Densification Behavior, Microstructure, and Property of ZnO with Multi-Oxides Glass Addition at Different Sintering Temperatures

Boen Houng[1,*], Wei-Chueh Chien[1], Chen-Kai Sun[2]

[1]Department of Materials Science and Engineering, I-Shou University, Kaohsiung, Taiwan

[2]Emerging Display Technologies Corporation, Kaohsiung, Taiwan

Abstract

Zinc Oxide (ZnO) mixed with various amount of glasses were sintered at different temperatures. The densification behavior of zinc oxide with glass addition and its microstructure and dielectric constant sintered from 900° to 1200°C have been investigated. A unique glass composition contained GeO_2, MoO_3, and V_2O_5 (GMV) was designed to act as the sintering aid to enhance the densification and to adjust the dielectric constant of ZnO. The effect of sintering temperature on the densification behavior and dielectrics properties of ZnO was investigated by dilatometer, x-ray diffractometer, scanning electron microscopy and LCR meter. The glass additive formed a thin continuous liquid phase and rearranged ZnO particles into a dense microstructure at relatively low temperature. The dielectric constants of glass added ZnO ceramics were found to vary with the glass concentration and sintering temperature.

Keywords: ZnO, glasses, densification behavior, dielectric constant

1. Introduction

ZnO has been extensively studied because of its remarkable chemical, optical and electronic properties which give a large perspective to its practical applications such as gas sensors, surface acoustic wave devices, optical waveguides blue/UV light emitting devices as well as photocatalysts [1-7]. In addition, ZnO with high dielectric constants and low dielectric loss have received special attention due to the rapid developments in microwave telecommunications, satellite broadcasting, discrete and multilayer capacitors, dynamic random access memories and low-loss substrates for microwave integrated circuits. [8-9]. Moreover, the development of the Low-Temperature Co-Fired Ceramic technology (LTCC) becomes an important fabricating technology that allows the incorporation of the multilayer structure into a monolithic bulk module with minimal processing steps, thus leading to thin and compact communication devices. Therefore, the LTCC with high electrical conductivity metallization such as silver has been identified to be a feasible solution for applications in the area of wireless communications [10].

Large numbers of materials have been studied with excellent dielectric properties, however, most of them need to be sintered at a higher sintering temperature greater than 1200°C and longer soaking time to achieve high enough density. To solve this problem, low-melting oxides such as Bi2O3, MoO3, CuO, and MnO2-Cr2O3-Sb2O3-Co3O4 are generally mixed with dielectric ceramics to reduce the sintering temperature [11-15]. On the other hand, by using nano-sized particles as starting ceramic materials has also shown an improvement in reducing sintering temperature [16-17]. However, these

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* Corresponding author. E-mail address: boyen@isu.edu.tw

approaches are far from the requirement for LTCC that a firing temperature below 900°C is essential. Since the metal Ag, melted at 961°C, has been used as a conductive electrode in LTCC, thus it is required to develop low-firing temperature ceramics with desirable dielectric properties. Applying a liquid-phase sintering process, refractory ceramics can be sintered at a lower temperature by forming thin continuous or semicontinuous liquid phases at grain boundaries [18-19]. During sintering, the ceramic particles are soluble in the liquid. This solubility causes the liquid to wet the solid, leading a capillary force that pulls the particles together. At the same time, the high temperature softens the solids, further promoting densification. High-diffusion rates are also associated with liquids, resulting in fast sintering or lower sintering temperatures. In addition, ZnO with high dielectric constants and low dielectric loss have received special attention due to the rapid developments in microwave telecommunications, satellite broadcasting, discrete and multilayer capacitors, dynamic random access memories and low-loss substrates for microwave integrated circuits.

In this work, we have designed a unique glass composition containing GeO2, MoO3, and V2O5 as a sintering aid that allows the ZnO to densify at many low temperatures by viscous flow and liquid-phase sintering mechanisms. On the other hand, this glass additive can also adjust the dielectric constant of ZnO by varying the concentration of glass additive. The effect of the glass concentration on the densification behavior, microstructure and dielectric properties of ZnO were investigated.

2. Experimental

The glass composition used as a sintering aid was made up of GeO_2, MoO_3, V_2O_5 in 1:1:3 molar proportion (all with purity ≥99.99%, Aldrich, St. Louis, USA). The traditional twin-roller quencher is used to prepare glass additives. The starting powders were first mixed to form a 60 g batch and then melted in a 90% Pt-10% Rh crucible at 1000°C for 30 minutes using an electric furnace. The melts were stirred to ensure the homogeneity of the glass composition. The molten glasses were subsequently quenched into a twinned roller, yielding thin ribbons of approximately 0.2 mm thickness. The resulting glasses were fully amorphous, as was confirmed by X-ray diffractometry. The ribbon glasses were then ground into powders (<325 mesh) and mixed with ZnO powders in the proportion of 1 to 10 wt % using ethanol solvent and zirconia milling media for 24 h. After drying, the mixtures were die-pressed at 80 MPa to yield several disk type pellets (12 mm in diameter and 3 mm in thickness). The pellets were then sintered at 800, 900, 1000, and 1100°C for 4 h with a heating rate of 5°C/min. The bulk density of samples was measured by the Archimedes method. An X-ray diffractometer (XRD, Panalyical, X'pert Pro) with Cu Kα radiation (λ= 0.1542 nm) was used to characterize the crystallization of the sintered ceramics. Fractured surfaces of the sintered samples were examined using field emission scanning electron microscopy (FESEM, Philips, XL-40FEG). X-ray Energy Dispersive Spectroscopy (EDS) was used to obtain the chemical compositions of the ZnO grain. Shrinkage behavior of the samples during heating from room temperature to 1300°C was measured using a horizontal loading dilatometer with alumina rams and boats (DIL-402C, Netzsch Instrument). The sintered samples were electroded with DC-sputtered films of gold on both sides for dielectric property measurement using an impendence analyzer (Agilent, 4263B, Palo Alto, USA).

3. Results and Discussion

The shrinkage history of ZnO various GMV glass concentrations as a sintering aid was examined by dilatometer as shown in Fig. 1. It can be seen from the diagram that as the number of glass additives increased shrinkage curves were shifted towards much lower temperatures than the typical sintering temperature of pure ZnO. Pure ZnO appears to start shrinkage at a slow rate approximately 1200°C. Nevertheless, ZnO ceramics with 1 and 5 wt % glass additives showed the apparent shrinkage above 900°C. As the number of glass additives increased to 10 wt%, ZnO exhibited a large shrinkage of

approximately 8 % at 900°C. The results suggest that GMV glass is an effective sintering aid for ZnO. The Differential Thermal Analysis (DTA) curve revealed that the GMV glass softened at 435°C and melted at 608°C, respectively. The decrease of sintering temperature was caused by the viscous liquid phase effect of GMV glass and served as a bond for the ZnO body, therefore the densification of ZnO occurred at much lower temperatures.
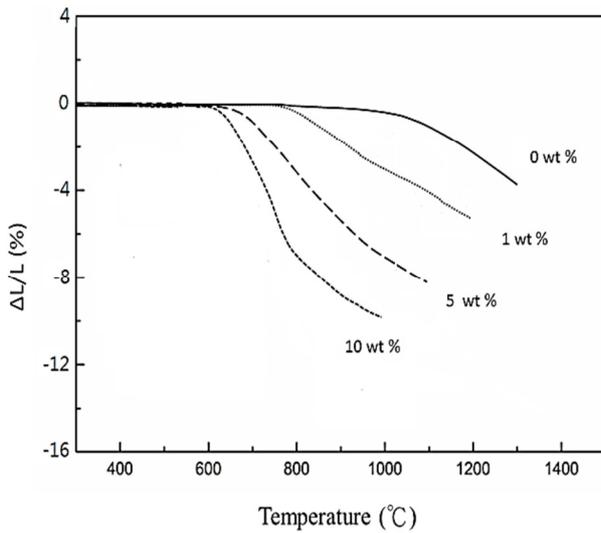
Fig. 1 The shrinkage behavior of the ZnO with and without GMV glass additives
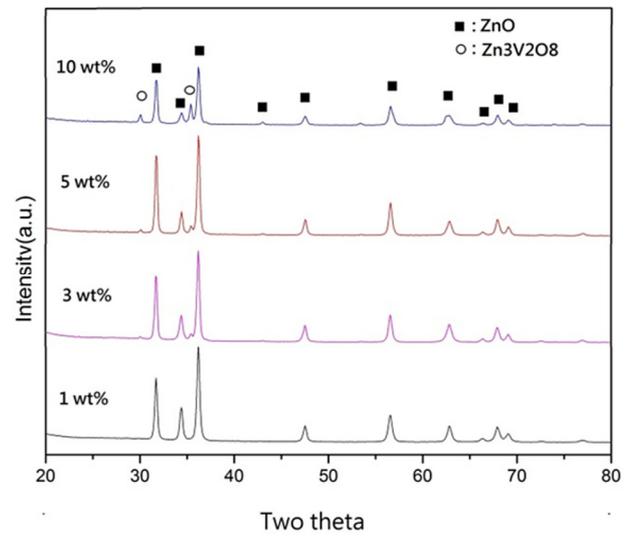
Fig. 2 X-ray diffraction patterns of ZnO with different GMV glass concentrations

XRD patterns of ZnO with different concentrations of GMV glass is shown in Fig. 2. It is found that the main crystal phase of the sample is wurtzite ZnO at a glass doping concentration of 1 wt %. However, in addition to the wurtzite ZnO phase, $Zn_3V_2O_8$ phase was also detected as glass additives increased to 3 wt% according to JCPDS 34-378. The formation of $Zn_3V_2O_8$ might be attributed to the reaction between the ZnO matrix and the liquid glass phase. Because of the composition of glass contained a greater amount of V_2O_5, ZnO matrix reacted with liquid glass to precipitate a stable $Zn_3V_2O_8$ phase during sintering processing.

Fig. 3 is the cross-sectional FESEM micrographs of ZnO ceramics sintered at 900°C for 1 hour with 0, 1, 5, and 10 wt% GMV glass. The sample without glass additives shows an obvious porous microstructure with the smallest grain size. Increasing the glass additives greatly promoted the densification and the grain size of ZnO. The bulk density and the grain size of ZnO as a function of glass concentrations is illustrated in Fig. 4. It can be seen that the density increased from 4.45 to 5.05 g/cm^3 and the grain size increased from 11 to 17 μm as glass concentration increased from 0 to 10 wt %.
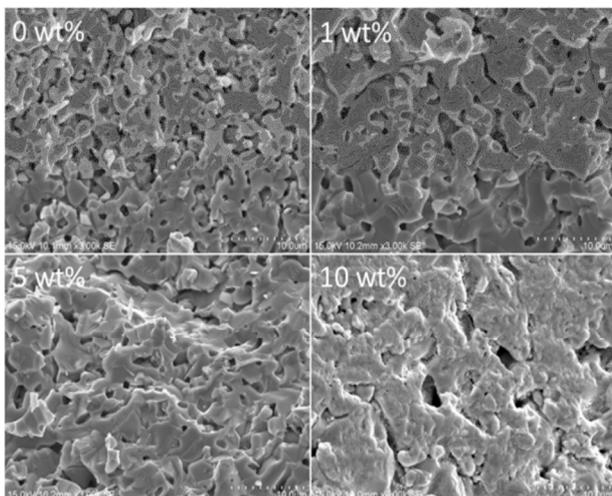
Fig. 3 FESEM images of ZnO with GMV glass concentrations at 0, 1, 5, and 10 wt %
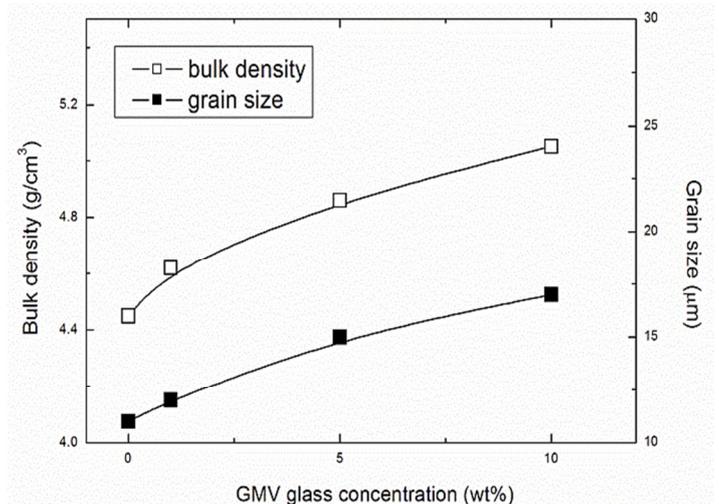
Fig. 4 The bulk density and the grain size of ZnO as a function of GMV glass concentration

In addition, the sintering temperature also has a significant effect on the microstructure development of ZnO, especially at higher GMV glass concentrations. Fig. 5 are FESEM images of ZnO with 10 wt % GMV glass sintered from 800 to 1100°C for 4 h. It can be seen that the morphologies of the ZnO are homogeneous without any abnormal grain growth. The grain size increased from approximately 9-10 µm at 800°C to 30-40 µm at 1100°C. This increase in densification and grain size is attributed to the dissolution of smaller particles and the growth of larger particles during sintering by material transfer through glass liquid phase. Fig. 6 is quantitative Energy Dispersive X-ray Spectrometer (EDS) analyses of the ZnO crystalline phase. The results revealed the presence of Ge, Mo, and V ions in ZnO crystalline phase, indicating that the ZnO shows a certain limited solubility in the liquid at the sintering temperature; the essential part of such lower sintering process is the dissolution and re-precipitation of ZnO particles to give increased grain size and densification.
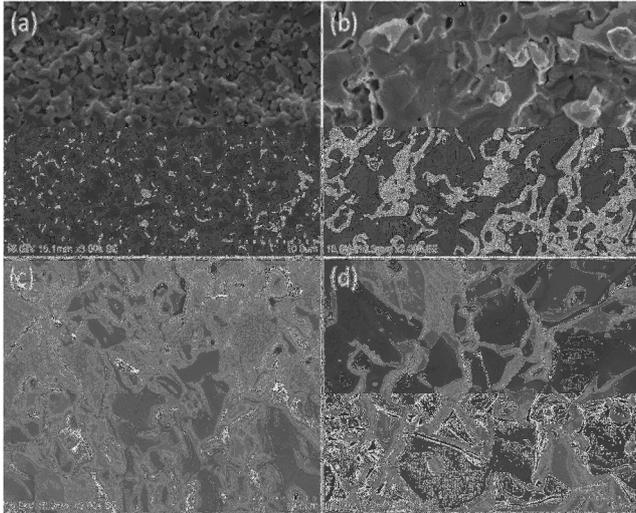
Fig. 5 FESEM images of ZnO with 10 wt% of GMV glass concentrations sintered at (a) 800, (b) 900, (c) 1000, and (d) 1100°C
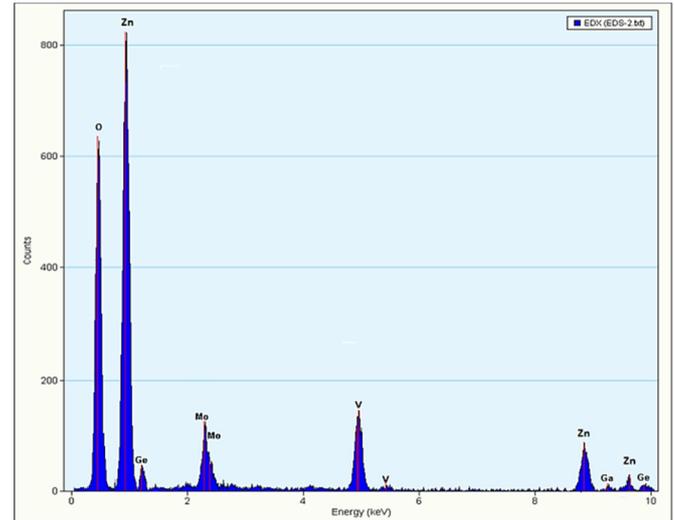
Fig. 6 The Energy Dispersive X-ray Spectra (EDS) of ZnO crystalline phases

Table 1 The dielectric properties of ZnO doped with different GMV glass concentrations

GMV Glass Concentration (wt%)	$\varepsilon\gamma$ (Theoretical)	$\varepsilon\gamma$ (Measured)	$\tan\delta$ (Dielectric Loss)
0	19	12	0.096
1	25	20	0.085
5	29	23	0.066
10	27	25	0.035

The theoretical and the measured dielectric properties of the ZnO with different concentrations of GMV glass sintered at 900 °C are summarized in Table1. The theoretical dielectric constant, ε_γ, was calculated using the logarithmic mixing rule [20] of Eq. (1) with the data of ZnO ($\varepsilon_1 = 38$), $Zn_3V_2O_8$ ($\varepsilon_2 = 31$), and GMV glass ($\varepsilon_3 = 12$).

$$\log\varepsilon\gamma = V_1\log\varepsilon_1 + V_2\log\varepsilon_2 + V_3\log\varepsilon_3 \tag{1}$$

where v_1, v_2, and v_3 represent the volume fractions of ZnO, $Zn_3V_2O_8$, and glass phase in the mixture, respectively. Whereas, the dielectric constant of GMV glass was measured after the as-quenched ribbon was heat-treated at 900°C. The volume fractions of ZnO, $Zn_3V_2O_8$, and glass phase in the samples were determined using the method developed by Chipera1 et al. according to the crystalline peak intensity present in the XRD pattern [21]. The measured dielectric constant of ZnO was found to agree well with the theoretical values. As the GMV glass concentration increased to 10 wt %, the dielectric constant showed an increase to approximately 25. The increase of the dielectric constant in the sample with GMV glass concentrations is due to the improvement of densification of ZnO ceramics. The presence of glass phases in high GMV concentration samples decreased the dielectric constant of ZnO. While the dielectric loss almost linearly decreased with the

increase of GMV glass concentrations. As well known, the value of the dielectric loss is mainly caused by the extrinsic effect that is related to the microstructure of materials such as porosities, grain boundaries, grain sizes and impurities [22]. In this work, ZnO ceramics doped with a high concentration of GMV glass showed a better microstructure in term of homogeneous grain size and less porosity, therefore resulting in lower dielectric losses.

4. Conclusions

This research demonstrated that the glass additives containing GeO_2, MoO_3, and V_2O_5 has an effect on lowering the sintering temperature of ZnO from 1100 to 800°C as a combination of viscous flow and liquid phase sintering effects. This allows the LTCC processing of ZnO ceramic for telecommunications application to be feasible. The densification and the grain size of ZnO were found to increase with the glass concentration and sintering temperature as a result of the mass transfer through the liquid phase. The dielectric constants of ZnO decreased to 25 with the glass concentration increased to 10 wt % because of the presence of the lower dielectric constant of glass phase. While the dielectric loss of ZnO decreased with the glass concentration due to the denser and homogenous microstructure of ZnO. In this study, the glass additive not only can be used as the sintering aid to enhance the densification of ZnO but also be able to modify the dielectric constant of ZnO by varying the glass concentration. In summary, the multiple oxides glass-doped ZnO ceramics have attained optimal properties at glass concentration of 10 wt% with a dielectric constant of 25 and dielectric loss of 3.5% as a result of high density and larger grain size associated with less porosity.

Conflicts of Interest

The authors declare no conflict of interest.

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