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Short communication

A novel low firing microwave dielectric ceramic $NaCa_2Mg_2V_3O_{12}$

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Abstract

A novel low-firing microwave dielectric ceramic $NaCa_2Mg_2V_3O_{12}$ was prepared by the conventional solid state ceramic route. The phase composition, microstructure, and sintering behavior were investigated. The $NaCa_2Mg_2V_3O_{12}$ ceramic could be well densified at around 915 °C and exhibited favorable microwave dielectric properties with a low relative permittivity of ~10, a high quality factor (Q $Q_u \times f$) of ~50,600 GHz, and a negative temperature coefficient of resonant frequency (τ_f) of −47 ppm/°C. The $NaCa_2Mg_2V_3O_{12}$ ceramic can be compatible with Ag electrode, which makes it a promising ceramic for LTCC technology application. $CaTiO_3$ was added into the $NaCa_2Mg_2V_3O_{12}$ ceramic to obtain a near zero τ_f, and $0.8NaCa_2Mg_2V_3O_{12}$–$0.2CaTiO_3$ ceramic sintered at 930 °C for 4 h showed improved properties with $\varepsilon_r=11.5$, $Q_u \times f=37{,}500$ GHz, and $\tau_f=2$ ppm/°C.

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

1. Introduction

Low-temperature co-fired ceramics (LTCC) has been generating considerable interest due to the benefits offered for the fabrication of miniature multilayer devices [1–4]. A typical LTCC module is a multilayered compact of ceramic substrates and common internal electrode material Ag which will melt at 961 °C. Advanced substrate materials for microwave integrated circuits should possess a high quality factor ($Q_u \times f$), a small temperature coefficient of resonant frequency (τ_f), and especially a low relative permittivity ($\varepsilon_r < 15$) to avoid signal delay [5].

Several ceramics such as Al_2O_3 [6], Mg_2SiO_4 [7], $Mg_4Nb_2O_9$ [8], and $MgSiO_3$ [9] have been developed and regarded as low ε_r microwave dielectric ceramics. However, these ceramics suffer the disadvantage of high sintering temperatures. In order to reduce the sintering temperature of dielectric ceramics, adding sintering aids, such as low-melting glass or oxides, is the common method. But the microwave dielectric properties of the materials will be degraded seriously as the glass or oxides will produce a large amount of amorphous phase in the materials.

Recently, some potential candidates for LTCC substrates have been concentrated on the compounds containing low melting point oxides [10–15]. Among these compounds, $Mg_2V_2O_7$ and $R_2V_2O_7$ (R=Ba, Sr, and Ca) ceramics possessed a good combination of microwave dielectric characteristics: ε_r=10~12.1, $Q_u \times f$=15,200–58,300 GHz, and τ_f=−26~35 ppm/°C [14,15]. However, no investigations on their chemical compatibility with silver has been reported to date. Recently, we reported a low ε_r and high $Q_u \times f$ microwave dielectric ceramic $LiCa_3MgV_3O_{12}$ with cubic garnet-structure, which could be well sintered at 900 °C and was compatible with Ag electrode [16]. In Na_2O–CaO–MgO–V_2O_5 system, $NaCa_2Mg_2V_3O_{12}$ also adopts the cubic garnet structure reported by Bayer and was synthesized at 750 °C [17]. Therefore, the $NaCa_2Mg_2V_3O_{12}$ ceramic might have a low sintering temperature as well as good microwave dielectric properties to meet the requirement for LTCC application. In the present paper, the preparation and microwave dielectric properties of $NaCa_2Mg_2V_3O_{12}$ ceramic were reported for the first time, and its chemical compatibility with silver electrode was also investigated to check whether the $NaCa_2Mg_2V_3O_{12}$ ceramic is suitable for the LTCC

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technology. Adjusting the temperature coefficients of resonant frequency (τ_f) of $NaCa_2Mg_2V_3O_{12}$ ceramic by the addition of $CaTiO_3$ with a large positive τ_f value (~+800 ppm/°C)[18] was also studied.

2. Experimental procedure

$NaCa_2Mg_2V_3O_{12}$ ceramics were prepared using the solid-state ceramic route from high-purity powder of Na_2CO_3, $CaCO_3$, MgO, and V_2O_5 (> 99%, Guo-Yao Co. Ltd., Shanghai, China). Since MgO is hygroscopic, it was calcined at 800 °C for 2 h to remove moisture retains. Powders were mixed and milled for 4 h using a planetary mill (Nanjing Machine Factory, Nanjing, China) operating at a running speed of 150 rpm with ZrO_2 media using alcohol as a medium. The mixtures were dried and calcined at 800 °C for 4 h. The calcined powder was re-milled for 6 h using 5 wt% of polyvinyl alcohol solution as a binder. The obtained powder was then crushed into a fine powder through a sieve with a 200 mesh. The obtained fine powder was then pressed into pellets of 12 mm in diameter and 7 mm in height by uniaxial pressing under a pressure of 200 MPa. The pellets were heated at 600 °C for 4 h to remove the PVA and then sintered on a Pt foil at 885–945 °C for 4 h.

The phase composition of the samples was analyzed by an X-ray diffraction measurement (Cu$K\alpha_1$, 1.54059 Å, Model X'Pert PRO, PANalytical, Almelo, Holland) with Cu$K\alpha$ radiation generated at 40 kV and 100 mA. The bulk densities of sintered ceramics were measured by Archimedes' method. The surface microstructure of the samples was examined using a 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 analyzed using a network analyzer (Model N5230A, Agilent Co., Palo Alto, Canada) and a temperature chamber (Delta 9039, Delta Design, San Diego, CA). The temperature coefficient of resonant frequency τ_f values were calculated using the following formula:

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

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 of the $NaCa_2Mg_2V_3O_{12}$ (NCMV) ceramic sintered at 915 °C for 4 h is shown in Fig. 1, and it can be fully indexed as single-phase with cubic garnet structure, which agreed well with the result reported by Bayer [17]. The FE-SEM micrograph of the surface of NCMV ceramic is also shown in Fig. 1. Homogenous microstructure with grains size in the range 1–5 μm and few pores could be observed for NCMV ceramic sintered at 915 °C for 4 h.

The variations of relative density, ε_r, $Q_u \times f$, and τ_f of $NaCa_2Mg_2V_3O_{12}$ ceramics as a function of the sintering

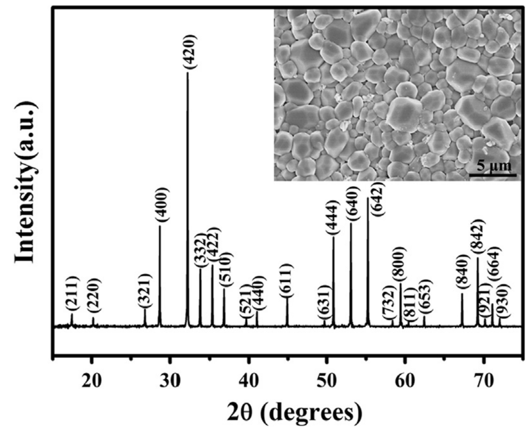


Fig. 1. X-ray diffraction result and FE-SEM image for the surface of a $NaCa_2Mg_2V_3O_{12}$ ceramic sintered at 915 °C for 4 h.

temperature were presented in Fig. 2. The relative density of $NaCa_2Mg_2V_3O_{12}$ ceramic increased with increasing sintering temperature, reached a maximum value (95.8%) at 915 °C, and then decreased slightly. Microwave dielectric properties versus sintering temperature of NCMV ceramics exhibited a trend similar to that of the relative density. ε_r increases from 8.8 to 10 as sintering temperature increases from 885 to 915 °C. Then ε_r reaches saturation and maintains stability, which indicates that the ε_r of ceramic is associated with the elimination of the pores [10,19]. The influence of the porosity on the microwave permittivity could be eliminated by applying Bosman and Havinga's correction [20] as shown in Eq. (2).

$$\varepsilon_{corrected} = \varepsilon_m(1 + 1.5p) \quad (2)$$

where $\varepsilon_{corrected}$ and ε_m are corrected and measured values of permittivity, respectively. p is the fractional porosity (0.042 in this work). The porosity corrected permittivity is about 10.75. The $Q_u \times f$ value of NCMV ceramics reaches the maximum with a value of 50,600 GHz. Thereafter, the $Q_u \times f$ values decrease with further increasing temperature, which may be due to the decreased densification caused by the evaporation of Na_2O [21]. τ_f values of NCMV ceramic do not change remarkably with increasing sintering temperature and remain stable at about −47 ppm/°C.

$NaCa_2Mg_2V_3O_{12}$ ceramic developed in the present study has a low sintering temperature (915 °C), a good combination of microwave dielectric properties (ε_r=9.9, $Q_u \times f$=50,600 GHz), low bulk density (< 3.5 g/cm^3) and low cost (cheap raw materials). However, the temperature stability of resonant frequency is poor (τ_f=−47 ppm/°C) which precludes its use as substrate material for 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) [18]. A similar approach was recently used by Huang and Tseng to tailor τ_f of $Ca_4MgNb_2TiO_{12}$ ceramics [22]. The addition of 30 mol% $CaTiO_3$ to $Ca_4MgNb_2TiO_{12}$ (τ_f~−32 ppm/°C) results in a ceramic composite exhibiting ε_r~43.88, $Q_u \times f$~20,200 GHz and τ_f~−6.9 ppm/°C [23]. In this paper, the microwave dielectric properties and XRD patterns of (1−x) $NaCa_2Mg_2V_3O_{12}$–$x$$CaTiO_3$ (0≤x≤0.2) ceramics sintered at

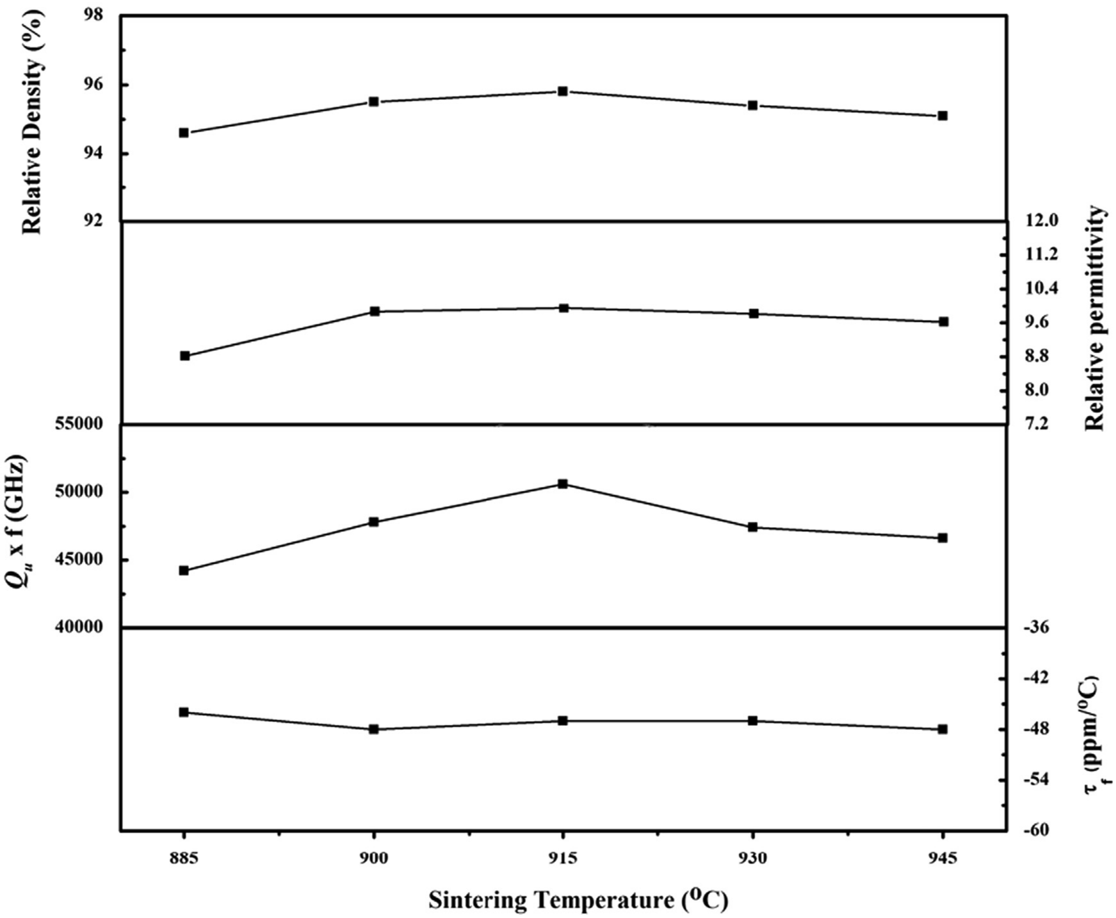


Fig. 2. The relative density, relative permittivity, quality factor, and temperature coefficient of the resonant frequency of $NaCa_2Mg_2V_3O_{12}$ ceramic as a function of sintering temperature.

Table 1
Bulk density and microwave dielectric properties of $(1-x)NaCa_2Mg_2V_3O_{12}$–$xCaTiO_3$ ($0 \leq x \leq 0.2$) ceramics sintered at 930 °C for 4 h.

x value	Bulk density (g/cm^3)	ε_r	$Q_u \times f$ (GHz)	τ_f (ppm/°C)
0	3.28	9.8	47,400	−47
0.05	3.25	10.1	45,600	−40
0.1	3.20	10.7	41,900	−28
0.2	3.16	11.5	37,500	2

930 °C for 4 h are shown in Table 1 and Fig. 3. The ε_r values increased from 9.8 to 11.5 and the τ_f values increased from −47 to 2 ppm/°C with increasing x values from 0 to 0.6. All the sintered ceramics exhibited high $Q_u \times f$ values. The $0.8NaCa_2Mg_2V_3O_{12}$–$0.2CaTiO_3$ ceramic sintered at 930 °C exhibits favorable microwave dielectric properties with $\varepsilon_r = 11.5$, $Q_u \times f = 37{,}500$ GHz, and $\tau_f = 2$ ppm/°C. Fig. 4 shows the result from energy-dispersive spectroscopy of second phase in $0.8NaCa_2Mg_2V_3O_{12}$–$0.2CaTiO_3$ ceramic sintered at 930 °C. Ca and Ti element are detected at a ratio of approximately 1:1, which confirms $CaTiO_3$ as the secondary phase.

For chemical compatibility experiment, mixtures of ceramic powders with 20 wt% Ag powders were cofired and analyzed to detect interactions between the low-fired samples and electrodes. The X-ray powder diffraction pattern (XRPD) and the backscattered electron image of $NaCa_2Mg_2V_3O_{12}$ cofired with Ag at 915 °C are presented in Fig. 5. Since the XRD pattern does not show the formation of any other phase except for $NaCa_2Mg_2V_3O_{12}$ and Ag, and the backscattered electron image of $NaCa_2Mg_2V_3O_{12}$/Ag sample cofired at 915 °C for 2 h reveals no interaction to form new phases after firing, then it is considered that the $NaCa_2Mg_2V_3O_{12}$ compound has a chemical compatibility with silver.

4. Conclusions

Novel low firing temperature vanadate garnet $NaCa_2Mg_2V_3O_{12}$ ceramic was investigated as promising low-loss dielectric ceramic

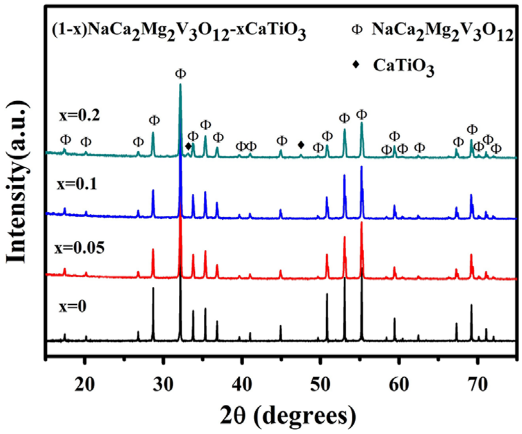
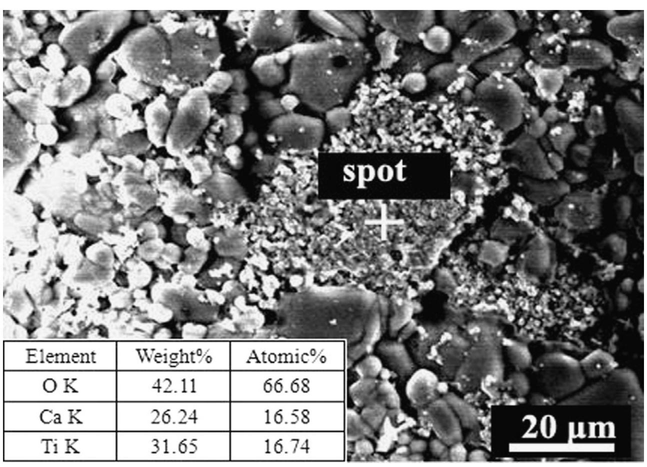


Fig. 3. XRD patterns of $(1-x)NaCa_2Mg_2V_3O_{12}$–$xCaTiO_3$ ($0 \leq x \leq 0.2$) ceramics sintered at 930 °C for 4 h.



Element	Weight%	Atomic%
O K	42.11	66.68
Ca K	26.24	16.58
Ti K	31.65	16.74

Fig. 4. FE-SEM image of $0.8NaCa_2Mg_2V_3O_{12}$–$0.2CaTiO_3$ ceramic sintered at 930 °C. Inset shows result of energy-dispersive spectroscopy of second phase in $0.8NaCa_2Mg_2V_3O_{12}$–$0.2CaTiO_3$.

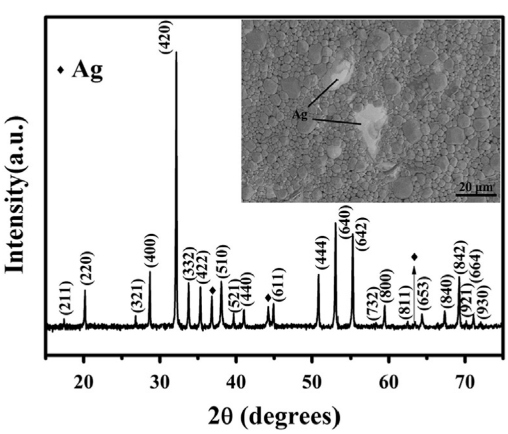


Fig. 5. XRD pattern of a $NaCa_2Mg_2V_3O_{12}$ ceramic mixed with 20 wt% Ag sintered at 915 °C for 2 h. Inset shows a backscattered electron image of $NaCa_2Mg_2V_3O_{12}$ sample cofired with Ag.

for microwave applications. NCMV ceramic can be densified at a relatively low sintering temperature of 915 °C and exhibited promising microwave dielectric properties of $\varepsilon_r = 10$, $Q_u \times f = 50{,}600$ GHz, and $\tau_f = -47$ ppm/°C. It was showed that the microwave properties were improved by adding a small amount of $CaTiO_3$ into NCMV, and the $0.8NaCa_2Mg_2V_3O_{12}$–$0.2CaTiO_3$ ceramic sintered at 930 °C for 4 h exhibited improved properties of $\varepsilon_r = 11.5$, $Q_u \times f = 37{,}500$ GHz, and $\tau_f = 2$ ppm/ °C. The backscattered electron image and XRD analysis confirmed that the ceramic did not react with silver powders, indicating that $NaCa_2Mg_2V_3O_{12}$ might be an attractive promising candidate for LTCC application.

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