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Ceramics International 40 (2014) 5015–5018

CERAMICS INTERNATIONAL

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Short communication

$LiCa_3ZnV_3O_{12}$: A novel low-firing, high Q microwave dielectric ceramic

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Received 4 August 2013; received in revised form 17 August 2013; accepted 19 August 2013
Available online 29 August 2013

Abstract

A novel low-firing microwave dielectric ceramic $LiCa_3ZnV_3O_{12}$ with low dielectric loss was synthesized by the solid-state reaction method. The phase composition, microstructure, and sintering behavior were investigated. The $LiCa_3ZnV_3O_{12}$ ceramic could be well densified at around 900 °C and exhibited favorable microwave dielectric properties with a low relative permittivity (ε_r) of 11.5, a fairly high quality factor (Q_uf) of 81,100 GHz, and a negative temperature coefficient of resonant frequency (τ_f) approximately -72 ppm/°C. The $LiCa_3ZnV_3O_{12}$ ceramic can be co-fired with Ag electrode, which makes it a promising ceramic for low temperature co-fired ceramic (LTCC) applications as substrate. Furthermore, $0.8LiCa_3ZnV_3O_{12}$–$0.2CaTiO_3$ ceramic sintered at 925 °C for 4 h exhibited improved microwave dielectric properties of $\varepsilon_r=13.2$, $Q_uf=59{,}600$ GHz, and $\tau_f=1.3$ ppm/°C.

Keywords: A. Sintering; C. Dielectric properties; E. Functional applications; Garnet

1. Introduction

The ever increasing demand for the low permittivity (ε_r), high quality factor (Q_uf) dielectrics in microelectronic industry constantly accelerates the search for novel microwave dielectrics for substrate, packaging, and antenna applications [1,2]. In general, the advanced substrate materials should have low relative permittivity to increase signal speed, a high quality factor to increase the frequency selectivity, and a near-zero temperature coefficient of resonant frequency (τ_f) to ensure the stability of the frequency against temperature changes. Several ceramics such as silicates and aluminates [3–6] have been developed and regarded as low ε_r and high Q_uf microwave dielectric ceramics. However, their high sintering temperatures (≥ 1300 °C) limit their application in low-temperature co-fired ceramic (LTCC)-based devices. The microwave dielectric materials used in the fabrication of LTCC devices have to be sintered below 950 °C for being co-fired with Ag electrode, of which the melting point is approximately 961 °C.

To reduce the sintering temperature of dielectric ceramics, adding sintering aids, such as low-melting glass or oxides, is a common method. However, this usually degrade seriously the microwave dielectric properties of the dielectric materials as the glass or oxides will produce a large amount of amorphous phase in the materials. Therefore, new materials with a low ε_r, a high Q_uf, and a near zero τ_f, as well as the ability to be sintered at <950 °C without requiring glass or oxide additives should be developed for application as the substrate of the LTCC devices.

Recently, many V_2O_5-rich microwave dielectric ceramics with intrinsic low sintering temperatures have attracted much attention, such as $Mg_2V_2O_7$ [7], $R_2V_2O_7$ (R=Ba, Sr, and Ca) [8], $LiCa_3MgV_3O_{12}$ [9], $Ca_5A_4(VO_4)_6$ (A^{2+}=Mg, Zn) [10], etc. These ceramics not only could be well sintered below 950 °C, but also exhibit a good combination of microwave dielectric characteristics: $\varepsilon_r=9\sim12.1$, $Q_uf=15{,}200\sim74{,}700$ GHz, and $\tau_f=-26\sim83$ ppm/°C. Furthermore, the cubic garnet structure of $LiCa_3MgV_3O_{12}$ was advantageous in terms

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http://dx.doi.org/10.1016/j.ceramint.2013.08.081

of low bulk density (for lightness of the electronic module) and good compatibility with Ag electrode [9].

In our previous work, V_2O_5-rich garnet compound $LiCa_3MgV_3O_{12}$ was investigated and regarded as an attractive promising candidate for LTCC substrate [9]. The Shannon's effective ionic radii of Zn^{2+} (0.74 Å) is very similar to that of Mg^{2+} (0.72 Å) [11], so it is worthwhile to investigate the Zn analog ceramic. In the present work, a new low-firing and low loss microwave dielectric ceramic $LiCa_3ZnV_3O_{12}$ (LCZV) was prepared, and its sintering behavior, microwave dielectric properties and chemical compatibility with silver were reported. Tuning the temperature coefficients of resonant frequency (τ_f) by the addition of $CaTiO_3$ with a large positive τ_f value (approximately +800 ppm/°C) was also carried out [12].

2. Experimental procedure

$LiCa_3ZnV_3O_{12}$ ceramics were prepared by conventional mixed oxide route from the high-purity oxide powders of Li_2CO_3, $CaCO_3$, ZnO, and V_2O_5 (>99%, Guo-Yao Co. Ltd., Shanghai, China). Stoichiometric amounts of the powders were weighed and milled in alcohol medium using zirconia balls for 4 h. The mixtures were dried and calcined at 750 °C for 4 h. The calcined powders were ground well and mixed with 5 wt% of polyvinyl alcohol solution as the binder. The powders were then uniaxially pressed into cylindrical disks of 12 mm diameter and 7 mm height under a pressure of 200 MPa. The samples were heated to 600 °C for 4 h to remove the organic binder and then sintered at 870~930 °C for 4 h.

The phase compositions of sintered samples were determined using an X-ray diffractometer (XRD) (CuKα_1, 1.54059 Å, Model X'Pert PRO, PANalytical, Almelo, The Netherlands). The bulk densities of sintered ceramics were measured by Archimedes' method. The microstructure observation of the samples was performed using field-emission scanning electron microscope (FE-SEM, Model S4800, Hitachi, Japan). Composition analysis was performed using energy-dispersive spectroscopy (EDS, IE 350; INCA, Oxford, U.K.). The microwave dielectric properties were measured using a network analyzer (Model N5230A, Agilent Co., Palo Alto, CA) and a temperature chamber (Delta 9039, Delta Design, San Diego, CA). The temperature coefficient of resonant frequency (τ_f) was measured in the temperature range from 25 °C to 85 °C. The τ_f value was calculated as follows:

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

where f_{85} and f_{25} are the resonant frequencies at 85 °C and 25 °C, respectively.

3. Results and discussion

The X-ray diffraction pattern as well as the FE-SEM image for the surface of LCZV ceramic sintered at 900 °C for 4 h are given in Fig. 1. Comparison of our experimental data with those in literatures [13] shows that the LCZV adopts the same garnet-structure as $LiCa_3MgV_3O_{12}$ (PDF files 00-024-1212).

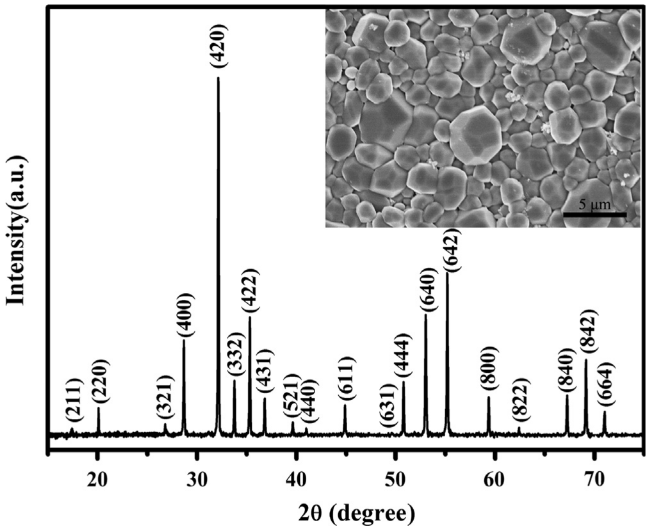


Fig. 1. X-ray diffraction result and FE-SEM image for the surface of a $LiCa_3ZnV_3O_{12}$ ceramic sintered at 900 °C for 4 h.

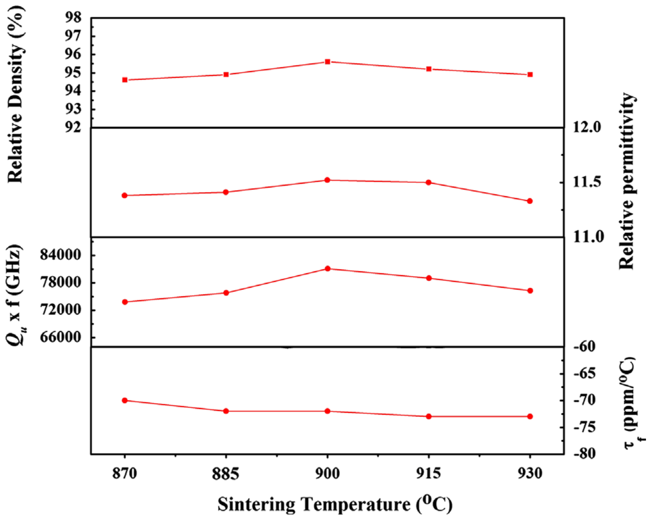


Fig. 2. The relative density, relative permittivity, quality factor, and temperature coefficient of the resonant frequency of $LiCa_3ZnV_3O_{12}$ ceramic as a function of sintering temperature.

All the peaks could be well indexed using the cubic garnet cell and there was no evidence of any secondary phases present. The lattice parameters of LCZV were calculated as $a = 12.439$ Å, and its theoretical density calculated by the lattice parameters was 3.71 g/cm^3. Homogenous microstructures with little pores can be observed for the LCZV ceramic sintered at 900 °C for 4 h. The grain sizes of the ceramic were between 1 and 5 μm.

Fig. 2 shows the variations of relative density, ε_r, Q_uf, and τ_f of LCZV ceramics as a function of the sintering temperature. The relative density of LCZV ceramic increased with increasing sintering temperature, reached a maximum value (95.6%) at 900 °C, and then decreased slightly. As the sintering temperature increases, ε_r increases with a trend similar to their density since the density and ε_r of ceramic are associated with the elimination of the pores [14,15]. With increasing sintering temperature, the Q_uf value of LCZV ceramics reaches the maximum with a value of 81,100 GHz (at 10.902 GHz) and decreases thereafter. Many factors are believed to affect the microwave dielectric loss and these can be divided into two parts: the intrinsic loss and the extrinsic loss [16]. Intrinsic loss is mainly caused by lattice vibration modes whereas extrinsic loss is dominated by second phase, oxygen vacancies, grain sizes, and densification or porosity. The densification plays an important role in controlling the dielectric losses. The improvements in quality factor of the ceramics can be attributed to the increase in densification. On the other hand, the deterioration of Q_uf might be due to the decreased densification caused by the evaporation of lithium at elevated temperatures [17,18]. The τ_f values of LCZV ceramics do not change remarkably with increasing sintering temperature and remain stable at approximately −72 ppm/°C.

$LiCa_3ZnV_3O_{12}$ ceramic developed in the present study has a low sintering temperature (900 °C), a good combination of microwave dielectric properties (ε_r=11.5, Q_uf=81,100 GHz), low bulk density (<4 g/cm^3) and low cost (cheap raw materials). However, the temperature stability of resonant frequency is poor (τ_f=−72 ppm/°C) which precludes its use as substrate material for the practical applications. The value of τ_f can be tuned nearly to zero by adding ceramics with a large positive τ_f value like $CaTiO_3$ (τ_f=+800 ppm/°C) [12]. In this paper, the microwave dielectric properties and XRD patterns of $(1–x)LiCa_3ZnV_3O_{12}–xCaTiO_3$ ($0 \le x \le 0.2$) ceramics sintered at 925 °C for 4 h are showed in Table 1 and Fig. 3. The ε_r values increased from 11.3 to 13.2 and the τ_f values increased from −72 to 1.3 ppm/°C with increasing x values from 0 to 0.2. All the sintered ceramics exhibited high Q_uf values. The $0.8LiCa_3ZnV_3O_{12}–0.2CaTiO_3$ ceramic sintered at 925 °C exhibits favorable microwave dielectric properties with ε_r=13.2, Q_uf=59,600 GHz (at 9.985 GHz), and τ_f =1.3 ppm/°C. EDS analysis was carried out to identify the second phase. Fig. 4 shows the result from energy-dispersive spectroscopy of second phase in $0.8LiCa_3ZnV_3O_{12}–0.2CaTiO_3$ ceramic sintered at 925 °C. Ca and Ti element are detected at a ratio of approximately 1:1, which confirms $CaTiO_3$ as the secondary phase.

To evaluate the chemical compatibility of LCZV ceramic with silver electrode, LCZV was cofired with 20% Ag powders at 900 °C for 2 h and the product was analyzed to detect interactions between the low-fired samples and electrodes. The X-ray powder diffraction pattern and the backscattered electron image of LCZV cofired with Ag at 900 °C are presented in Fig. 5. As the XRD pattern does not show the formation of any other phase except for LCZV and Ag, and the backscattered electron image of LCZV/Ag sample cofired at 900 °C for 2 h reveals no interaction to form new phases after firing, then it is considered that the LCZV compound has an excellent chemical compatibility with silver.

Table 1
Bulk densities and microwave dielectric properties of $(1–x)LiCa_3ZnV_3O_{12}–xCaTiO_3$ ($0 \le x \le 0.2$) ceramics sintered at 925 °C for 4 h.

x value	Bulk density (g/cm^3)	ε_r	Q_uf (GHz)	τ_f (ppm/°C)
0	3.51	11.3	72,400	−72
0.05	3.49	11.6	70,800	−69
0.1	3.45	12.3	67,200	−46
0.2	3.39	13.2	59,600	+1.3

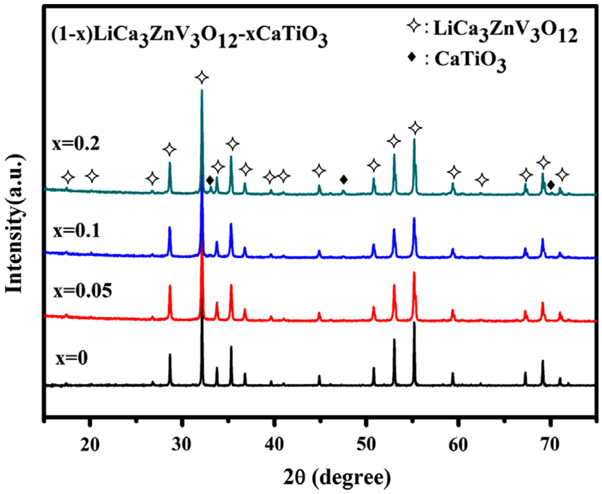
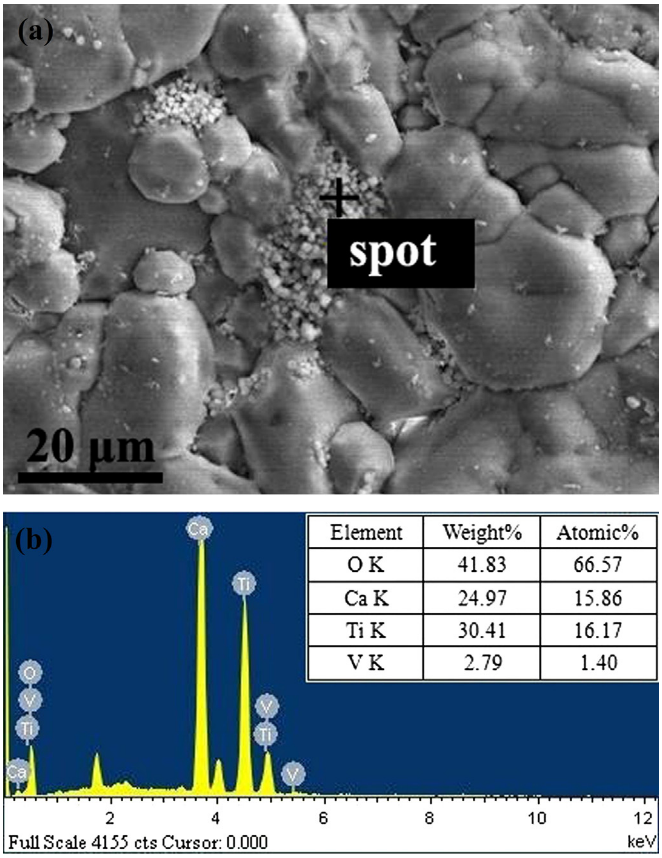


Fig. 3. X-ray diffraction patterns of $(1-x)LiCa_3ZnV_3O_{12}–xCaTiO_3$ ($0 \le x \le 0.2$) ceramics sintered at 925 °C for 4 h.



Element	Weight%	Atomic%
O K	41.83	66.57
Ca K	24.97	15.86
Ti K	30.41	16.17
V K	2.79	1.40

Fig. 4. FE-SEM image of $0.8LiCa_3ZnV_3O_{12}–0.2CaTiO_3$ ceramic sintered at 925 °C, and result of energy-dispersive spectroscopy of second phase in 0.8LCZV–0.2CTO.

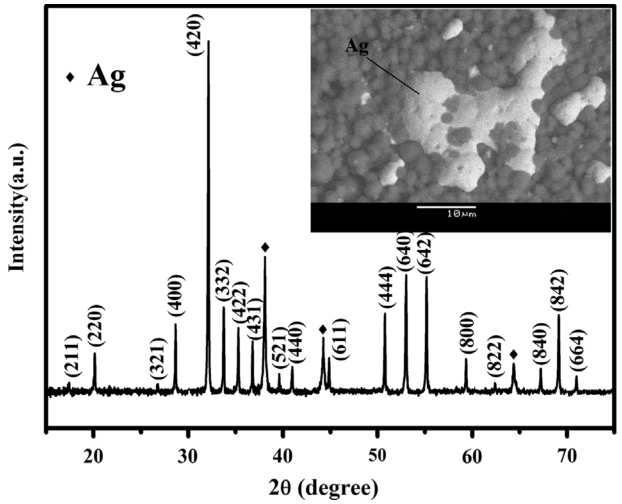


Fig. 5. XRD patterns of a $LiCa_3ZnV_3O_{12}$ ceramic mixed with 20 wt% Ag sintered at 900 °C for 2 h. Inset shows a backscattered electron image of $LiCa_3ZnV_3O_{12}$ sample cofired with Ag.

4. Conclusions

A novel low-firing vanadate garnet $LiCa_3ZnV_3O_{12}$ ceramic was investigated as promising low-loss dielectric ceramic for microwave applications. LCZV ceramic can be densified at a relatively low sintering temperature of 900 °C and exhibited good microwave dielectric properties of $\varepsilon_r = 11.5$, $Q_uf = 81{,}100$ GHz, and $\tau_f = -72$ ppm/°C. By adding $CaTiO_3$ into LCZV, the microwave properties were improved. $0.8LiCa_3ZnV_3O_{12}$–$0.2CaTiO_3$ ceramic sintered at 925 °C for 4 h exhibited improved properties of $\varepsilon_r = 13.2$, $Q_uf = 59{,}600$ GHz, and $\tau_f = 1.3$ ppm/°C. The backscattered electron image and XRD analysis confirmed that the ceramic did not react with silver powders, indicating that LCZV might be an attractive promising candidate for LTCC application.

Acknowledgment

This work was supported by Natural Science Foundation of China (Nos. 21261007, 21061004, and 51102058), the Natural Science Foundation of Guangxi (Grant no. 2012GXNSFDA053024), Project of Department of Science and Technology of Guangxi (No. 11107006-42) and Guilin (Nos. 20120112-1 and 20120112-2), and Program to Sponsor Teams for Innovation in the Construction of Talent Highlands in Guangxi Institutions of Higher Learning.

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