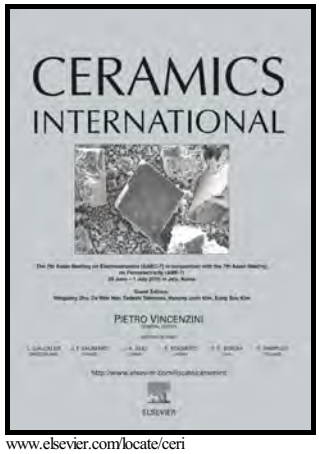

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Microwave dielectric properties of novel glass-free low temperature firing $ACa_2Mg_2V_3O_{12}$ (A = Li, K) ceramics

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Abstract

Two novel low-firing microwave dielectric ceramics $ACa_2Mg_2V_3O_{12}$ (A = Li, K) were prepared using the solid state reaction method. The phase composition, sintering behavior, and microwave dielectric properties were investigated. X-ray diffraction (XRD) analysis showed that both ceramics crystallized into a cubic garnet structure. Both ceramics were well densified at temperatures lower than 960 ^{o}C. $LiCa_2Mg_2V_3O_{12}$ ceramic sintered at 940 ^{o}C with relative density of ~ 96.3% obtained the optimum microwave dielectric properties with ε_r ~ 9.8, $Q\times f$ ~ 24,900 GHz (at 11.0 GHz), τ_f ~ +259.2 ppm/^{o}C. For $KCa_2Mg_2V_3O_{12}$, the ceramic sintered at 900 ^{o}C had a relative density of ~ 96.1%, a relative permittivity (ε_r) ~ 10, a quality factor ($Q\times f$) ~ 30,330 GHz and a large positive temperature coefficient of resonance frequency τ_f ~ +190.9 ppm/^{o}C. Both $ACa_2Mg_2V_3O_{12}$ (A = Li, K) ceramics were chemically compatible with Ag electrodes. The large positive τ_f of $LiCa_2Mg_2V_3O_{12}$ ceramic could

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be compensated by forming sold solution with $NaCa_2Mg_2V_3O_{12}$, and improved properties with a near-zero τ_f = +2 ppm/^{o}C, ε_r = 9.9, $Q \times f$ = 45,500 GHz was obtained for $0.16LiCa_2Mg_2V_3O_{12}$-$0.84NaCa_2Mg_2V_3O_{12}$ ceramic sintered at 920 ^{o}C for 4 h.

Keywords: Microwave dielectric properties; Garnet; Vanadate

1. Introduction

In recent years, low-temperature co-fired ceramic (LTCC) has been generating considerable interest due to the requirement of miniaturization and integration [1, 2]. Generally, advanced ceramics for microwave integrated circuits should have a high quality factor ($Q\times f$), a low dielectric constant (ε_r), and a near-zero temperature coefficient of resonance frequency (τ_f). Furthermore, for LTCC technology, ceramics should be sintered at temperatures lower than 960 ^{o}C (the melting temperature of the inner electrode, such as Ag). Often low-melting point additives are used to reduce the sintering temperatures which results in deterioration of the microwave dielectric properties of the ceramic materials [3, 4].

More recently, some vanadate compounds with garnet structure have been reported to be potential microwave dielectric ceramics for LTCC applications because of their intrinsically low sintering temperatures and promising microwave dielectric properties. For example, $LiCa_3MgV_3O_{12}$ ceramic sintered at 900 ^{o}C has a relative permittivity (ε_r) ~ 10.5, a quality factor ($Q\times f$) ~ 74,700 GHz and a temperature coefficient of resonant frequency (τ_f) ~ -61 ppm/^{o}C) [5]. $NaCa_2Mg_2V_3O_{12}$ ceramic has a ε_r = 10, $Q\times f$ = 50,600 GHz and τ_f = -47 ppm/^{o}C when sintered at 915 ^{o}C [6]. By comparison, it is found that the large negative τ_f value is a common feature for vanadate garnets (as shown in Table 1). This would impede their practical applications to a large extent. Generally, two approaches have been proposed to adjust the τ_f value. The first method is formation of a composite between two compounds with opposite signs of τ_f value. In our previous work [6], near-zero τ_f garnets were achieved by

compensating the large negative τ_f with $CaTiO_3$ having a positive one (~ +800 ppm/^oC). This approach, in spite of the effective adjustment of the τ_f values, could cause an abrupt degradation of the quality factor. Forming solid solution is another accepted method for temperature adjustment. This method is desirable because of its ability to maintain the high $Q \times f$ while successfully tuning the τ_f. Thus, it is worthwhile to search for novel microwave dielectrics with positive τ_f values in vanadate garnets as temperature compensators.

The synthesis of $ACa_2Mg_2V_3O_{12}$ (A = Li, K) was first reported by Neurgaonkar et al [11]. They reported that both compounds with cubic garnet structure could be easily achieved at 750 ^oC for 24 h. Li *et al.* [12] studied the fluorescence and luminescent properties of $KCa_2Mg_2V_3O_{12}$ although so far, their microwave dielectric properties have not been reported yet. In this work, $ACa_2Mg_2V_3O_{12}$ (A = Li, K) ceramics were prepared by the conventional solid state reaction method, and its crystal structure, sintering behavior and microwave dielectric properties were studied.

2. Experimental Procedure

$ACa_2Mg_2V_3O_{12}$ (A = Li, K) ceramics were prepared by the conventional solid-state route from high-purity (99%) powders of Li_2CO_3, K_2CO_3, $CaCO_3$, MgO, and NH_3VO_3 (Guo-Yao Co.Ltd., Shanghai, China). As MgO is hygroscopic, it was calcined at 800 ^oC for 2h to remove moisture retains. Powders were milled with zirconia balls for 6h using a planetary mill (Nanjing Machine Factory, Nanjing, China) operating at a running speed of 150 rpm. The mixtures were dried, and calcined at 700 ^oC for 4h, followed by re-milling for 4h. Subsequently, the obtained powder was

mixed with polyvinyl alcohol as a binder and then crushed into a fine powder through a sieve with 200 mesh. The obtained powder was pressed into pellets with 12 mm diameter and 7 mm height by uniaxial pressing under a pressure of 200 MPa. The pellets were heated at 550 ^{o}C for 4h to remove the PVA and then sintered at 890-950 ^{o}C for 4h. To research the chemical compatibility of $ACa_2Mg_2V_3O_{12}$ (A = Li, K) with Ag powders, 20 wt% Ag was mixed with the compounds, co-fired at 940 ^{o}C and 900 ^{o}C for 4h, respectively.

The crystal structure and phase composition of the specimens were analyzed with X-ray diffraction (XRD; Model X'Pert PRO, PANalytical, Almelo, the Netherlands). The bulk densities of the sintered ceramics were measured using Archimedes' method. The surface microstructures of the samples were examined by scanning electron microscopy (SEM; JSM6380-LV, JEOL, Tokyo, Japan). The microwave dielectric properties were measured using a network analyzer (N5230A, Agilent Co., Palo Alto, California) and a temperature chamber (Delta 9039; Delta Design, San Diego, California). The temperature coefficient of the resonant frequency τ_f values were calculated with the formula as follows:

$$\tau_f = \frac{f_{85} - f_{25}}{60 \times f_{25}} \quad (1)$$

where, f_{85} and f_{25} are the resonant frequencies at the measuring temperatures 85 and 25 ^{o}C, respectively.

3. Results and Discussion

Fig.1 shows the XRD patterns of $ACa_2Mg_2V_3O_{12}$ (A = Li, K) recorded from the calcined powders at 700 ^{o}C. All the detected peaks could be indexed based on the

JCPDS file number 00-24-1044 for $KCa_2Mg_2V_3O_{12}$, and no additional peaks were observed. It is notable that the peaks for $LiCa_2Mg_2V_3O_{12}$ shifted to higher angle compared with the K-based compound. Both compounds crystallized into a cubic garnet structure with lattice parameter of a = 12.3865 Å and a = 12.5000 Å for $LiCa_2Mg_2V_3O_{12}$ and $KCa_2Mg_2V_3O_{12}$, respectively. The difference in lattice parameter and the peak shift can be explained by the smaller effective ionic radius of Li^+ (0.078 Å) than that of K^+ (0.151 Å) [13].

SEM micrographs of $LiCa_2Mg_2V_3O_{12}$ ceramics sintered at different temperatures (920-950 ^oC) are shown in **Fig.2**. As shown in **Fig.2** (a), a porous microstructure with an average grain size of ~ 2-3 μm was observed. As the sintering temperature increased, the amount of porosity decreased along with a slight increase in the grain size. The sample sintered at 940 ^oC exhibited a dense microstructure with homogeneously distributed grains and an average grain size of ~ 3-4 μm. As illustrated in **Fig.2** (d), some large grains (9-10 μm) appeared in the sample sintered at 950 ^oC. $KCa_2Mg_2V_3O_{12}$ ceramic could be densified at relatively lower temperature ranges (880-910 ^oC). **Fig.3** shows the SEM images of the surfaces of the sintered $KCa_2Mg_2V_3O_{12}$ samples. Similarly, with increasing sintering temperature, the amount of porosity decreased while the grain size increased. A dense microstructure with an average grain size of ~ 3-4 μm was observed in the sample sintered at 900 ^oC.

XRD pattern, backscattered electron image (BSE) and energy dispersive spectrometer (EDS) analysis of the co-fired $LiCa_2Mg_2V_3O_{12}$ with 20 wt % Ag sintered at 940 ^oC for 4 h are shown in **Fig.4.** From the XRD patterns, only the peaks of

$LiCa_2Mg_2V_3O_{12}$ and Ag (JCPDS No. 004-0783) could be observed and no secondary phase was detected. Two different kinds of grains with different elemental contrast were distinguished and were marked as spots 1 and 2 in the BSE image. EDS analysis revealed that the bright grains (spot 1) were Ag while the slight dark grains (spot 2) were rich in Ca, Mg, and V elements. These results indicates that $LiCa_2Mg_2V_3O_{12}$ did not react with Ag when sintered at 940 ^oC for 4 h. Similar results were observed in $KCa_2Mg_2V_3O_{12}$ and the respective XRD pattern, BSE image, and EDS analysis of the co-fired $KCa_2Mg_2V_3O_{12}$ with 20 wt % Ag sintered at 900 ^oC for 4 h are shown in **Fig.5.**

The relative densities of the sintered ceramics are shown in **Fig.6** as a function of sintering temperature. As the sintering temperature increased to 940 ^oC, the relative density of $LiCa_2Mg_2V_3O_{12}$ increased to a maximum value of ~ 3.25 g/cm^3 (96.3 % of theoretical density 3.37 g/cm^3), and then decreased slightly due to the over-sintering. A similar change in density was observed for $KCa_2Mg_2V_3O_{12}$. A maximum relative density of ~ 3.35 g/cm^3 (about 96.1 % of theoretical density 3.49 g/cm^3) was achieved in the sample sintered at 900 ^oC. These results are in accordance with the SEM analysis.

The variation of microwave dielectric properties (ε_r, $Q\times f$, and τ_f values) of both ceramics are shown in **Fig.6** as a function of sintering temperature. For both compounds, the variation trend of the relative permittivity and quality factor with increasing sintering temperature is similar to that of the bulk density. The largest ε_r and $Q\times f$ values were achieved at the sintering temperatures corresponding to the

highest bulk densities. However, no significant change in τ_f value was detected as the sintering temperature increased. As shown in **Fig.6**, the τ_f values of $ACa_2Mg_2V_3O_{12}$ (A = Li, K) ceramic are about 255 ± 5 and 188 ± 2 ppm/^oC, respectively. The best microwave dielectric properties of $LiCa_2Mg_2V_3O_{12}$ ceramic were obtained for the sintering temperature of 940 ^oC with a ε_r value of ~ 9.8, a $Q\times f$ value of ~ 24,900 GHz, and a τ_f ~ +259.2 ppm/ ^oC. For $KCa_2Mg_2V_3O_{12}$ ceramic, the optimum microwave properties were obtained at 900 ^oC with a ε_r ~ 10, a $Q\times f$ value of ~ 30,300 GHz, and a τ_f ~ +190.9 ppm/ ^oC.

The theoretical relative permittivity can be calculated by the Clausius-Mossotti equation [14, 15].

$$\varepsilon_r = \frac{1+2b\alpha_D^T / V_m}{1-b\alpha_D^T / V_m} \qquad (2)$$

where, $b = 4\pi/3$, α_D^T is the sum of ionic polarizabilities of individual ions and V_m is the molar volume. The theoretical relative permittivity of $ACa_2Mg_2V_3O_{12}$ (A = Li, K) ceramic is 10.4 and 11.9, respectively. This could partly explain the lower ε_r of $LiCa_2Mg_2V_3O_{12}$ than that of $KCa_2Mg_2V_3O_{12}$.

It is well known that the quality factor ($Q\times f$) is affected by the intrinsic factors like lattice vibration and ionic polarization, and the extrinsic factors, such as grain boundaries, impurities, defects, order-disorder, etc. [16]. In the present system, the effects from secondary phase and impurities could be eliminated based on the XRD and SEM results that confirmed the formation of single phase ceramics with high relative density (>95 %).

The $Q\times f$ strongly depends on the packing fraction [17] which can be calculated

by Eq (3).

$$\text{pakcing fraction (\%)} = \frac{\text{volume of packed ions}}{\text{volume of primitive unit cell}} \quad (3)$$

The packing fraction of $LiCa_2Mg_2V_3O_{12}$ is 68.5%, much larger than that of $KCa_2Mg_2V_3O_{12}$ (71.2%). Thus, the $Q\times f$ of $LiCa_2Mg_2V_3O_{12}$ is lower than that of $KCa_2Mg_2V_3O_{12}$ might be partly due to the smaller packing fraction.

It is worth noting that the τ_f of $ACa_2Mg_2V_3O_{12}$ (A = Li, K) ceramic are largely positive. It may be possible to design solid solution between $ACa_2Mg_2V_3O_{12}$ and other cubic garnet ceramics with negative τ_f values to obtain novel temperature stable microwave dielectrics. More recently, a low-firing garnet ceramic $NaCa_2Mg_2V_3O_{12}$ with a negative $\tau_f \sim$ -47 ppm/^{o}C, a $\varepsilon_r \sim 10$, and a $Q\times f \sim$ 50,600 GHz was reported [6]. In this paper, the τ_f of $LiCa_2Mg_2V_3O_{12}$ ceramic was tuned by forming solid solution with $NaCa_2Mg_2V_3O_{12}$. The microwave dielectric properties of $(Li_{1-x}Na_x)Ca_2Mg_2V_3O_{12}$ ($0 \le x \le 0.84$) ceramic sintered at 920 ^{o}C for 4h were shown in Table 2. All the sintered ceramics exhibited high $Q\times f$ values. The τ_f value decreased form +259.2 to +2 ppm/^{o}C with increasing x values form 0 to 0.84. The $(Li_{0.16}Na_{0.84})Ca_2Mg_2V_3O_{12}$ ceramic sintered at 920 ^{o}C for 4h showed improved properties with $\varepsilon_r \sim 9.9$, $Q\times f \sim$ 45,500 GHz, $\tau_f \sim$ +2 ppm/^{o}C.

4. Conclusions

In summary, $ACa_2Mg_2V_3O_{12}$ (A = Li, K) ceramics were prepared through a solid-state reaction method. Both ceramics could be well densified at temperatures lower than 960 ^{o}C. $LiCa_2Mg_2V_3O_{12}$ ceramics exhibited good microwave dielectric properties with a $\varepsilon_r \sim 9.8$, a $Q\times f$ value of ~ 24,900 GHz, and a $\tau_f \sim$ +259.2 ppm/ ^{o}C.

For $KCa_2Mg_2V_3O_{12}$ ceramic, the optimum microwave dielectric properties were: ε_r ~ 10, $Q \times f$ ~ 30,300 GHz, and τ_f ~ +190.9 ppm/ ^oC. The large positive τ_f of $LiCa_2Mg_2V_3O_{12}$ ceramic could be tuned by forming solid-solution with $NaCa_2Mg_2V_3O_{12}$, and the $(Li_{0.16}Na_{0.84})Ca_2Mg_2V_3O_{12}$ ceramic sintered at 920 ^oC for 4 h showed improved properties with ε_r ~ 9.9, $Q \times f$ ~ 45,500 GHz, τ_f ~ +2 ppm/^oC. Additionally, XRD, EDS analysis revealed that both ceramics were chemically compatible with silver electrodes at their respective sintering temperatures.

Acknowledgments

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Table 1 Microwave Dielectric Properties of Some vanadate garnets

Composition	S. T. (°C)	ε_r	$Q\times f$ (GHz)	τ_f (ppm/°C)	Reference
$LiCa_3MgV_3O_{12}$	900	10.5	74700	-61	[5]
$Na_2YMg_2V_3O_{12}$	850	12.3	23180	-4.1	[7]
$NaMg_4V_3O_{12}$	690	12.5	35900	-58.1	[8]
$LiMg_4V_3O_{12}$	740	10.7	24000	-11.7	[9]
$LiCa_3ZnV_3O_{12}$	900	11.5	81100	-72	[10]

Table 2 Bulk density and microwave dielectric properties of $(Li_{1-x}Na_x)Ca_2Mg_2V_3O_{12}$ ceramics sintered at 920 °C for 4 h

x value	ε_r	$Q\times f$ (GHz)	τ_f (ppm/°C)
0	9.8	24,900	259.2
0.3	9.8	32,300	165
0.5	9.9	36,750	105
0.7	9.8	40,120	57
0.84	9.9	45,500	2

Figure Captions:

Fig.1 XRD patterns of $ACa_2Mg_2V_3O_{12}$ (A = Li, K) powders calcined at 700 ^oC/4h.

Fig.2 SEM micrographs of $LiCa_2Mg_2V_3O_{12}$ ceramics sintered at different temperatures: (a) 920 °C; (b) 930 °C; (c) 940 °C; (d) 950 °C.

Fig.3 SEM micrographs of $KCa_2Mg_2V_3O_{12}$ ceramics sintered at different temperatures: (a) 880 °C; (b) 890 °C; (c) 900 °C; (d) 910 °C.

Fig.4 (a) XRD patterns of the $LiCa_2Mg_2V_3O_{12}$ with 20 wt% silver powder and **(b)** Backscattered electron (BSE) and EDS analysis of the co-fired ceramics.

Fig.5 (a) XRD patterns of the $KCa_2Mg_2V_3O_{12}$ with 20 wt% silver powder and **(b)** Backscattered electron (BSE) and EDS analysis of the co-fired ceramics.

Fig.6 The relative densities, ε_r, $Q \times f$ values, and τ_f of $LiCa_2Mg_2V_3O_{12}$ and $KCa_2Mg_2V_3O_{12}$ ceramics sintered at different temperatures.

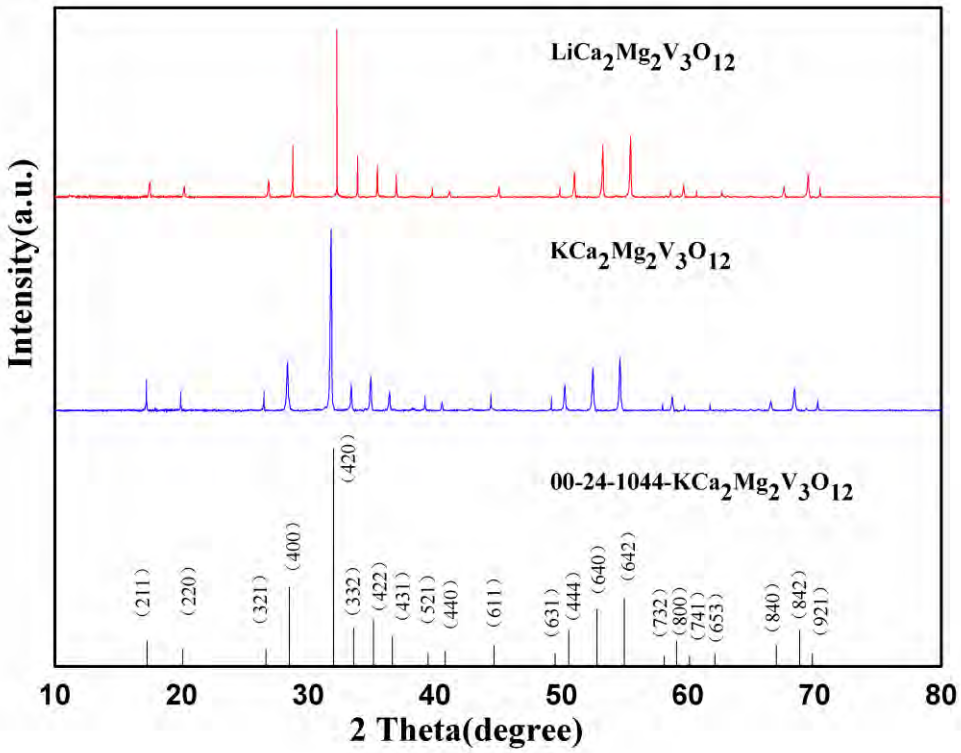


Fig.1

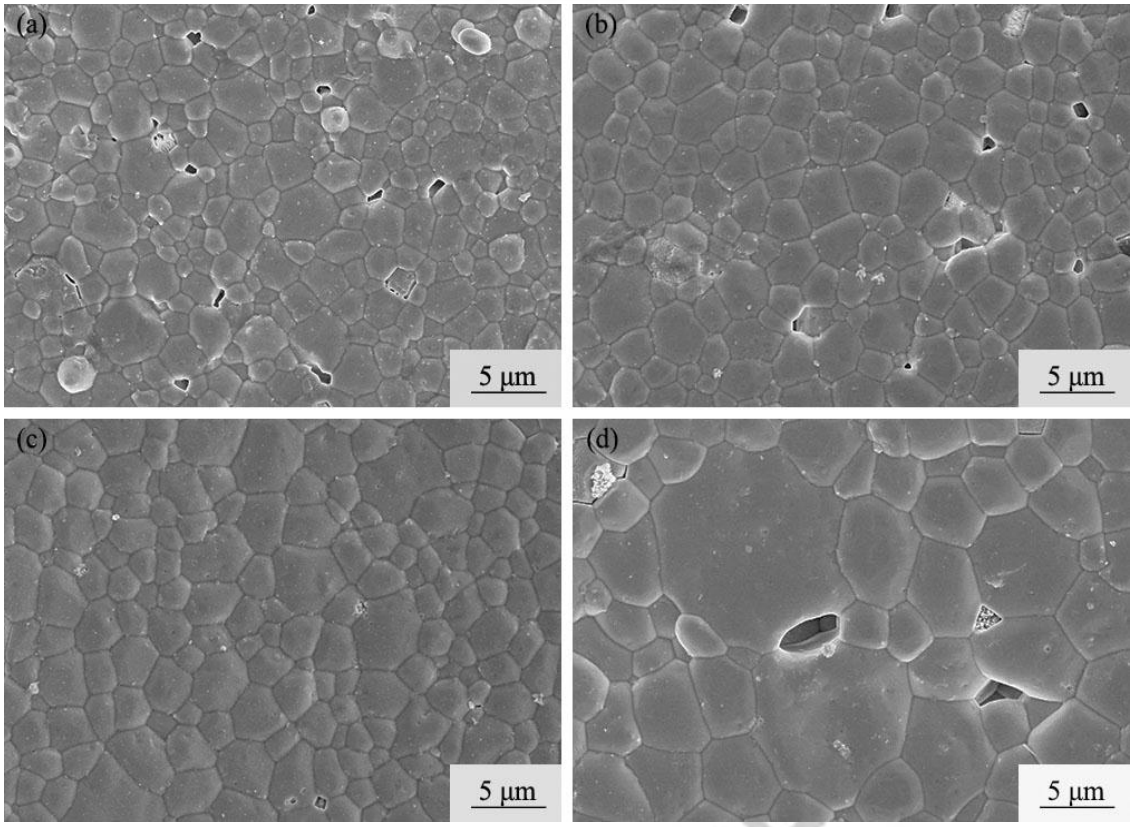
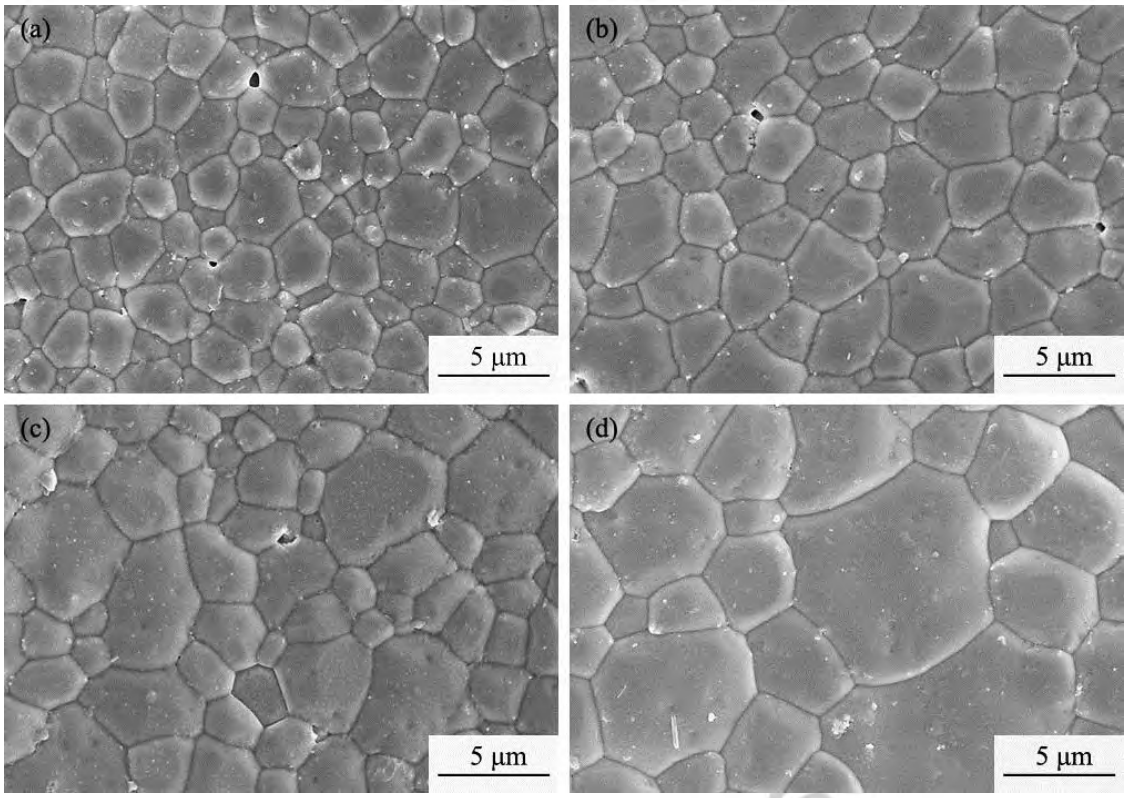


Fig.2



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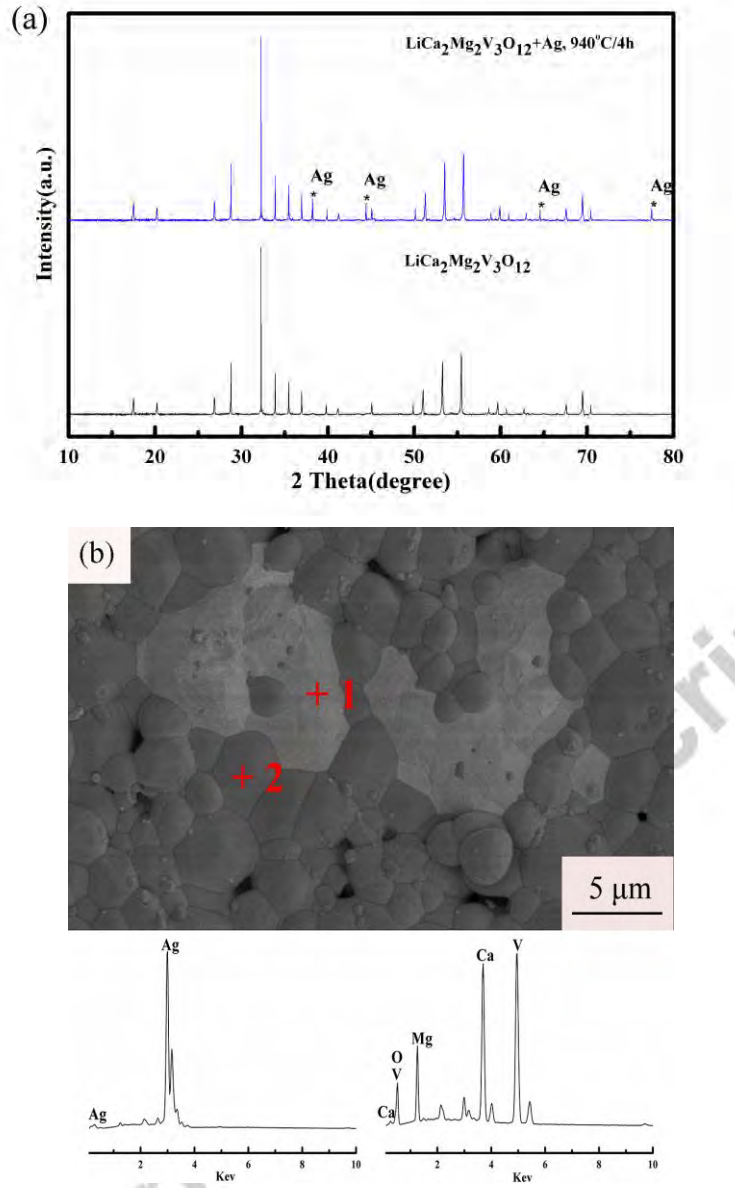

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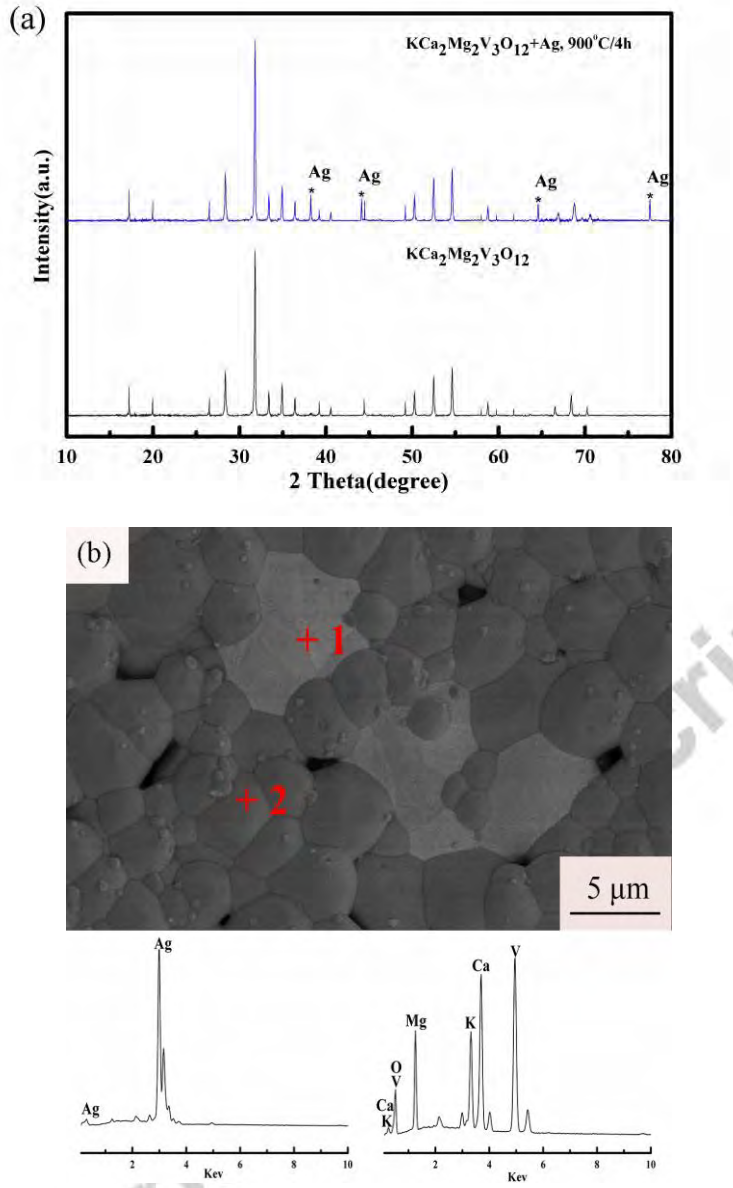

Fig. 5

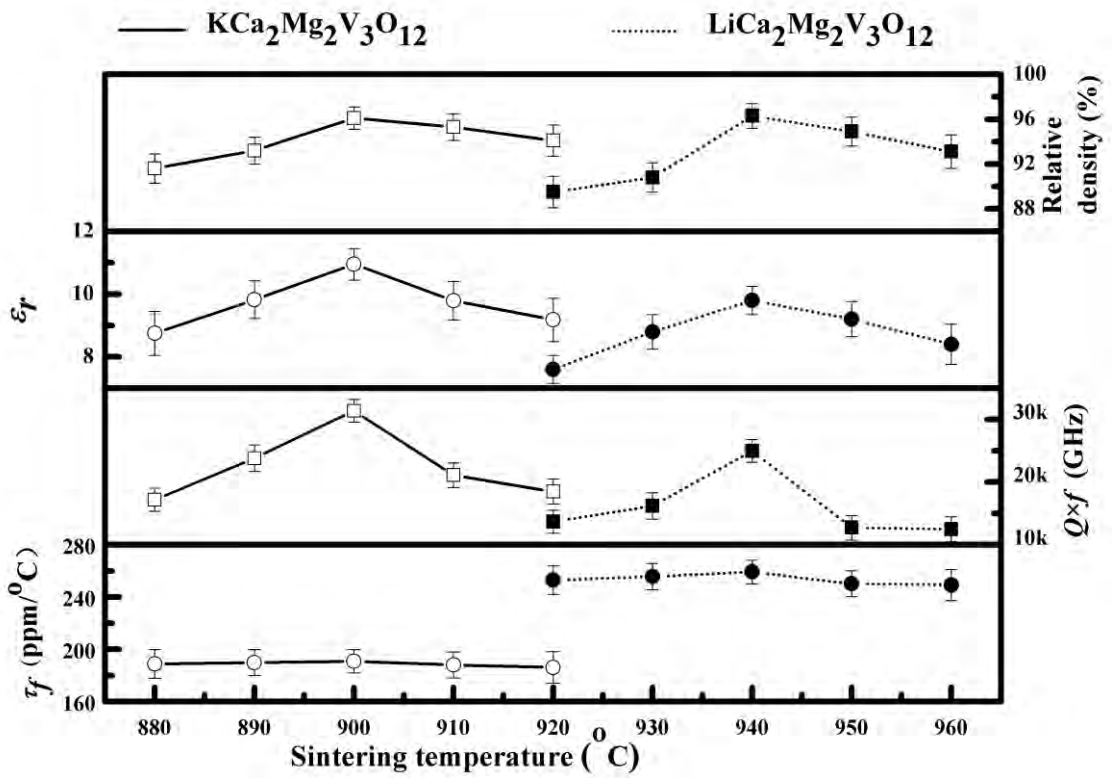

Fig. 6