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Novel thermal-stable low temperature sintered $Ba_2LiMg_2V_3O_{12}$ microwave dielectric ceramics with ZnO-P_2O_5-MnO_2 glass addition

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ABSTRACT

Novel $Ba_2LiMg_2V_3O_{12}$ ceramics with different amount of ZnO-P_2O_5-MnO_2 (ZPM) glass addition were densified at 850 °C via a solid-state reaction route. No reaction between the ceramic matrix and Ag was detected. A $Ba_3(VO_4)_2$ secondary phase generated in the $Ba_2LiMg_2V_3O_{12}$ matrix made a positive contribution to the τ_f value. Further addition of the ZPM glass adjusted the τ_f value to near zero. Among all specimens, the sample with 2 wt.% of the ZPM addition (marked as BZ20) possessed good microwave dielectric properties: ε_r = 13.47, Q × f = 16272 GHz (11.18 GHz), τ_f = (+)0.4 ppm/°C. All experimental results suggested that a novel thermal-stable microwave dielectric ceramic system was designed for LTCC applications.

1. Introduction

Rapid development of wireless communication demands vast amount of microwave components. For most microwave devices, dielectric ceramic materials are widely adopted due to their advantages in compactness, thermal stability, light weight, and low cost for high frequency applications [1]. Further development of device miniaturization and integration requires that the ceramic could be cofired with the internal metal electrodes. Low-temperature co-fired ceramic (LTCC) technology is a superior solution for miniaturization and integration [2]. Silver (Ag), due to its high conductivity and low cost, has been widely used as the internal electrodes, but its melting temperature is only about 961 °C [3]. Thus it is essential to explore new low-temperature sintered ceramic systems with good compatibility between the dielectric matrix and silver electrodes [4,5].

For most microwave devices, the frequency determining components require that the dielectric materials should possess moderate permittivity (ε_r), low dielectric loss (high Q), and nearly zero temperature coefficient of resonant frequency (τ_f) with low cost [1]. However, it is always a challenge to balance and realize these performance indexes within one single material. Therefore, various material systems with different crystal structure were investigated to break the limitations [6–9]. Among these materials, garnet-type compounds were reported as promising candidates in the field of lasers, phosphors, and ferrite materials [10–12], whereas few results were related with their microwave dielectric properties. Recently, the microwave dielectric properties of the $Re_3Ga_5O_{12}$ (Re = Nd, Sm, Eu, Dy, Yb, and Y) garnets were uncovered and promising microwave dielectric performance were obtained: high Q × f (>40000 GHz), low ε_r value (~12), and relatively stable τ_f values (−33.7 to −12.4 ppm/°C) [13]. However, their sintering temperatures are usually too high (1350 °C–1500 °C) to apply for LTCC technology. Fortunately, some modified garnet vanadates were reported with low sintering temperatures and good microwave dielectric properties, which are potential for LTCC applications [14–16]. Fang et al. reported that the $LiCa_3MgV_3O_{12}$ ceramic sintered at 900 °C showed a low ε_r value of 10.5, a high Q × f value of 74700 GHz, and a τ_f value of −61 ppm/°C [14]. Further exploration on $NaCa_2Mg_2V_3O_{12}$ ceramics reached to a similar result: a low ε_r value of 10, a relative high Q × f value of 50600 GHz, and a τ_f value of −47 ppm/°C when sintered at 915 °C [15]. These results indicated that the modified garnet vanadates possess relatively high Q × f values when sintered at low temperature, but their large negative τ_f values prohibited their practical applications. Therefore, it is essential to search for new garnet microwave dielectric systems with a near-zero temperature coefficient of resonant frequency.

As known, phosphate glass is promising for its eco-friendly compatibility with low-melting-point below 600 °C, which is

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beneficial for LTCC technology [17–19]. But the P_2O_5 based phosphate glass usually possesses relatively poor chemical stability, thus different oxides such as ZnO, MnO_2, Al_2O_3, and CuO have been adopted to improve its performance [20–22]. Among these modified systems, ZnO-P_2O_5-MnO_2 based system is promising due to its lower ternary eutectic temperature and better performance in low temperature, which is widely applied in electronic packaging area. Based on these promising characteristics, ZnO-P_2O_5-MnO_2 glass might be a suitable sintering aid for garnet-structured microwave dielectrics.

In this study, novel $Ba_2LiMg_2V_3O_{12}$ ceramic system with different amount of ZnO-P_2O_5-MnO_2 (ZPM) glass addition were fabricated via a solid-state reaction route. The microstructure and microwave dielectric properties were investigated systematically. It was revealed that the combined $Ba_3(VO_4)_2$ secondary phase generated in the $Ba_2LiMg_2V_3O_{12}$ matrix with the ZPM glass addition made a positive contribution on τ_f, adjusting its value to near zero, which was promising for microwave applicaitons.

2. Experimental procedure

$Ba_2LiMg_2V_3O_{12}$ powders were synthesized with reagent grade $BaCO_3$, Li_2CO_3, MgO, and V_2O_5 (all purity > 99%, Sinopharm Chemical Reagent Co. Ltd, Shanghai, China). The starting materials were accurately weighed in stoichiometric ratios, mixed with zirconia media and ethanol by ball milling for 24 h. After drying, the mixture were calcined at 800 °C for 4 h to form the $Ba_2LiMg_2V_3O_{12}$ phase. To ensure the sintering temperature of the $Ba_2LiMg_2V_3O_{12}$ ceramics stay lower, ZnO-P_2O_5-MnO_2 (ZPM) glass addition was added. The ZPM powders were synthesized with a composition of 65 mol% of ZnO, 30 mol% of P_2O_5, and 5 mol% of MnO_2, using reagent grade ZnO, P_2O_5, and MnO_2 (all purity > 99%, Sinopharm Chemical Reagent Co. Ltd, Shanghai, China). The ZPM mixture was melted at 1100 °C for 30 min in a platinum crucible and followed by a quenching process in cold deionized water to form amorphous ZPM glass. Then the quenched glass was dried and crushed into powders, milled again for 10 h. Then different amount of the ZPM powders (x = 0 wt.%, 0.5 wt.%, 1 wt%, and 2 wt.%) were added into the $Ba_2LiMg_2V_3O_{12}$ matrix. For convenience, we abbreviated these samples as BZx: BZ (0 wt.%), BZ05 (0.5 wt.%), BZ10 (1 wt.%), and BZ20 (2 wt.%), respectively. After re-milling for another 10 h, the dried BZx powders were subsequently granulated with PVA binder and pressed into cylinder-shaped bulks with 12 mm in diameter and 6 mm in thickness. The green bulks were sintered in a temperature range of 800–900 °C for 4 h in air atmosphere.

The bulk densities of the as-sintered samples were measured by Archimedes method. The phase structure of the as-sintered samples were examined by an X-ray diffractometer (XRD: Philips X' pert Pro MPD, PANalytical Company, Almelo, Holland) at a scanning rate of 10°/min in the range of $10° \leq 2\theta \leq 80°$, using CuKα radiation. The microstructure of the as-sintered ceramics was observed using a scanning electron microscope (SEM: JEOL JSM-6490, Tokyo, Japan). The dielectric properties at microwave frequencies were measured by the Hakki-Coleman dielectric resonator method in TE011 mode by using a network analyzer (Agilent N5230A, 300 MHz—20 GHz, Agilent Technologies, Palo Alto, CA, USA) combined with a temperature chamber (Delta 9023, Delta Design, USA). The temperature coefficient of resonant frequency value (TCF, τ_f) can be determined via the following equation [23]:

$$\tau_f = \frac{f_T - f_{T_0}}{f_{T_0} \times (T - T_0)} \times 10^6 \text{ppm}/°\text{C}$$

where f_T and f_{T_0} were the resonant frequencies at temperature T (85 °C) and T_0 (25 °C), respectively.

3. Results and discussions

Fig. 1 shows the bulk density of the ZPM modified $Ba_2LiMg_2V_3O_{12}$ ceramics at different sintering temperatures. It is observed that the bulk density values for all specimens increase with the sintering temperature, approaching to a maximum value around 850 °C, then decline. It should be pointed out that the densification temperature is slightly shifted towards lower temperatures while the bulk density is increased with introducing the ZPM glass, as the arrow marked in Fig. 1. This sintering behavior demonstrates that pure $Ba_2LiMg_2V_3O_{12}$ ceramics can be fired blow 950 °C without any sintering aids, which meets the basic requirements of the LTCC technology; the addition of the ZPM glass can lower the sintering temperature and assist to densify the $Ba_2LiMg_2V_3O_{12}$ ceramics. Based on the above sintering behavior, we select the specimens fired at 850 °C for further investigation.

Fig. 2 shows the XRD patterns of the ZPM modified $Ba_2LiMg_2V_3O_{12}$ ceramics sintered at 850 °C for 4 h. Besides the cubic garnet structured $Ba_2LiMg_2V_3O_{12}$ phase with a lattice parameter of a = 12.5408 Å, as indexed with rhombus shape in red, a secondary phase of $Ba_3(VO_4)_2$ with hexagonal crystal structure (R-3m, PDF# 29-0211) is detected (marked with heart shape). As $Ba_3(VO_4)_2$ is also a promising microwave dielectric system with positive τ_f values and high Q × f values [24,25], this secondary phase may not deteriorate the dielectric performance of this $Ba_2LiMg_2V_3O_{12}$ system. No third phase related with the ZPM glass can be detected.

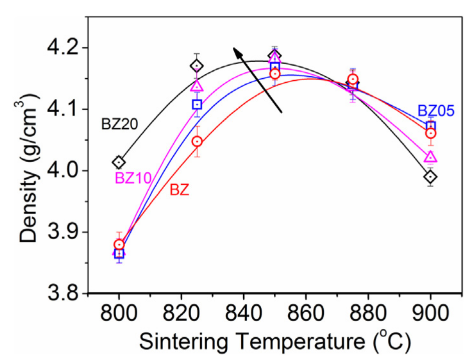

Fig. 1. Bulk density of the ZPM modified $Ba_2LiMg_2V_3O_{12}$ ceramics at different sintering temperatures.

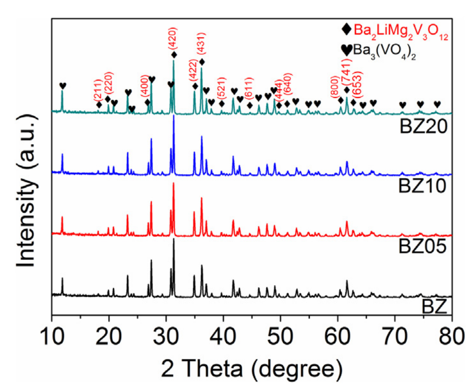

Fig. 2. XRD patterns of the ZPM modified $Ba_2LiMg_2V_3O_{12}$ ceramics sintered at 850 °C for 4 h.