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Microstructure and properties evaluation of TiO_2 ceramics with multi-oxides glass additions

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Abstract

A unique glass composition based on GeO_2, MoO_3 and V_2O_5 (GMV) was designed to act as a sintering aid to enhance the densification and to adjust the dielectric constant of TiO_2. This allows the low temperature co-fired ceramic processing (LTCC) of approximately 750 °C to be feasible with a desirable dielectric property. The effect of GMV glass concentration on the densification behavior and dielectrics properties of TiO_2 was investigated by dilatometer, x-ray diffractometer, scanning electron microscopy and transmission electron microscopy. The addition of glass not only was found to accelerate the TiO_2 phase transformation from anatase to rutile, but also to increase the densification rate and the grain size of TiO_2. The glass additive formed a thin continuous liquid phase and rearranged TiO_2 particles into a dense microstructure at much lower temperature. The dielectric constants of TiO_2 were ranged from 28 to 45 depending on the concentration of glass additive, while the dielectric loss was decreased with the glass concentration as a result of denser TiO_2 microstructure.

Keywords: Densification; Microstructure; Dielectric; Liquid phase

1. Introduction

TiO_2 has been extensively studied because of its remarkable optical, chemical and electronic properties which give a large prospective to its practical applications such as gas sensors, photocatalytic devices and solar cells [1–3]. More recently, the dielectric properties of TiO_2 have been of great interest for applications in the telecommunications industry due to its unusually high dielectric constant, low dielectric loss and near zero temperature coefficient of resonant frequency [4]. 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 have been identified to be feasible solution for applications in the area of wireless communications [5].

A 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 ZnO, Bi_2O_3, MoO_3 and CuO are generally mixed with TiO_2-based dielectric ceramics to reduce the sintering temperature [6–8]. Particularly, by using nano-size TiO_2 particles as starting materials has also shown an improvement in reducing sintering temperature [9,10]. However, these 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 lower temperature by forming thin continuous or semicontinuous liquid phases at grain boundaries [11–14]. During sintering, the ceramic particles are soluble in the liquid. This solubility causes

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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 this work, we have designed a unique glass composition containing GeO_2, MoO_3 and V_2O_5 as a sintering aid that allows the TiO_2 to densify at much low temperatures by viscous flow and liquid-phase sintering mechanisms. On the other hand, this glass additive can also adjust the dielectric constant of TiO_2 by varying the concentration of glass additive. The effect of the glass concentration on the densification behavior, microstructure and dielectric properties of TiO_2 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 M proportion (all with purity $\geq$ 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 min using an electric furnace. The melts were stirred to ensure the homogeneity of 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 grinded into powders ($<$ 325 mesh) and mixed with TiO_2 powders in proportion of 1 to 20 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 750, 850, 950 and 1050 °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 filed emission scanning electron microscopy (FESEM, Philips, XL-40FEG). A transmission electron microscopy (TEM, FEI, Tecnai G^2) equipped with X-ray energy dispersive spectroscopy (EDS) was used to obtain the chemical compositions of the TiO_2 grains and the triple points. To perform TEM/EDS analysis the specimen was cut in 0.3 mm thick disk with a low speed diamond wheel saw and polished to a thickness of approximately 30 μm. This was affixed to copper ring and then thinned by an argon ion-beam milling method (Gatan, 691 model).

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 a impendence analyzer (Agilent, 4263B, Palo Alto, USA).

3. Results and discussions

The shrinkage behavior of TiO_2 containing various concentrations of GMV glass as sintering aid was examined by dilatometer as shown in Fig. 1. As quantity of glass additives increased shrinkage curves were shifted towards much lower temperatures than the typical sintering temperature of pure TiO_2. The shrinkage of pure TiO_2 appears to occur slowly at approximately 1200 °C. Nevertheless, TiO_2 ceramics with 1 and 5 wt% glass additives showed the apparent shrinkage above 900 °C. As the amount of glass additives increased greater than 10 wt%, TiO_2 exhibited a large shrinkage of approximately 10% at 900 °C. The results suggest that GMV

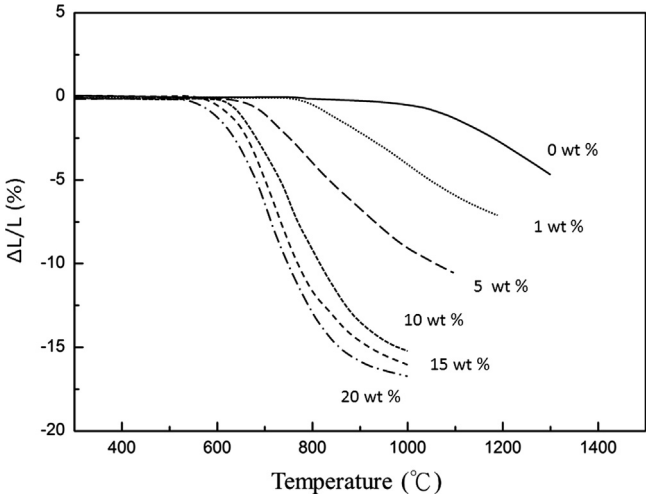

Fig. 1. The shrinkage behavior of the TiO_2 with and without GMV glass additives as a function of firing temperature.

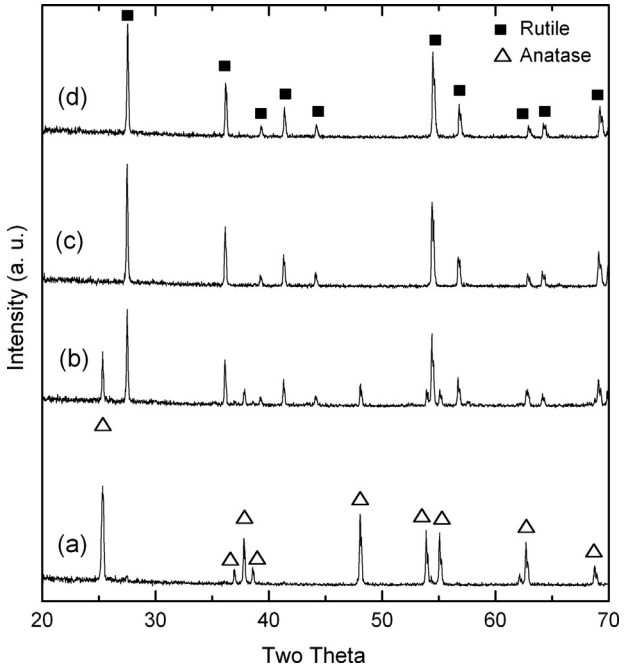

Fig. 2. X-ray diffraction patterns of TiO_2 with GMV glass concentrations at (a) 0, (b) 5, (c) 10, and (d) 20 wt% sintered at 750 °C.

glass is an effective sintering aid for TiO2. 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 TiO_2 body, therefore the densification of TiO_2 occurred at much lower temperatures.

Fig. 2 shows the XRD patterns of TiO_2 with different concentrations of GMV glass. It is clearly observed that the main crystal phase of pure TiO_2 is anatase. As glass additives increased to 5 wt%, the rutile phase crystallized along with anatase. Further increase of the glass additives to 10 wt% anatase phase disappeared and the phase transition was completed. The results of Fig. 2 imply that GMV glass accelerated the TiO_2 phase transition from anatase to rutile. It is believed that the supply of nuclei or the increase of the concentration of anion vacancies formed by reduction of foreign ions such as Ge, Mo and V in anatase grains promotes the TiO_2 anatase to rutile phase transformation [15,16].

The cross-sectional FESEM micrographs of TiO_2 ceramics sintered at 750 °C with 0, 5, 10 and 20 wt% GMV glass are shown in Fig. 3. 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 TiO2. Fig. 4 illustrated the bulk density and the grain size of TiO_2 as a function of glass concentrations. It was found that the density increased from 3.48 to 4.09 g/cm^3 and the grain size increased from 0.2 to 1.5 μm as glass concentration increased from 0 to 20 wt%.

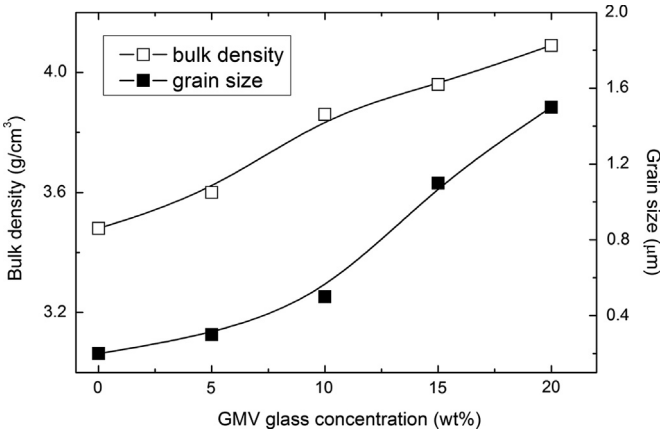

Fig. 4. The bulk density and the grain size of TiO_2 as a function of GMV glass concentration.

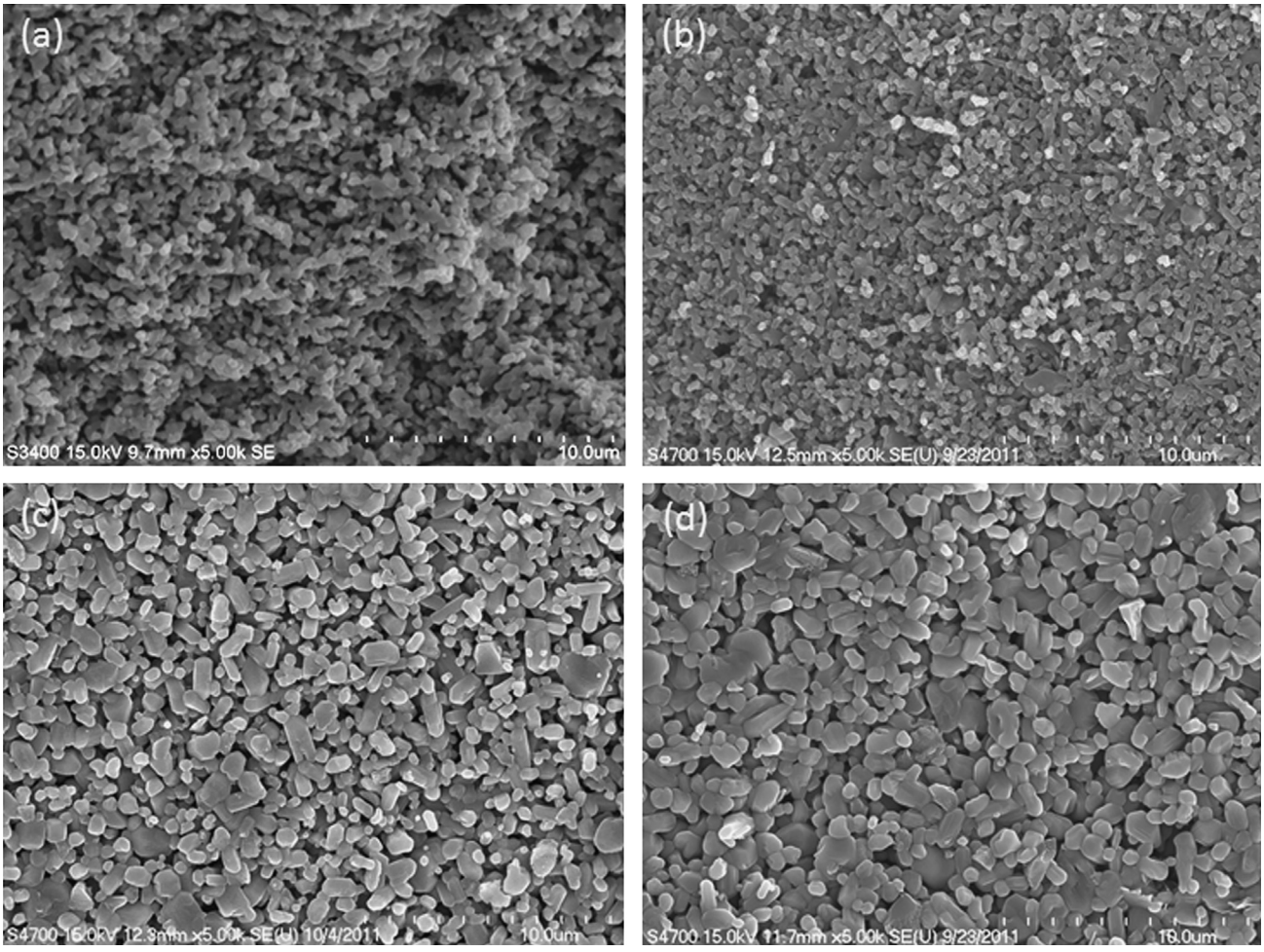

Fig. 3. FESEM photo images of TiO_2 with GMV glass concentrations at (a) 0, (b) 5, (c) 10, and (d) 20 wt%.

The sintering temperature also has a significant effect on the microstructure development of TiO_2, especially at higher GMV glass concentrations. Fig. 5 are FESEM images of TiO_2 with 20 wt% GMV glass sintered from 750 to 1050 °C for 4 h. It can be seen that the morphologies of the TiO_2 are homogeneous without any abnormal grain growth. The grain size increased from approximately 1–2 μm at 750 °C to 7–8 μm at 1050 °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 liquid phase. A TEM image of the TiO_2 sintered at 750 °C with 10 wt% GMV glass is shown in Fig. 6 that reveals a microstructure of the residual glass-phase at TiO_2 triple-grains junction. Fig. 7 (a) and (b) are quantitative energy dispersive X-ray spectrometer (EDS) analyses of the TiO_2 crystalline phase and glass phase, respectively. The results revealed the presence of Ge, Mo and V ions in TiO_2 crystalline phase and Ti ion in glass phase, indicating that the TiO_2 shows a certain limited solubility in the liquid at the sintering temperature; the essential part of such lower sintering process is the dissolution and reprecipitation of TiO_2 particles to give increased grain size and densification [17].

The theoretical and the measured dielectric properties of the TiO_2 with different concentrations of GMV glass sintered at

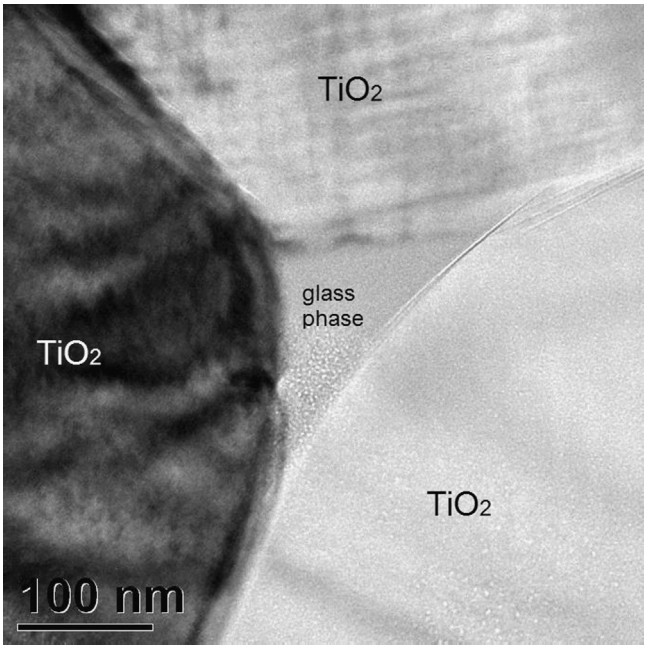

Fig. 6. TEM bright field image of TiO_2 with 10 wt% GMV glass showed a residual glass phase at TiO_2 triple-grain junction.

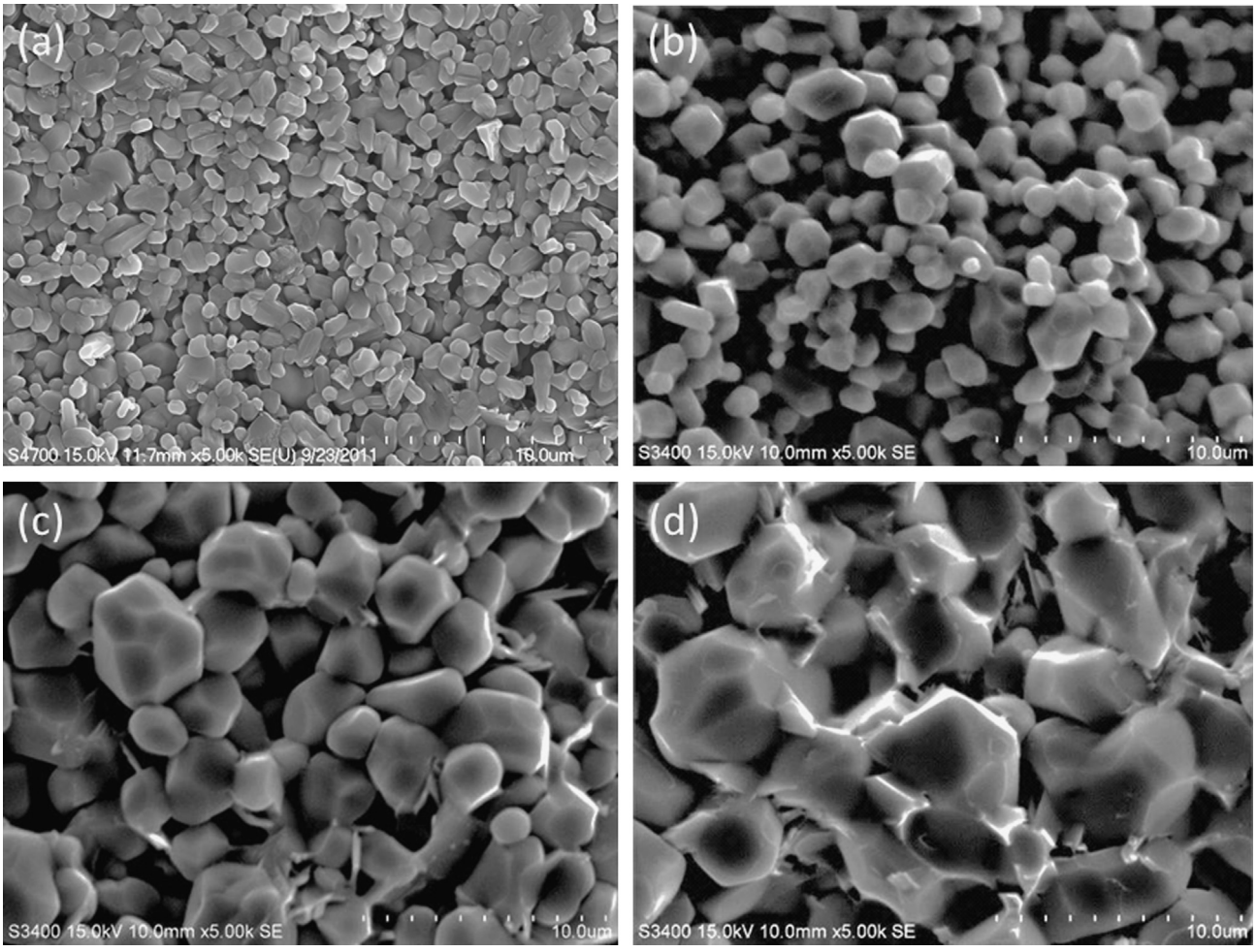

Fig. 5. FESEM photo images of TiO_2 with 20 wt% GMV glass concentration sintered at (a) 750, (b) 850, (c) 950, and (d) 1050 °C for 4 h.

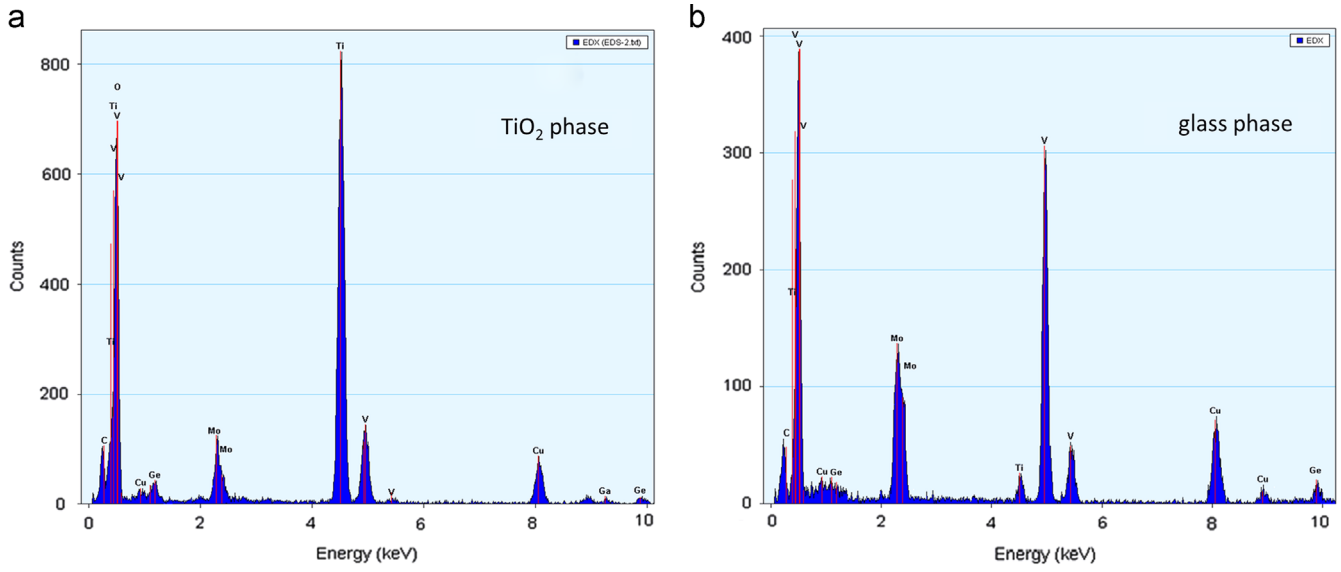

Fig. 7. The energy dispersive X-ray (EDS) spectra of (a) TiO_2 and (b) glass phases presented in Fig. 5.

Table 1
The dielectric properties of TiO_2 with different GMV glass concentrations.

GMV glass concentration (wt%)	ε_γ (theortical)	ε_γ (measured)	tan δ (Dielectric loss)
0	19	15	0.113
5	33	28	0.065
10	48	45	0.039
15	44	40	0.024
20	42	37	0.017

750 °C are summarized in Table 1. The theoretical dielectric constant, ε_γ, was calculated using the logarithmic mixing rule [18] of Eq. (1) with the data of anatase TiO_2 ($\varepsilon_1=75$), rutile TiO_2 ($\varepsilon_2=105$), and GMV glass ($\varepsilon_3=11$).

$$\log \varepsilon_\gamma = v_1 \log \varepsilon_1 + v_2 \log \varepsilon_2 + v_3 \log \varepsilon_3 \quad (1)$$

where v_1, v_2, and v_3 represent the volume fractions of anatase, rutile TiO_2, and glass phase in the mixture, respectively. The volume fractions of anatase and rutile TiO_2 in the samples were determined using the method developed by Spurr and Myers [19] according to the following Eq. (2):

$$f = 1/[(1+1.26(I_A/I_R)] \quad (2)$$

where f is the content of anatase crystal phase, I_A and I_R are the XRD peak intensities of the anatase (101) and the rutile (110), respectively. Whereas, the dielectric constant of GMV glass was measured after the as-quenched ribbon was heat treated at 750 °C. The measured dielectric constant of TiO_2 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 45 and then decreased after the maximum. The increase of the dielectric constant in the sample with low GMV glass concentrations is due to the crystallization of rutile TiO_2 phase. The presence of glass phases in high GMV concentration samples decreased the dielectric constant of TiO_2. While the dielectric loss almost linearly decreased with the increase of GMV glass concentrations. As well known, the value of 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 [20]. In this work, TiO2 ceramics with high concentration of GMV additives 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 of GeO_2, MoO_3 and V_2O_5 has an effect on lowering sintering temperature of TiO_2 from 1200 to 750 °C as a combination of viscous flow and liquid phase sintering effects. This allows the LTCC processing of TiO_2 ceramic for telecommunications application to be feasible. The densification and the grain size of TiO_2 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 TiO_2 decreased to 37 with the glass concentration increased to 20 wt% because of the presence of the lower dielectric constant of glass phase. While the dielectric loss of TiO_2 decreased with the glass concentration due to the denser and homogenous microstructure of TiO_2. In this study, the glass additive not only can be used as sintering aid to enhance the densification of TiO_2, but also be able to modify the dielectric constant of TiO_2 by varying the glass concentration.

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