Materials Letters 139 (2015) 169–172

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Low-temperature densification of Mg_2SnO_4 ceramics with LiF-Fe_2O_3-V_2O_5 additive

Juehui Zhou [a], Nuoxin Xu [a], Qilong Zhang [a,*], Di Zhou [b], Xin Tang [a], Hui Yang [a]

[a] Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China
[b] Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an 710049, China

ARTICLE INFO

Article history:
Received 21 July 2014
Accepted 11 October 2014
Available online 22 October 2014

Keywords:
Sintering
Microstructure
Dielectrics
Electroceramics
Electrical properties

ABSTRACT

The effects of LiF-Fe_2O_3-V_2O_5 (LFV) additive on the sinterability, microstructure, phase composition, and microwave dielectric properties of Mg_2SnO_4 is investigated. By adding LFV additive, the densification temperature of Mg_2SnO_4 ceramics is significantly lowered from 1550 °C to 1050 °C. XRD shows all doped samples are single-phase Mg_2SnO_4 with *Fd*3*m* space group. TEM image and EDS spectra indicate that an amorphous phase is formed in the intergranular region, and Fe^{3+} ions presents in Mg_2SnO_4 matrix. Mg_2SnO_4 with 4 wt.% LFV additive sintered at 1050 °C provides the attractive combination of dense microstructure and excellent dielectric properties: ε_r=7.90, $Q\times f$=41,400 GHz and τ_f=−82 ppm/°C. In addition, the ceramic is compatible with Ag/Pd electrodes, suggesting the potential application in millimeter-wave communication.

1. Introduction

In recent years, with the rapid development of wireless and mobile communication, high-quality microwave dielectric ceramics have significantly attracted scientific and commercial attention. In the case of microwave substrate application and higher frequency applications (such as millimeter wave or higher), dielectric ceramics with low dielectric constant ($\varepsilon_r \leq 10$) (low-K) are preferred for integrated circuits [1–3]. Up till now, several kinds of low-K materials, such as $Mg_3B_2O_6$, Al_2O_3, Mg_2SiO_4, Mg_2SnO_4, and Zn_2GaO_4, have been investigated [2,4–6], among which spinel Mg_2SnO_4 is a relatively new candidate with low dielectric constant (ε_r=8.41) and high quality factor ($Q\times f$=55,100 GHz for pure Mg_2SnO_4 sintered at 1550 °C) [7]. Recently, the microwave dielectric properties were further enhanced by ion substitution of Mg(II) with Zn(II), Ni(II) or Co(II) [8–10], and Mg-nonstoichiometry [11]. However, the sintering temperatures of these Mg_2SnO_4-based ceramics are rather high ($T_{sint.} \geq 1550$ °C), making them unavailable for electrode co-fire process [12]. To the best of our knowledge, few investigations on the low-temperature sintering of Mg_2SnO_4-based ceramics have been reported.

In this work, LiF-Fe_2O_3-V_2O_5 (LFV) additive is employed to lower the sintering temperature of Mg_2SnO_4 ceramic. The sintering mechanism and corresponding effects of additive on the microstructure and dielectric properties of Mg_2SnO_4 ceramics are studied. In addition, the co-firing behavior of ceramic with Ag/Pd electrode is investigated.

2. Experimental

High-purity powders of MgO (≥99.9%), SnO_2 (≥99.95%), LiF (≥98%), Fe_2O_3 (≥99%), and V_2O_5 (≥99%) were used as precursors. Mg_2SnO_4 was prepared by calcining MgO and SnO_2 powder mixtures at 1,200 °C for 4 h. The resulting Mg_2SnO_4 was added by 1∼5 wt. % LiF-Fe_2O_3-V_2O_5 (LFV, sintering additive with the weight ratio of LiF:Fe_2O_3:V_2O_5=4:1:2), then ball-milled for 4 h in ethanol medium. The granulated powders were pressed into pellets with a diameter of 18 mm and a thickness around 9 mm. The pellets were sintered at temperature ranging from 1000 °C to 1100 °C for 4 h in covered crucibles.

Bulk density of sintered samples were measured using the Archimedes method. The crystalline phases were identified by X-ray diffraction (XRD, EMPYREAN, PANalytical Co., the Netherlands) with Cu Kα_1 radiation. The fracture morphology of the sintered samples was observed by the field emission scanning electron microscope (FE-SEM, SU-70, Hitachi Ltd., Japan). Microstructure and element distribution of samples were investigated by the transmission electron microscope (TEM, Tecnai G2 F20 S-TWIN, FEI, USA), and energy-dispersive X-ray spectroscopy (EDS),

* Corresponding author. Tel.: +86 571 87951408; fax: +86 571 87953054.
E-mail address: mse237@zju.edu.cn (Q. Zhang).

http://dx.doi.org/10.1016/j.matlet.2014.10.064
0167-577X/

respectively. Microwave dielectric properties of dielectric constants (ε_r), quality factors ($Q \times f$ values), and temperature coefficient of resonant frequency (τ_f) between 25 °C and 80 °C were measured in the TE_{011} mode using Hakki–Coleman method with an Agilent HP-4294 A Network Analyzer. Ceramic sheet with Ag/Pd (with 20% Pd) was co-fired and analyzed to detect interactions between the low-fired samples and Ag/Pd electrodes.

3. Results and discussion

To reveal the effect of LFV additive on the sintering behavior of Mg_2SnO_4 ceramics, a TEM equipped with an EDS system is employed to analyze Mg_2SnO_4 sample sintered at 1050 °C with 4 wt.% LFV additive. It is observed that LFV melt and form an amorphous phase as shown in Fig. 1a (marked as region B). It indicates that LFV wet the grains of Mg_sSnO_4 at sintering process, thereby promoting the densification of ceramic through a typical liquid-phase sintering mechanism [12]. It is worth noting that Fe ions is detected in both the grain (region A) and the intergranular glassy region (region B), while F and V ions are found only in the intergranular region (region B). Thus, Fe^{3+} ions were assumed to dissolved in the Mg_2SnO_4 matrix, which was further proved by XRD analysis.

XRD patterns of pure Mg_2SnO_4 sintered at 1620 °C, Mg_2SnO_4 with xLFV ($x=2\sim5$ wt.%) ceramics sintered at 1050 °C, and Mg_2SnO_4 sintered at 1000∼1100 °C are shown in Fig. 1c. Samples over the whole composition range show a single spinel Mg_2SnO_4 phase (JCPDS card: 24–0732) with $Fd3m$ space group. With the increasing of x, peak positions shift toward higher angles (Fig. 1d), indicating that the volume of unit cell decreases. Spinel Mg_2SnO_4 has the inversed configuration, with half the Mg^{2+} ions occupying the tetrahedral sites and the other half Mg^{2+} ions together with all of the Sn^{4+} ions occupying the octahedral sites [13]. On octahedral sites, the cation radius of Fe^{3+} with coordination number of 6 [R($^{VI}Fe^{3+}$)=0.645 Å] is smaller than that of Mg^{2+} [R($^{VI}Mg^{2+}$)=0.720 Å] and Sn^{4+} [R($^{VI}Sn^{4+}$)=0.690 Å]. On tetrahedral sites, the cation radius of Fe^{3+} with coordination number of 4 [R($^{IV}Fe^{3+}$)=0.490 Å] is also smaller than that of Mg^{2+} [R($^{IV}Mg^{2+}$)=0.570 Å] [14]. Therefore, the Fe^{3+} substitution might occur on either octahedral or tetrahedral sites. In both cases, such Fe^{3+} substitution would decrease the cell volume of Mg_2SnO_4. The previous study indicates that Fe^{3+} occupies both the octahedral and tetrahedral sites in the Mg_2TiO_4-$MgFe_2O_4$ spinel system [15]. Similarly, we could assume that heterovalent substitution of Mg^{2+} and Sn^{4+} takes place, and the solid solution of $Mg_{1-\lambda}Fe_\lambda[Mg_{1-\delta+\lambda}Fe_{2\delta-\lambda}Sn_{1-\delta}]O_4$ is formed. As the sintering temperature increased, the solubility of Fe ion increased so that the peak positions further shift toward higher angles is as shown in Fig. 1d.

Fig. 2 demonstrates the SEM micrographs of 4 wt.% LFV-doped Mg_2SnO_4 ceramics sintered at different temperatures. At 1000°C, the fracture morphologies show a porous structure. As the sintering temperature increases, the structure becomes denser. Well-

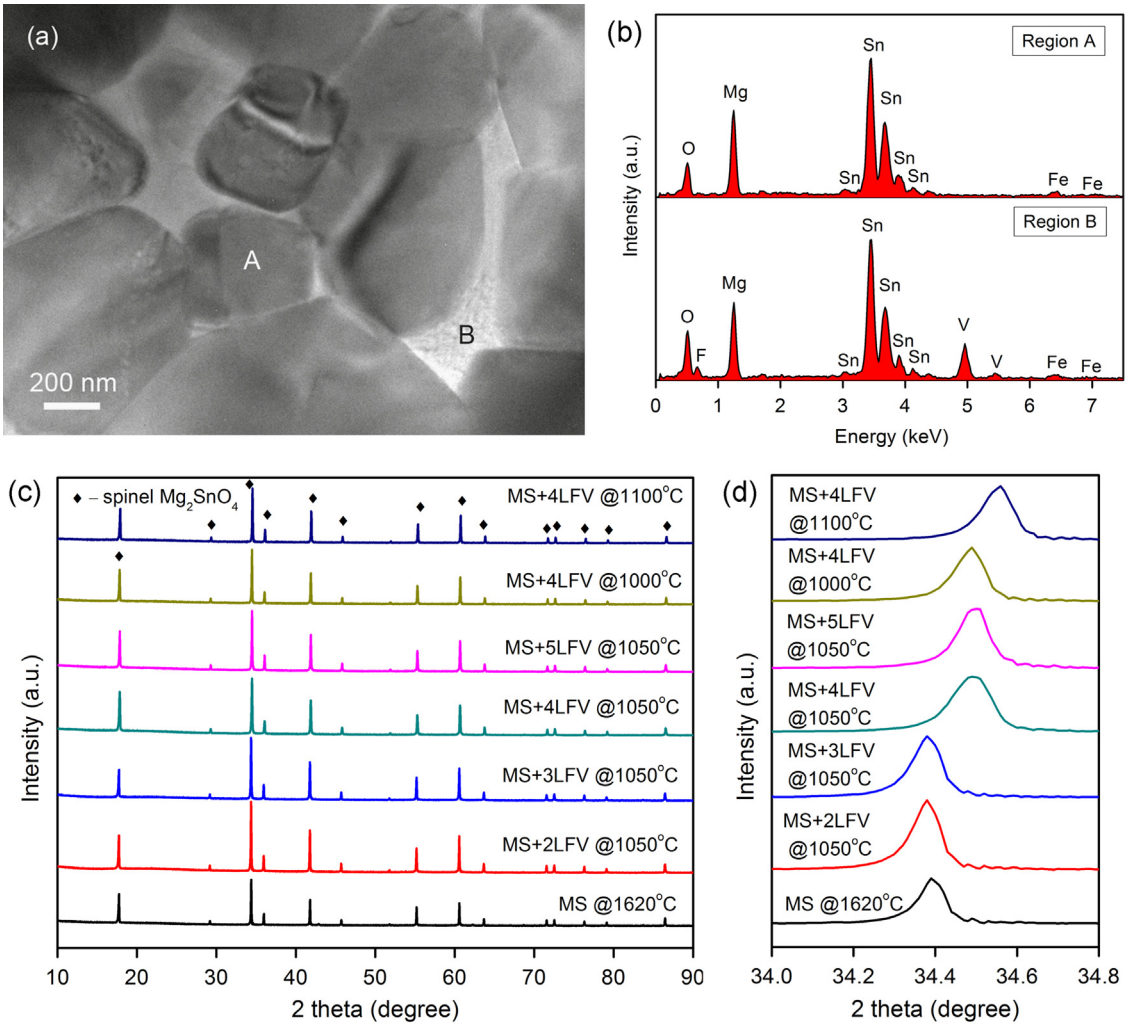

Fig. 1. (a) TEM image of Mg_2SnO_4 ceramic with 4 wt.% LFV additive sintered at 1050 °C, (b) EDS spectra of marked regions, (c) XRD patterns, and (d) (3 1 1) peaks of Mg_2SnO_4 ceramics with different LFV content sintered at different temperatures. MS+xLFV represents Mg_2SnO_4 ceramic with x wt.% LFV additive.