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Pseudo Phase Diagram and Microwave Dielectric Properties of Li_2O–MgO–TiO_2 Ternary System

Yi-Ding Zhang[‡] and Di Zhou[‡,§,¶,†]

[‡]Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China

[§]Xi'an Jiaotong University Suzhou Academy, Suzhou, Jiangsu 215123, China

[¶]Department of Materials Science and Engineering, University of Sheffield, Sheffield S1 3JD, UK

Li_2O–MgO–TiO_2 ternary system is an important microwave dielectric ceramic material with excellent properties and prospect in both scientific research and application. A phase diagram of the Li_2O–MgO–TiO_2 ternary system was established in this article, based on earlier research results and our present work. Microwave dielectric properties with compositions in different regions of the phase diagram have been analyzed. We found that the 0.33 $Li_2MgTi_3O_8$–0.67 Li_2TiO_3 ceramics sintered at 1200°C exhibited excellent dielectric properties: $Q \times f$ value = 80 476 GHz (at 7.681 GHz), ε_r = 24.7, τ_f = +3.2 ppm/°C. We also designed two ceramic systems in the Li-rich region of the Li_2O–MgO–TiO_2 ternary system, which received little attention in the past decades, because many excellent single-phase ceramics, such as Li_2MgTiO_4, $Li_2MgTi_3O_8$ and $MgTiO_3$, have been found in the Ti-rich region. The ceramic systems have low sintering temperatures but also relatively poor dielectric properties.

Keywords: *dielectric materials/properties; phase diagrams; oxides*

I. Introduction

Since 1980s, modern wireless communication technology has witnessed unprecedented prosperity and it greatly promoted the research and application on the microwave dielectric ceramic materials. Generally, a dielectric ceramic material is judged with three key properties: high $Q \times f$ value, zero temperature coefficient at resonant frequency (TCF or τ_f) and high relative dielectric constant (ε_r). Dielectric ceramics with such excellent properties have been widely used in resonator, filter, duplexer, multiplexer, and other microwave or wireless devices.[1,2]

The Li_2O–MgO–TiO_2 (indexed as LMTO) ternary system is an important microwave dielectric ceramic system. It is derived from the Li_2O–ZnO–TiO_2 ternary system (indexed as LZTO), which was earned extensive investigation. In 1996, Hernandez et al.[3] first reported Li_2O–ZnO–TiO_2 ternary phase diagram at 1100°C, in which they studied different compositions of the Ti-rich region. Figure 1 shows a revised version of Hernandez's original phase diagram. The marked line on the left denotes the spinel-structured solid solution (spinel ss) between Zn_2TiO_4 and $Li_4Ti_5O_{12}$. The other two marked lines in the graph indicate the rock-salt-structured solid solution.

A few single-phase ceramics in the LZTO system, such as $Li_2ZnTi_3O_8$ and $Li_2Zn_3Ti_4O_{12}$, were found to possess high $Q \times f$ values (over 70 000 GHz) and relatively small TCF values (about −10 to −40 ppm/°C).[4,5] Researchers then tried to replace Zn^{2+} with other divalent ions, such as Mg^{2+} or Co^{2+}, to achieve even higher $Q \times f$ values.

Recently, various Li_2O–MgO–TiO_2 ceramics have been reported to possess high $Q \times f$ values, near-zero τ_f values or low sintering temperatures, but an overall LMTO ternary diagram has not been available. Therefore, we have attempted to make a comprehensive understanding on the Li_2O–MgO–TiO_2 ternary system. With the literature data, combined with our experimental results, we established a pseudo phase diagram for the LMTO system. Microwave dielectric properties and compositions in different regions of the phase diagram will be discussed. In addition, we found a couple of excellent ceramic samples in recent study, whose dielectric properties and the microstructures were analyzed and discussed in the paper.

II. Experimental Procedure

Ceramic samples were prepared using the conventional ceramic route as previously described.[1,2] The samples were divided into two groups, Ti-rich group and Li-rich group, for which calcination temperature is 600°C and 1000°C, respectively. After re-milling, powders were pressed into cylinders with binder addition. Li-rich samples were sintered at the temperature ranges from 600°C to 800°C for 4 h, while Ti-rich samples were sintered from 1150°C to 1300°C for 4 h.

Crystalline structures were identified using X-ray diffraction (XRD) with Cu-K_α radiation (Rigaku D/MAX-2400 X-ray diffractometer, Tokyo, Japan). Microstructures were studied using scanning electron microscopy (SEM) (JSM-6460, JEOL, Tokyo, Japan). Bulk densities were obtained through the Archimedes method. Dielectric properties at microwave region were measured using $TE_{01\delta}$ method with a network analyzer (8720ES, Agilent, Palo Alto, CA) and a programmable temperature chamber in 25°C–85°C. Temperature coefficient of resonant frequency (τ_f) was calculated as follows:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25}(85 - 25)} \times 10^6 \text{ppm/}^\circ\text{C}, \quad (1)$$

where f_{85} and f_{25} were the $TE_{01\delta}$ resonant frequencies at 85°C and 25°C, respectively.

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[†]Author to whom correspondence should be addressed. e-mail: zhoudi1220@gmail.com

III. Results and Discussion

Figure 2 demonstrates single-phase ceramics in the LMTO ternary system. Dielectric properties of these ceramics are listed in Table I.[6–15] Except TiO_2, they have dielectric constants (at microwave frequencies) ranging from 17 to 27. $Q \times f$ values of the ceramics are all above 40 000 GHz, with the highest value to be 160 000 GHz. TiO_2 has a very large positive τ_f of +465 ppm/°C, $Li_2MgTi_3O_8$ has a low τ_f of +3 ppm/°C, and Li_2TiO_3 has a medium positive

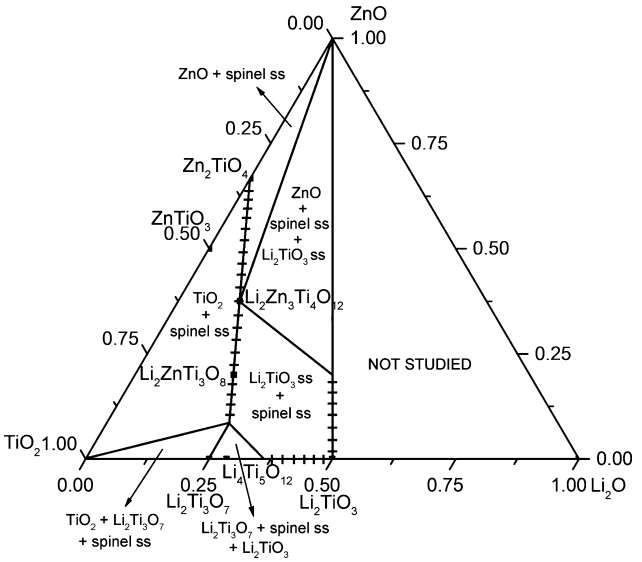

Fig. 1. Revised version of Hernandez's original LZTO pseudo phase diagram.[1]

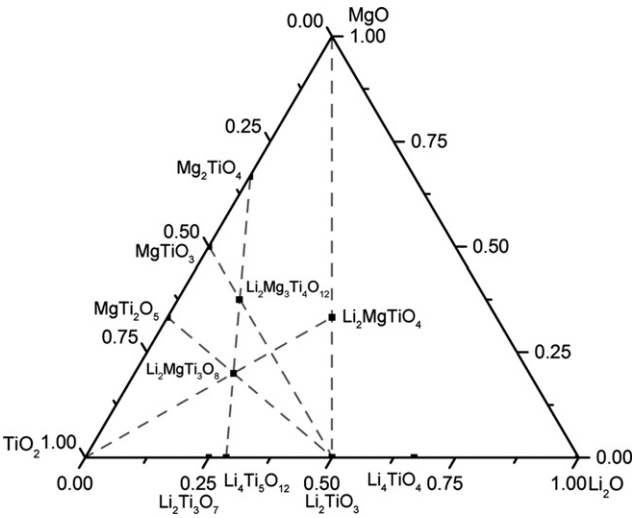

Fig. 2. The single-phase ceramics in the LMTO ternary system.

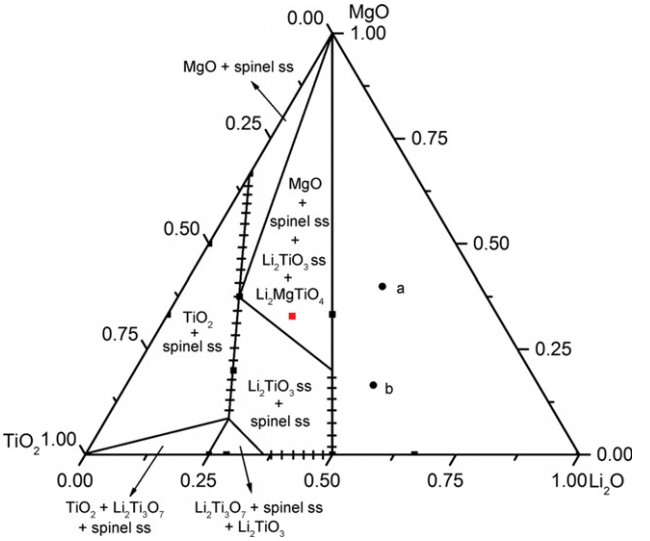

Fig. 3. Pseudo phase diagram of the LMTO ternary system.

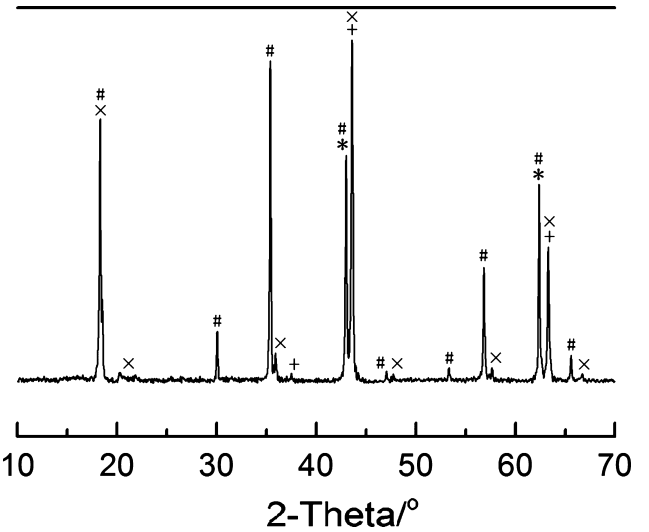

Fig. 4. The XRD pattern of the $0.4Mg_2TiO_4$–$0.6Li_2TiO_3$ ceramic system (*~MgO, $^{+}$~Li_2MgTiO_4, $^{\#}$~Mg_2TiO_4, $^{\times}$~Li_2TiO_3).

Table I. Dielectric Properties of the Single-Phase Ceramics in the LMTO Ternary System

Number	Phase	Li_2:Mg:Ti	Sintering temperature/°C	ε_r	$Q \times f$ value/GHz	τ_f/ppm/°C	Reference
A	TiO_2	0:0:1	–	~105	46 000	+465	6
B	Li_2TiO_3	1:0:1	1200	~22	60 000	+22	8
C	$MgTi_2O_5$	0:1:2	1500	~17	50 000	−60	9
D	$MgTiO_3$	0:1:1	1275	~17	110 000	−55	10,11
E	Mg_2TiO_4	0:2:1	1450	~17	160 000	−59	12
F	Li_2MgTiO_4	1:1:1	1250	~17	100 000	−27	15
G	$Li_2Mg_3Ti_4O_{12}$	1:3:4	1125	~20	62 000	−27	7
H	$Li_2MgTi_3O_8$	1:1:3	1000	~27	40 000	+3	13
I	$Li_4Ti_5O_{12}$	2:0:5	930	~19	9200	−10	14
J	$Li_2Ti_3O_7$	1:0:3	–	–	–	–	–
K	Li_4TiO_4	2:0:1	–	–	–	–	–

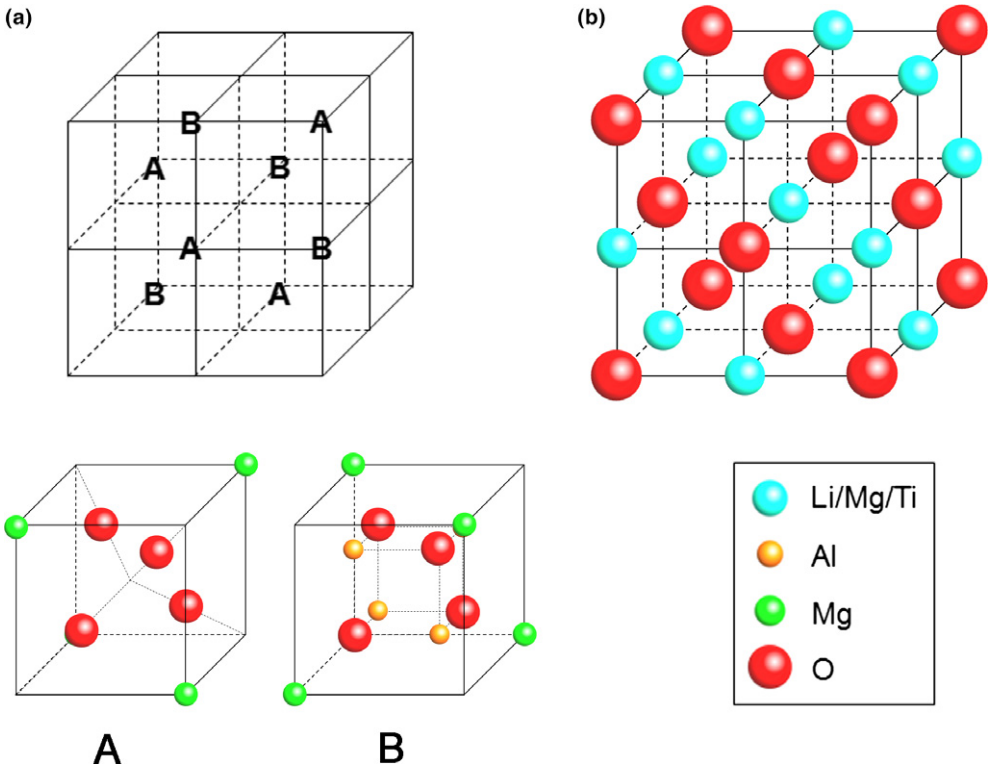

Fig. 5. Crystal structure diagram of (a) $MgAl_2O_4$ spinel and (b) Li_2MgTiO_4.

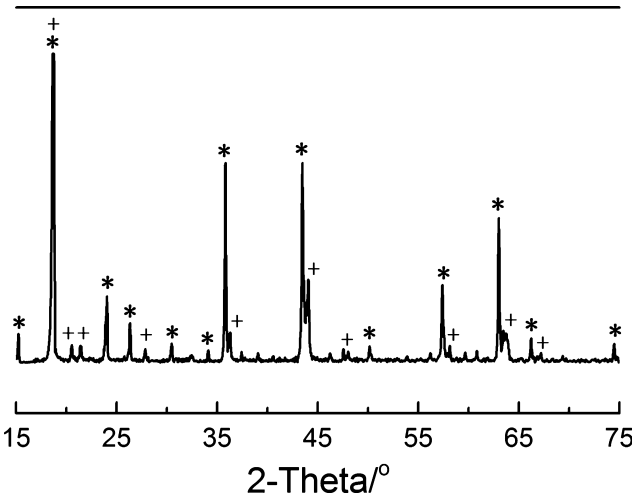

Fig. 6. XRD pattern of the 0.33 $Li_2MgTi_3O_8$–0.67 Li_2TiO_3 ceramic sample sintered at 1225°C (*~$Li_2MgTi_3O_8$, $^+$~Li_2TiO_3).

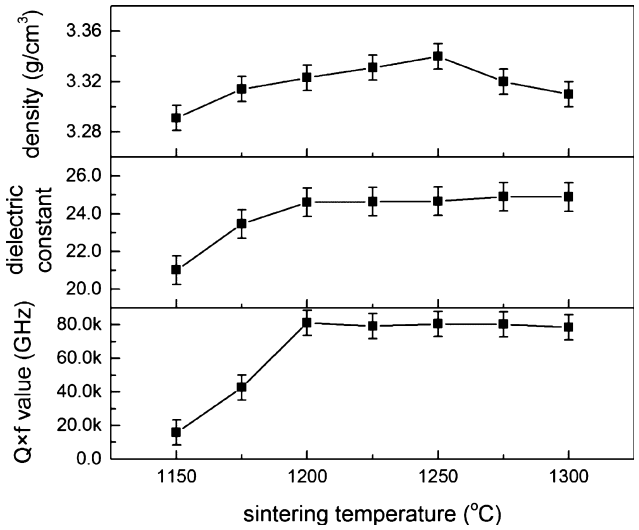

Fig. 7. Variation in the dielectric properties of the 0.33 $Li_2MgTi_3O_8$–0.67 Li_2TiO_3 ceramic samples as a function of sintering temperature.

τ_f = +22 ppm/°C. The rests of the ceramics have negative τ_f values. Therefore, Li_2TiO_3 becomes a common ceramic that can be combined with other ceramics to achieve temperature-stabled materials, as the τ_f value of $Li_2MgTi_3O_8$ is too small to neutralize those with large negative values. Among the 10 ceramics, the dielectric properties of $Li_2Ti_3O_7$ and Li_4TiO_4 have not been studied.

Figure 3 shows a pseudo phase diagram of the LMTO system. Unlike a standard phase diagram, the composition and dielectric properties of each point in this pseudo phase diagram was measured under its optimized sintering temperature. Different compositions in the Ti-rich region are shown in the figure. The LMTO system is quite similar to the LZTO system, but one exception was found in our recent study. That is the triangle region in the LMTO system, as indicated by the small red square in Fig. 3, which has different composition from the region in the LZTO phase diagram. The region in the LMTO system consists of MgO, Mg_2TiO_4 (spinel ss), $LiTiO_3$ and Li_2MgTiO_4, whereas the related region in the LZTO system consists of ZnO, Zn_2TiO_4 and $LiTiO_3$, without Li_2ZnTiO_4. Li_2ZnTiO_4 either does not exist or has not been reported in the open literatures. However, Li_2MgTiO_4 has been identified and investigated.[15–18] The red square in Fig. 3 represents the 0.4 Mg_2TiO_4–0.6 Li_2TiO_3, whose XRD pattern is shown in Fig. 4. There are four phases, Li_2MgTiO_4, MgO, Mg_2TiO_4, and Li_2TiO_3.

$Li_2MgTi_3O_8$, $Li_2Mg_3Ti_4O_{12}$, and Mg_2TiO_4 belong to spinel-related structure. Figure 5(a) shows the classic crystal structure with formula ABX_4. In this structure, X^{2-} ions form in a face-centered cubic close packing. A^{2+} ions, or bivalent cations, occupy one-eighth of the tetrahedral

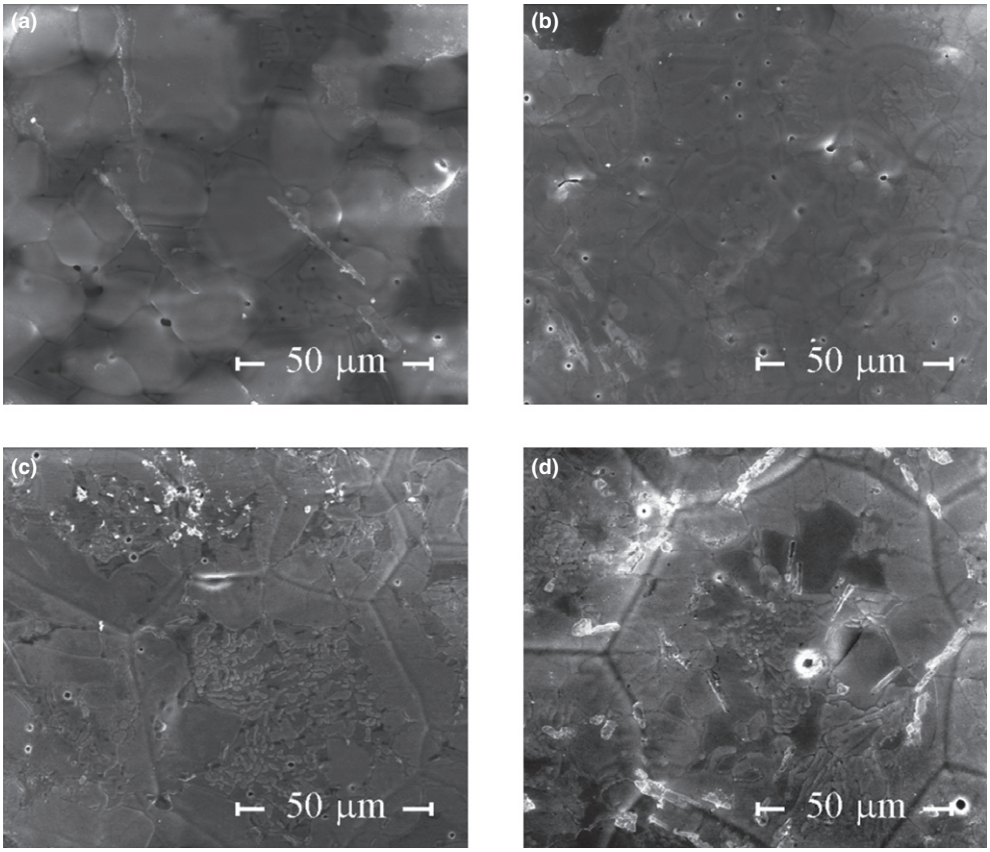

Fig. 8. SEM pictures of the 0.33 $Li_2MgTi_3O_8$–0.67 Li_2TiO_3ceramic samples sintered at different temperatures [(a) ~1150°C, (b) ~1200°C, (c) ~1250°C, (d) ~1300°C].

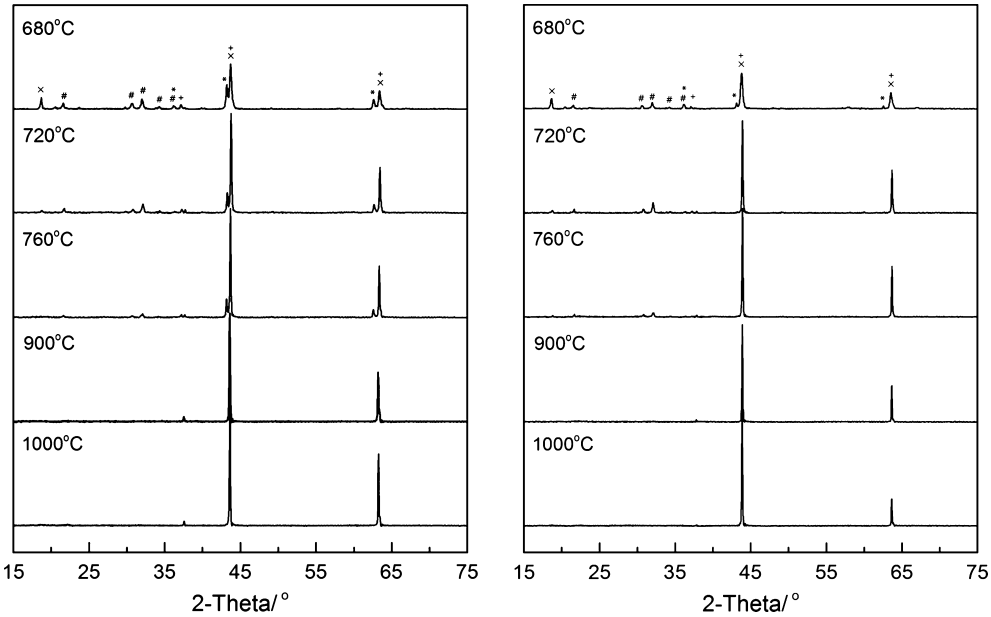

Fig. 9. XRD patterns of (a) 0.33 Li_4TiO_4–0.67 MgO and (b) 0.5 Li_2MgTiO_4–0.5 Li_4TiO_4 ceramic samples sintered at different temperatures (*~MgO, $^{+}$~Li_2MgTiO_4, $^{\#}$~Li_2CO_3, $^{\times}$~Li_2TiO_3).

interstices, and B^{3+} ions, or trivalent cations, occupy half of the octahedral interstices. If half of the B^{3+} were replaced by A^{2+}, it becomes inverse spinel structure, such as Mg_2TiO_4. For $Li_2MgTi_3O_8$ and $Li_2Mg_3Ti_4O_{12}$, Li^+, and Mg^{2+} together occupy A^{2+} sites, and Ti^{3+} occupy B^{3+} sites. In addition, because they are solid solutions, there could be various defects. Li_2MgTiO_4 has rock salt structure, which is also known as NaCl structure. The structure is illustrated in Fig. 5(b). In this structure, O^{2-} ions occupy Cl^- sites, and Mg^{2+}, Li^+, Ti^{4+} together occupy Na^+ site randomly.

Figure 6 shows XRD pattern of the 0.33 $Li_2MgTi_3O_8$–0.67 Li_2TiO_3 ceramic sample sintered at 1225°C for 4 h. There are two phases, Li_2TiO_3 and $Li_2MgTi_3O_8$.

Figure 7 demonstrates dielectric properties of the 0.33 $Li_2MgTi_3O_8$–0.67 Li_2TiO_3 ceramic samples as a function of sintering temperature. $Q \times f$ value and dielectric constant of

the samples are first increased as the sintering temperature is increased from 1150°C to 1200°C, and then kept steady. $Q \times f$ value is about 80 000 GHz when the sintering temperature is above 1200°C and the dielectric constant is about 24.5. Density of the samples is first increased as the sintering temperature is increased from 1150°C to 1250°C, and then slightly decreased as the temperature is further increased. The decrease in density may be attributed to abnormal grain growth.[19] The maximum density of the samples is 3.34 g/cm^3 at 1250°C. At this temperature, the sample has $Q \times f$ value and dielectric constant of 80 476 GHz (at 7.68 GHz) and 24.7, respectively. Temperature coefficients of all the samples are about +3 ppm/°C, and the value is +3.2 ppm/°C at 1250°C.

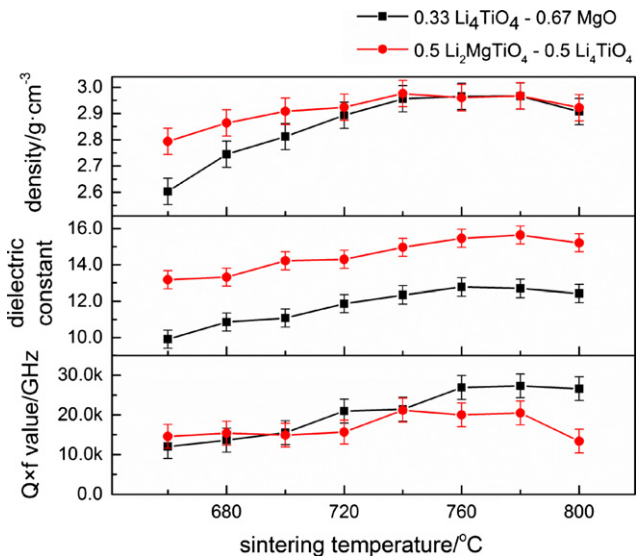

Fig. 10. Dielectric properties of 0.5 Li_2MgTiO_4–0.5 Li_4TiO_4 and 0.33 Li_4TiO_4–0.67 MgO ceramic samples sintered at different temperatures.

SEM images of the 0.33 $Li_2MgTi_3O_8$–0.67 Li_2TiO_3 ceramic samples are shown in Fig. 8. The grain size is increased with increasing sintering temperature. The abnormal grain growth, as shown in Fig. 8(d), could be the reason for the decrease in density.

In Li-rich region of the LMTO systems, two exemplary ceramic systems, (a) 0.33 Li_4TiO_4–0.67 MgO and (b) 0.5 Li_2MgTiO_4–0.5 Li_4TiO_4, as shown in the right side of Fig. 3 were studied. Both samples exhibit a low sintering temperature of less than 800°C and a low $Q \times f$ value.

Both ceramic samples have similar phase composition, as evidenced by the XRD patterns in Fig. 9. The major phase is Li_2MgTiO_4. Minor phases, such as MgO, Li_2TiO_3, and Li_2CO_3 are also identified, when the sintering temperature is below 700°C. As sintering temperature is increased, the Li_2MgTiO_4 phase becomes more and more dominant and no secondary phase is formed even the sintering temperature reaches 1000°C.

Microwave dielectric properties of the 0.5 Li_2MgTiO_4–0.5 Li_4TiO_4 and 0.33 Li_4TiO_4–0.67 MgO ceramic samples sintered at different temperatures are shown in Fig. 10. With increasing temperature, $Q \times f$ value, dielectric constant, and density of the samples are first increased, and then decreased. Fluctuation of the curve is due to the experimental error. The maximum values of the three properties are obtained at about 760°C. The 0.33 Li_4TiO_4–0.67 MgO ceramic sintered at 760°C has $Q \times f$ value = 26 000 GHz (at 10.72 GHz), $\varepsilon_r = 12.8$, $\tau_f = -78.4$ ppm/°C. The 0.5 Li_2MgTiO_4–0.5 Li_4TiO_4 ceramic sintered at 760°C has $Q \times f$ value = 20 000 GHz (at 9.65 GHz), $\varepsilon_r = 16.5$, $\tau_f = -48.7$ ppm/°C. The decrease in $Q \times f$ value and density of the samples sintered at high temperatures may be due to the abnormal grain growth.[19]

Figure 11 shows SEM images of the 0.5 Li_2MgTiO_4–0.5 Li_4TiO_4 and 0.33 Li_4TiO_4–0.67 MgO samples sintered at three temperatures. The grain size is increased with sintering temperature. At 800°C, giant grains are formed in the 0.5 Li_2MgTiO_4–0.5 Li_4TiO_4 sample. The pores among the grains could also cause a decrease in density and the $Q \times f$ value.

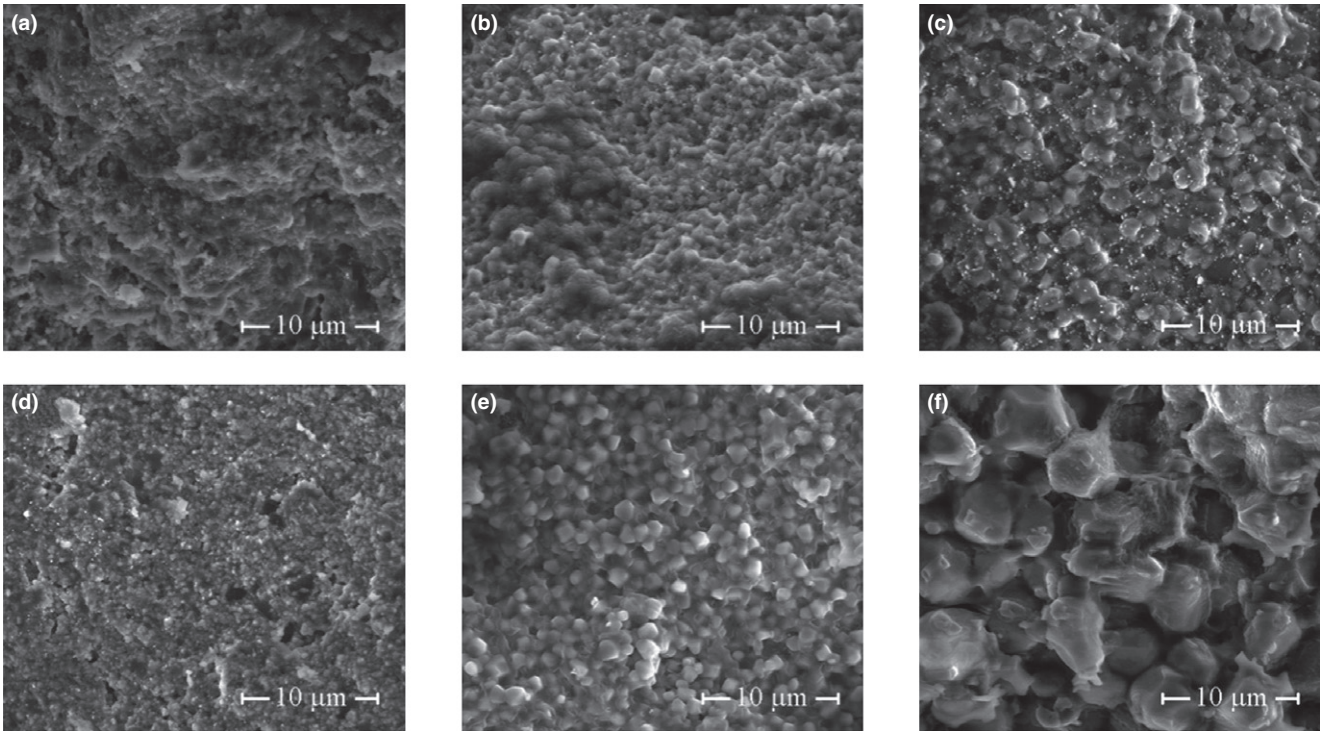

Fig. 11. SEM pictures of ceramic samples sintered at different temperatures: 0.5 Li_2MgTiO_4–0.5 Li_4TiO_4 [(a) ~660°C, (b) ~760°C, (c) ~800°C]. 0.33 Li_4TiO_4–0.67 MgO [(d) ~660°C, (e) ~760°C, (f) ~800°C].

IV. Conclusion

Dielectric properties and phase composition of the Li_2O–MgO–TiO_2 ternary ceramic system were discussed. A pseudo phase diagram of the LMTO system was established, which shows an overall phase composition in Ti-rich region of the LMTO system. Dielectric properties of some important single-phase ceramics were studied. The 0.33 $Li_2MgTi_3O_8$–0.67 Li_2TiO_3 ceramic system possesses excellent dielectric properties, with $Q \times f$ value of 80,476 GHz (at 7.68 GHz), dielectric constant of 24.7 and temperature coefficient of +3.2 ppm/°C, when the sample is sintered at 1250°C. The two Li-rich ceramics selected in the study have low sintering temperature of less than 800°C. They have $Q \times f$ values of lower than 30 000 GHz, dielectric constant of about 15 and large negative temperature coefficients. No new single-phase ceramic in the Li-rich region was found.

Acknowledgments

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