amount of B_2O_3 addition, the $Q\times f$ value slightly decreased from 36,000 GHz to 32,000 GHz. The excellent combination of microwave dielectric properties with ε_r = 28.0, $Q \times f$ = 32,000 GHz and τ_f = -7.8 ppm/°C (listed on Table 2) were obtained.

To investigate the chemical compatibility with metal electrodes, 15 wt% Ag was mixed into the sample powder x = 1.2 with 5 wt% B_2O_3 addition. The XRD patterns of the cofired sample is illustrated in Fig. 5 (a). Except the peaks of the $Li_4Ti_5O_{12}$ and Li_2TiO_3, the peaks of Ag can also be observed, indicating that there are no chemical interactions between Ag and the ceramic x = 1.2 with 0.5 wt% B_2O_3. The BSE image and EDS analysis of the cofired sample are shown in Fig. 6. The bright grain (Spot A) was confirmed as Ag, which had a highly visible grain boundary in the matrix ceramics. The results further confirm that Ag did not react with neither $Li_4Ti_5O_{12}$ nor Li_2TiO_3. Therefore, it is reasonable to conclude that the x = 1.2 ceramic with 0.5 wt% B_2O_3 sintered at 940 °C for 4 h could be a promising candidate for LTCC application, because of its low sintering temperature, promising microwave dielectric properties, chemical compatibility with Ag, light weight, and low cost.

4. Conclusions

Novel microwave dielectric ceramics $Li_{4+x}Ti_5O_{12}$ ($0 \leq x \leq 1.2$) were prepared by conventional solid-state reaction method. The phase evolution, sintering behavior, microstructure, and microwave dielectric properties were systematically investigated. The XRD, EDS and Raman analysis show that the pure spinel $Li_4Ti_5O_{12}$ solid solutions were obtained at x = 0.2 to x = 0.4, while TiO_2 appeared as a secondary phase at x = 0 and another phase Li_2TiO_3 appeared with further increasing x beyond

0.4. The quality factor of the ceramics within $0 \leq x \leq 0.4$ improved greatly with appropriate excessive amount of lithium. Moreover, the τ_f values could be adjusted to near zero. The ceramic with $x = 1.2$ sintered at 1000 °C has a relative permittivity (ε_r) of 25.1, a quality factor ($Q\times f$) of 36,000 GHz, and a temperature coefficient of frequency (τ_f) of +2.7 ppm/°C. The relationship between microwave dielectric properties and their compositions were investigated. We also studied their chemical compatibility with silver in consideration of LTCC applications.

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Table 1 Phase compositions, calculated ε_r and τ_f value of $Li_{4+x}Ti_5O_{12}$ ($0.6 \leq x \leq 1.2$) ceramics.

x	$Li_4Ti_5O_{12}$ (mol%)	Li_2TiO_3 (mol%)	ε_r (calculated)	τ_f (calculated) (ppm/℃)
0.6	89.9	10.1	26	-10
0.8	83.9	16.1	25.7	-6.7
1	78.1	21.9	25.4	-3.5
1.2	74.7	25.3	25.2	-1.6

Table 2 Sintering temperature, bulk density and microwave dielectric properties of $Li_{4+x}Ti_5O_{12}$ ($0 \leq x \leq 1.2$) ceramics.

x	*S.T.*(℃)	ρ (g/cm^3)	ε_r	$Q\times f$ (GHz)	τ_f (ppm/℃)
0	930	3.07	25.8	9000	-8.1
0.2	960	3.19	27.0	26000	-16.2
0.4	980	3.26	26.5	30000	-15.6
0.6	980	3.23	26	32000	-13.5
0.8	980	3.2	25.4	34000	-9.8
1	1000	3.19	25.2	35000	-5.2
1.2	1000	3.18	25.1	36000	2.7
1.2+0.5%B_2O_3	940	3.28	28.0	32000	-7.8
Li_2TiO_3	1150	3.14	21.9	42000	39.6

Figure Caption:

Fig. 1. X-ray patterns of the sintered $Li_{4+x}Ti_5O_{12}$ ($0 \leq x \leq 1.2$) ceramics.

Fig. 2. Raman spectra of the $Li_{4+x}Ti_5O_{12}$ ($0 \leq x \leq 1.2$) ceramics.

Fig. 3. SEM micrographs of the $Li_{4+x}Ti_5O_{12}$ ($0 \leq x \leq 1.2$) ceramics sintered at optimum temperature: (a) x = 0.2, (b) x = 0.4, (c) x = 0.6, (d) x = 0.8, (e) x = 1, and (f) x = 1.2 (the inset is the EDS results of spot 1 and 2).

Fig. 4. The variation in (a) bulk density,(b) permittivity, (c) $Q\times f$ and (d) τ_f of $Li_{4+x}Ti_5O_{12}$ ceramics at their optimum temperature as function of x.

Fig. 5. The XRD patterns of (a) x = 1.2 sample with 0.5 wt% B_2O_3 sintered at 940 ^oC for 4 h and (b) x = 1.2 sample with 0.5 wt% B_2O_3 cofired with 15 wt% Ag at 940 ^oC for 2 h.

Fig. 6. The BSE image (a) and EDS analysis (b) of sample x = 1.2 with 0.5 wt% B_2O_3 cofired with 15 wt% Ag at 940 ^oC for 2 h.

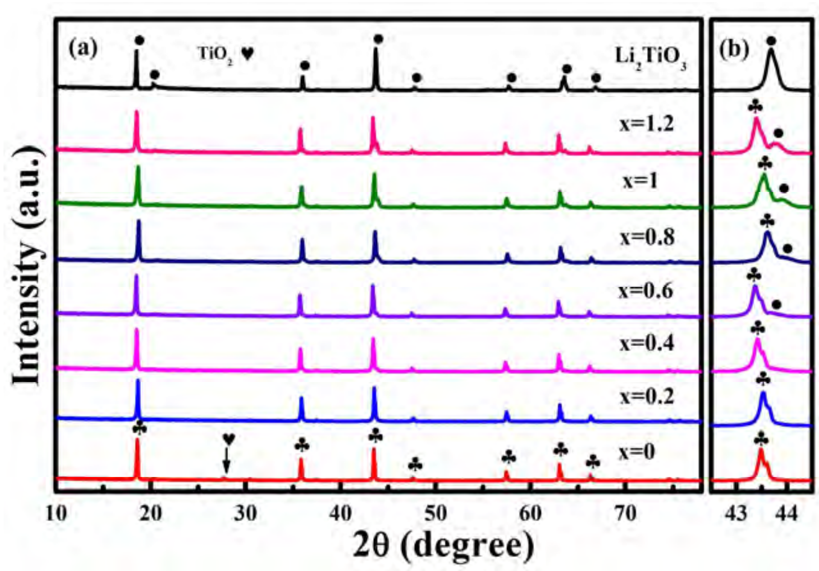
(a)
TiO2 ♥
Li2TiO3
x=1.2
x=1
x=0.8
x=0.6
x=0.4
x=0.2
x=0
Intensity (a.u.)
10
20
30
40
50
60
70
2θ (degree)
(b)
43
44

Fig. 1.

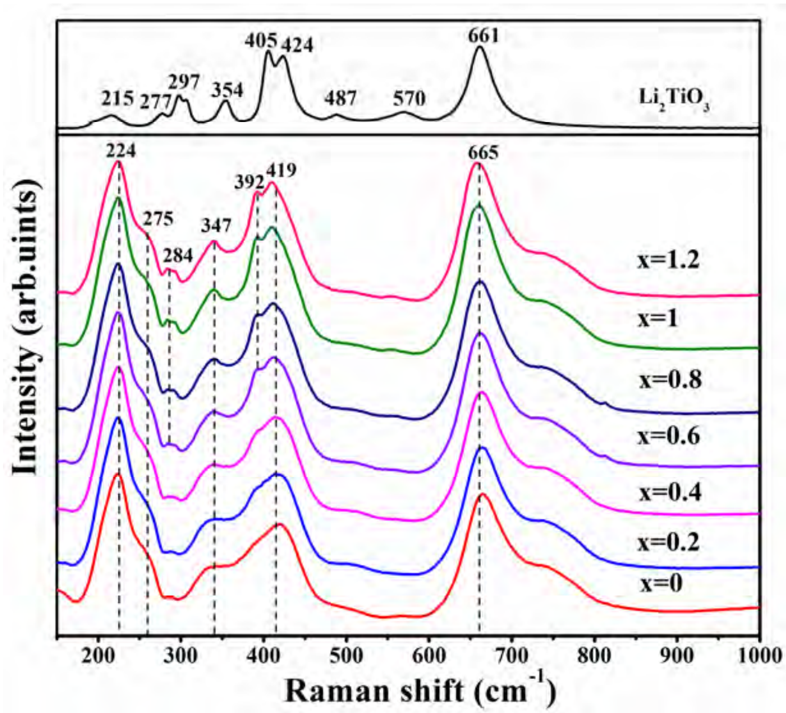
215
277
297
354
405
424
487
570
661
Li2TiO3
224
275
284
347
392
419
665
x=1.2
x=1
x=0.8
x=0.6
x=0.4
x=0.2
x=0
Intensity (arb.uints)
200 300 400 500 600 700 800 900 1000
Raman shift (cm-1)

Fig. 2.

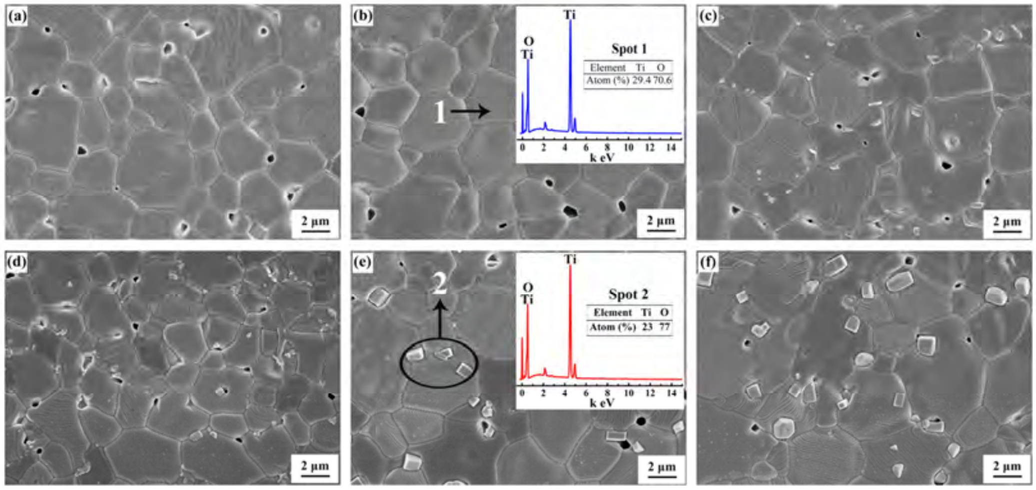
(a)
2 μm
(b)
1
Ti
O
Ti
Spot 1
Element Ti O
Atom (%) 29.4 70.6
0 2 4 6 8 10 12 14
k eV
2 μm
(c)
2 μm
(d)
2 μm
(e)
2
Ti
O
Ti
Spot 2
Element Ti O
Atom (%) 23 77
0 2 4 6 8 10 12 14
k eV
2 μm
(f)
2 μm

Fig. 3.

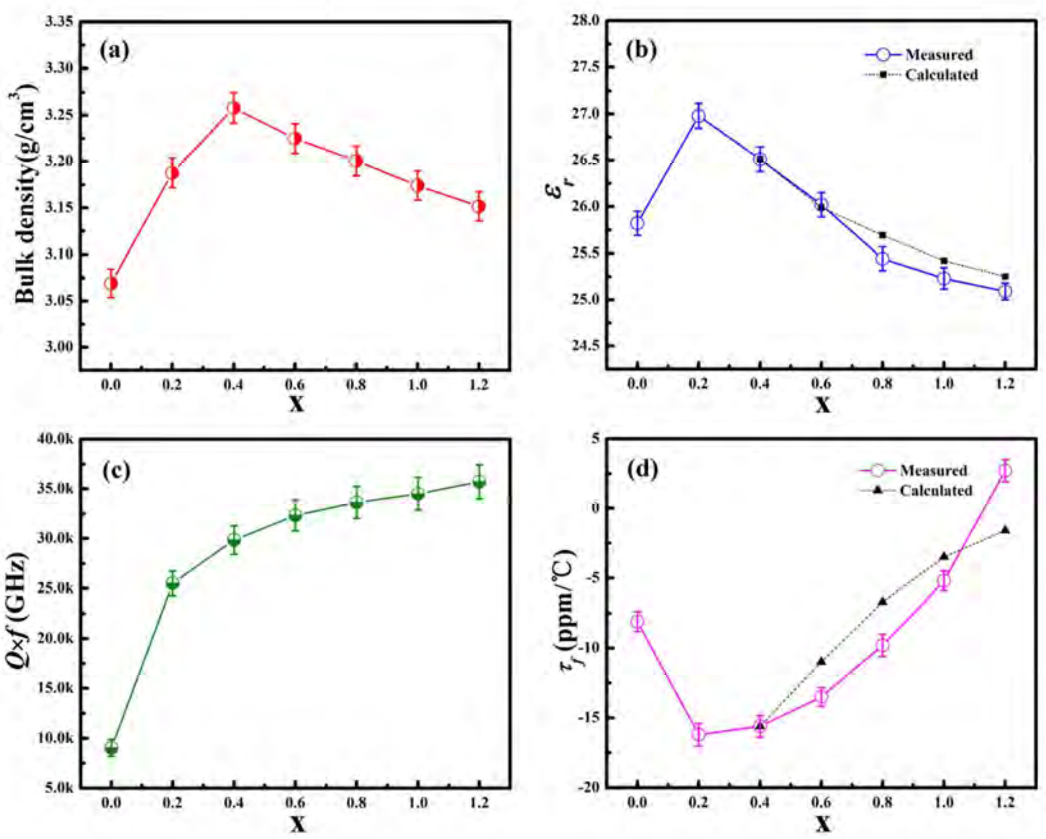
(a)
Bulk density(g/cm3)
X
(b)
Measured
Calculated
εr
X
(c)
Q×f (GHz)
X
(d)
Measured
Calculated
τf (ppm/℃)
X

Fig. 4.

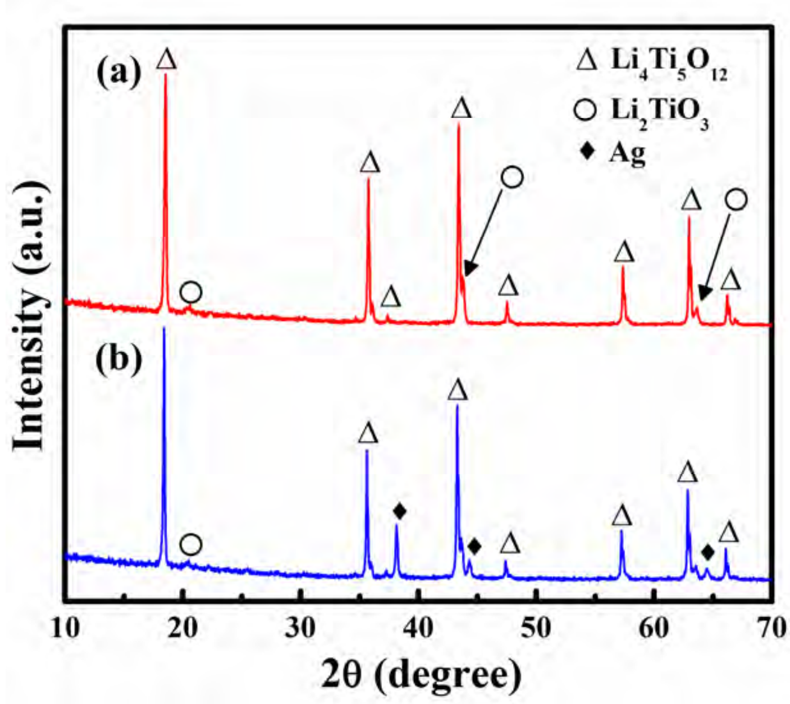
(a)
(b)
Δ Li4Ti5O12
○ Li2TiO3
♦ Ag
Intensity (a.u.)
10
20
30
40
50
60
70
2θ (degree)

Fig. 5.

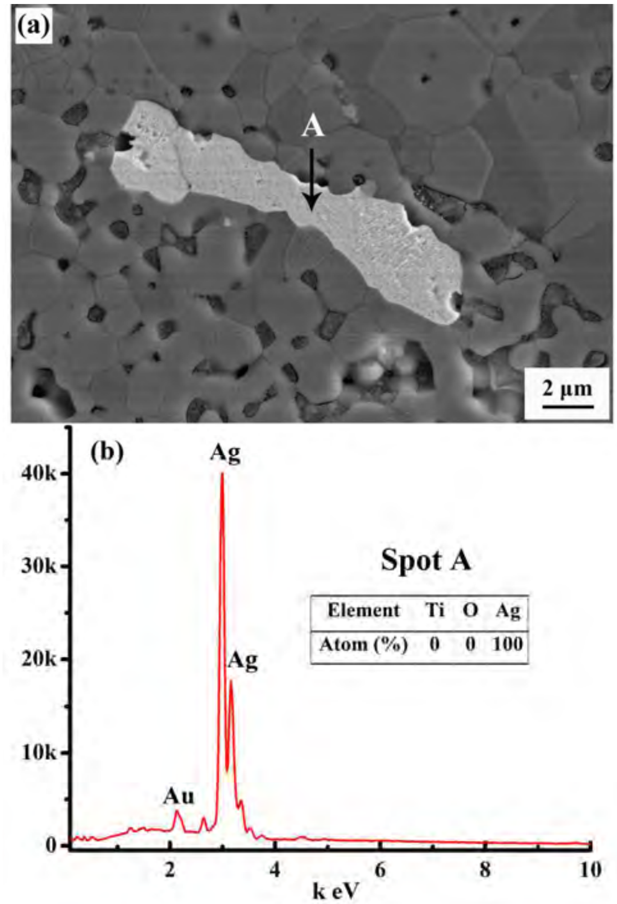
(a)
A
2 µm
(b)
Ag
Ag
Au
Spot A
Element Ti O Ag
Atom (%) 0 0 100
40k
30k
20k
10k
0
2
4
6
8
10
k eV

Fig. 6.

1. Dense and single phase $Li_4Ti_5O_{12}$ ceramics were obtained through appropriate amount of Li addition.

2. $Li_4Ti_5O_{12}$ and Li_2TiO_3 coexisted to form composite ceramics with near zero τ_f values and high quality factor.

3. The sintering temperature of $Li_{4+x}Ti_5O_{12}$ ceramics could be lowered with small amount of B_2O_3.

4. Chemical compatibility between $Li_{4+x}Ti_5O_{12}$ and silver electrode was confirmed.