Journal of Alloys and Compounds 709 (2017) 234–239

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Low-temperature firing and microwave dielectric properties of (1−x) $Ca_5Mg_4(VO_4)_6$-x$Ba_3(VO_4)_2$ temperature stable ceramics

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ARTICLE INFO

Article history:
Received 14 December 2016
Received in revised form
7 March 2017
Accepted 10 March 2017
Available online 14 March 2017

Keywords:
Microwave dielectric properties
LTCC
Vanadate
Temperature-stable dielectrics

ABSTRACT

(1−x)$Ca_5Mg_4(VO_4)_6$-x$Ba_3(VO_4)_2$ ($0.5 \leq x \leq 0.7$) ceramics were fabricated via the conventional solid-state reaction method. The phase composition, microstructure, and compatibility with silver were investigated using X-ray diffraction, Raman spectra and Scanning electron microscopy. The results confirmed that $Ca_5Mg_4(VO_4)_6$ and $Ba_3(VO_4)_2$ crystal phases can be well coexisted in the sintered ceramics. The temperature coefficient of resonant frequency could be tuned by the volume mixture rule of $Ca_5Mg_4(VO_4)_6$ and $Ba_3(VO_4)_2$. As for the addition of $Ba_3(VO_4)_2$, the ε_r showed to increase, while the Qxf declined. In particular, the $0.35Ca_5Mg_4(VO_4)_6$-$0.65Ba_3(VO_4)_2$ composite ceramics sintered at 900 °C for 5 h showed excellent combinational microwave dielectric properties: $\varepsilon_r = 11.9$, Qxf = 35 000 GHz, and $\tau_f = -2$ ppm/°C, which also exhibited good chemical compatibility with silver.

1. Introduction

Considerable attentions have been drawn to develop microwave dielectrics with high performance for applications in substrate, radar for Pre-Crash Safety System, and noncompressed digital video transmission system, which demand low dielectric constant ($\varepsilon_r < 15$), low dielectric loss (high quality factor $Q \times f$, $\tan\delta = 1/Q$), and a near-zero temperature coefficient of resonant frequency (τ_f) [1–3]. Another crucial factor that deserves tremendous attention is the low temperature cofired ceramic (LTCC) technology, which is benefited for low-cost and miniaturization in the microwave devices [4–7]. To meet the requirement of LTCC technology, the materials must have lower sintering temperature than the melting point cheap metal Ag electrode (961 °C). However, the sintering temperatures for most of the reported substrate materials are too high (>1000 °C) to be utilized as LTCC materials [8–10]. Therefore, it is desirable to develop new kinds of low-temperature sintering advance substrate ceramics with high performance for practical LTCC applications.

In our previous work, $Ca_5Mg_4(VO_4)_6$ ceramic was reported to possess intrinsic low sintering temperature (800 °C) and superior microwave dielectric properties ($\varepsilon_r = 9.2$, Qxf = 49 400 GHz, and $\tau_f = -50$ ppm/°C) [11]. However, the large negative τ_f limited its further application in LTCC devices. An easy and effective approach to compensate τ_f through zero is to combine two chemical compounds with τ_f of opposite signs to form composite materials [12]. Especially for diphasic ceramics with different crystal structures, it has been proved to be effectively inhibited the formation of the solid solutions or secondary phases, and guaranteed the desirable microwave dielectric properties [13–15]. $Ba_3(VO_4)_2$ exhibits an exceptionally relatively low ε_r but a large positive τ_f value (60 ppm/°C) [16]. It is often used as an end-member in composite ceramics with near-zero τ_f, such as $Ba_3(VO_4)_2$-$Zn_{2-x}SiO_{4-x}$ and $Ba_3(VO_4)_2$-$BaWO_4$, etc [17–19]. Hence, in the present work, (1−x)$Ca_5Mg_4(VO_4)_6$-x$Ba_3(VO_4)_2$ ($0.5 \leq x \leq 0.7$) ceramics with different crystal structure were prepared by the conventional solid-state reaction method, aiming to increase the thermal stability, while maintaining relatively low ε_r and reasonably high Qxf. The phase constitution, microstructure, compatibility with silver electrode, and microwave dielectric properties of resultant ceramics were performed in detail.

2. Experimental procedure

The starting materials are high-purity oxide or carbonate powders (>99.9%; Guo-Yao Co. Ltd., Shanghai, China): MgO, V_2O_5, $CaCO_3$, and

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http://dx.doi.org/10.1016/j.jallcom.2017.03.112
0925-8388/

$BaCO_3$. Predried raw materials were separately weighed in stoichiometric mixtures $Ca_5Mg_4(VO_4)_6$ (CMV) and $Ba_3(VO_4)_2$ (BV) and ball-milled for 8 h in a nylon jar with agate balls and ethanol as media. The CMV and BV powders were calcined at 700 °C for 3 h and 650 °C for 20 h, respectively. The calcined powders were mixed according to molar fraction (1−x)CMV-xBV ($0.5 \leq x \leq 0.7$) and then re-milled for 8 h again. The milled powders were dried. After drying, the powders with 5 wt% polyvinyl alcohol (PVA) as a binder were pressed into pellets 10 mm in diameter and 5 mm in thickness under a pressure of 100 MPa. These pellets were sintered from 875 to 950 °C for 5 h in air with a heating rate of 5 °C/min, and then cooled to room temperature.

The bulk densities of the sintered ceramics were measured by Archimedes' method. The crystal structures were analyzed using X-ray powder diffraction (XRD) with Cu Ka radiation (Rigaku D/MAX2550, Tokyo, Japan). The Raman spectra were collected at room temperature using a Raman Microscope (Horiba Jobin Yvon S.A.S., France) with Ar ion laser (514 nm) operated at 30 mw. The microstructure of pellets was investigated using a scanning electron microscope (SEM, Fei Quanta 200, Eindhoven, Holland) coupled with energy dispersive X-ray spectroscopy (EDS). The microwave dielectric properties of sintered samples were measured using a network analysis (ZVB20, Rohde & schwarz, Munich, Germany) with the $TE_{01\delta}$ shielded cavity method. The temperature coefficient of resonant frequency (τ_f) was calculated with the following equation (1):

$$\tau_f = \frac{f_{80} - f_{20}}{f_{20} \times (80 - 20)} \quad (1)$$

where f_{80} and f_{20} are the resonant frequency at 80 °C and 20 °C, respectively.

3. Results and discussion

Fig. 1 illustrates the XRD patterns of the (1-x)CMV-xBV ($0.5 \leq x \leq 0.7$) ceramics sintered at 900 °C for 5 h. All diffraction peaks could be well indexed by CMV (JCPDS #34-0014) and BV (JCPDS #29-0211) phases, and no obvious secondary phase was found, indicating that a stable diphasic system CMV-BV was formed in the studied range. Moreover, it can be seen that the intensity of the diffraction peaks of the CMV phase decreased gradually as the BV content increased. In the hexagonal structure BV with space

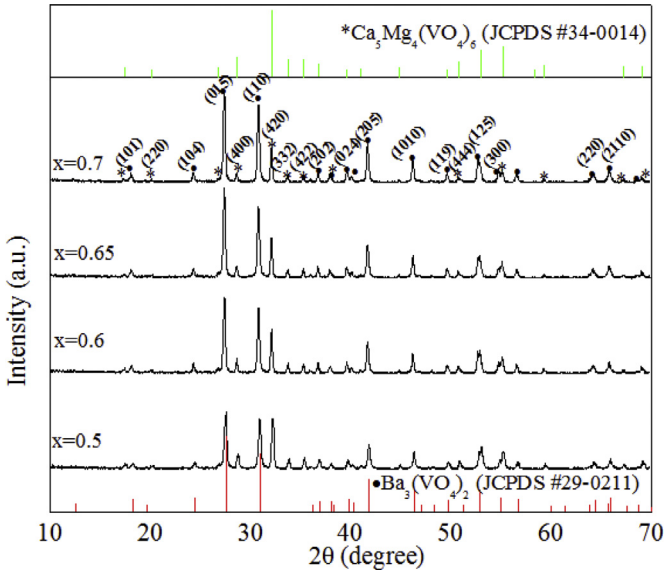

Fig. 1. XRD patterns of the (1−x)CMV-xBV ceramics sintered at 900 °C for 5 h.

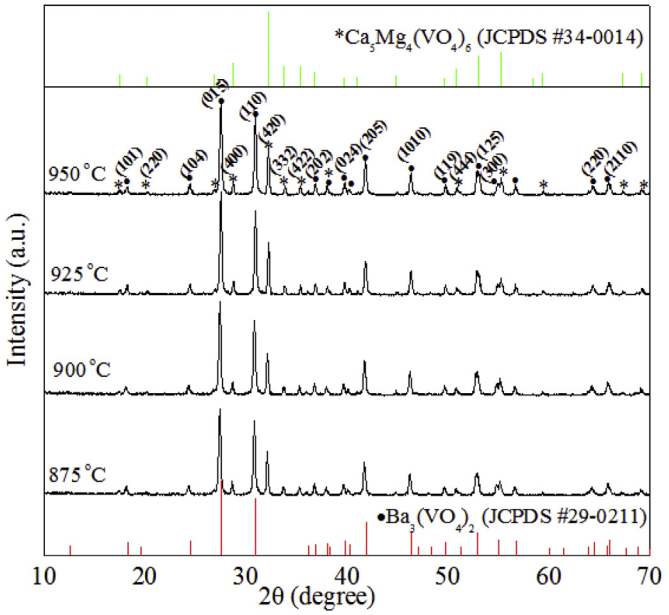

Fig. 2. XRD patterns of the 0.35CMV-0.65BV ceramics sintered at various temperatures.

group R-32/m, V^{5+} ions locate in the center of tetrahedral [VO_4] groups link by sixfold and tenfold coordinate Ba^{2+} ions [20]. CMV exhibits a cubic garnet structure with space group of Ia-3d, the octahedral [MgO_6] units connect to the tetrahedral [VO_4] units by corner-sharing forming three-dimensional structural framework and Ca ions are located inside the voids [21]. The formation of diphasic ceramics in samples can be attributed to the their visible differences in the crystal structure and linkages of polyhedral units, which inhibit the chemical reaction between them. In accordance with the pertinent literature, the good chemical compatibility of CMV and BV is benefit for the successful compensation of the dielectric properties, especially for τ_f [22].

The XRD patterns of the 0.35CMV-0.65BV ceramics sintered at various temperatures are illustrated in Fig. 2. In all samples, only the mixed phases CMV and BV could be detected and no other secondary phase was observed, regardless of the sintering temperature. This indicates the CMV-BV composite ceramics can coexist well in the temperature range of 875–950 °C.

Fig. 3 shows the Raman spectra of the (1−x)CMV-xBV ceramics

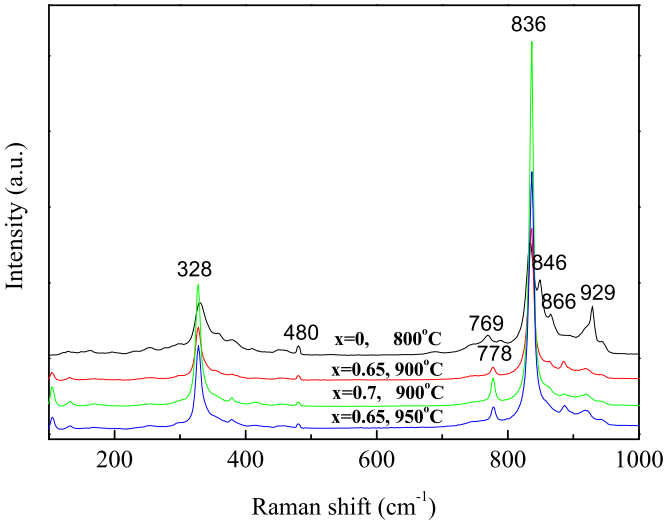

Fig. 3. Raman spectra of the (1−x)CMV-xBV ceramics sintered at different conditions.