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Low temperature sintering kinetics of BaO-0.15ZnO-4TiO_2 dielectric ceramic in the presence of a liquid phase

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ABSTRACT

The influence of Li_2O-B_2O_3-SiO_2 glass (LBS) on the activation energy, phase composition, reaction mechanisms, and microstructure of the BaO-0.15ZnO-4TiO_2 ceramics (Ba-Zn-Ti) were investigated to understand the mechanism of the sintering kinetic. The results reveal that the sintering process of the Ba-Zn-Ti significantly accelerated at a low temperature even with a higher activation energy, due to the reaction of Ba-Zn-Ti and LBS caused by the existence of liquid phase, which provides extra energy at the early stage of sintering, called reactive liquid-phase sintering. The sintering temperature of Ba-Zn-Ti significantly dropped from 1150 °C to 875 °C attribute to the presence of liquid phase caused by LBS, and obtained excellent dielectric microwave properties.

1. Introduction

Wireless communication system have been accelerated development by the technology of low-temperature cofired ceramics (LTCC) due to the miniaturization trend of circuit dimension, high level of passive integration, excellent reliability and low cost [1–3]. By this technology, microwave dielectrics are stacked in multilayers and cofired with internal electrodes, such as Ag, Cu, and Al. The approach to lower the sintering temperature is using compounds with intrinsically lower sintering temperatures. Zhou Di et al. reported Bi_2O_3-MoO_3 binary system, Bi_2O_3-TiO_2-V_2O_5 system, and $(Bi_{0.75}Ce_{0.25})VO_4$ ceramic could be sintered below 820 °C and 900 °C respectively with excellent microwave dielectric properties [4–6]. The other method to reduce the sintering temperature is addition of sintering aid [7]. In our previous work, the BaO-0.15ZnO-4TiO_2 ceramics with 5 wt% Li_2O-B_2O_3-SiO_2 glass sintered at 900 °C and obtained excellent microwave dielectric properties: ε_r=27.88, Q×f =14795 GHz [8]. However, the basic mechanism of this low temperature sintering have not been investigated. In this work, the experiments on the activation energy, phase evolution, reaction mechanisms and microstructure of the ceramics were carried out to understand the mechanism of the sintering kinetic in the process.

2. Experimental

The samples of Ba-Zn-Ti were prepared by solid-state reaction from high purity oxides: $BaCO_3$, ZnO and TiO_2 (> 99%). The raw materials were weighted and mixed as the mole ratio of the Ba-Zn-Ti and then milled with ZrO_2 media in deionized water for 3 h. The mixtures were dried and calcined at 950 °C for 3 h. The LBS was prepared by mixing Li_2CO_3, H_3BO_3 and SiO_2 according to the composition of 56.92 wt%, 37.59 wt%, and 5.49 wt%. The batches were dry-milled with ZrO_2 media for 2 h and melted at 1400 °C for about 2 h. The melt was then quenched using copper plate to form glass. The Ba-Zn-Ti powders re-milled with LBS in alcohol for 3 h with ZrO_2 media and then mixed together with acrylic acid to form pellets (15 mm diameter 8 mm height). The specimens sintered at 850–900 °C for 0.5 h at heating rate of 5 °C/min in air. The activation energy (E_a) of samples was calculated with a dilatometer (NETZSCH, Germany). The phases composition of samples and the reaction mechanisms were examined by X-ray diffraction (XRD) analysis (Rigaku Industrial Corporation, Japan) and a thermal analysis system (NETZSCHSTA449C, Germany). The microstructure of the sintered specimens was examined from polished surfaces by a scanning electron microscopy (SEM, JSM-6490LV, Japan).

3. Results and discussion

In our previous study [8], the LBS shows a low melting point at about 845 °C. The wetting behavior indicates that the liquid phase formed by LBS and then soaked by the Ba-Zn-Ti. The sintering temperature of Ba-Zn-Ti dropped from 1150 °C to 875 °C attribute to the liquid phase caused by LBS. To further understand the sintering behavior, the activation energy (E_a) of Ba-Zn-Ti and Ba-Zn-Ti +5 wt%

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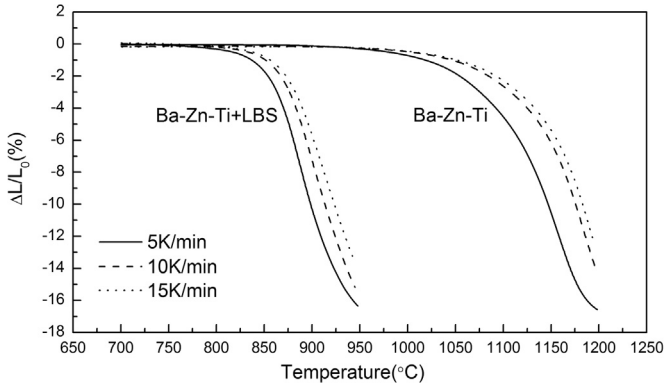

Fig. 1. The linear shrinkages curves and onset temperatures of shrinking for Ba-Zn-Ti and Ba-Zn-Ti+LBS fired at varying sintering rates of 5, 10, and 15 K/min respectively.

LBS was calculated. The pure Ba-Zn-Ti and Ba-Zn-Ti +5 wt% LBS ceramics were sintered from room temperature to 1200 °C and 950 °C respectively using different sintering rates (k) of 5,10, and 15 K/min (Fig. 1). The shrinkage (dL/L_0) of the samples was measured versus the varying temperature, and the dL/L_0 of 3, 6, 9, 12% was taken at different temperature for each heating rate k (Fig. 2). Then, for each given value of dL/L_0, ln k was obtained versus the inverse of temperature in Kelvin, 1/T [9]. The Ea can be calculated by using the follow Arrhenius expression [10]:

$$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln z$$

where the activation energy (Ea) will be the slope of the graph of ln k against 1/T multiplied by the gas constant, R(=8.3145 J/K/mol)...

The results, calculated from the dilatometric curves, give an average Ea of about 489.25 ± 60.65 KJ/mol for Ba-Zn-Ti (Fig. 2(a)), an average Ea of about 561.1 ± 60.2 KJ/mol for Ba-Zn-Ti + LBS (Fig. 2(b)), which demonstrate the significantly higher activation energy is required when Ba-Zn-Ti ceramic sintering at low temperature with LBS. However, the liquid-phase sintering mechanism as discussed before enhanced the sintering process should lead to a decrease of the Ea, as reported literatures [11]. To explain this phenomenon, more experiments were performed.

The XRD result indicates that the LBS lead to the formation of $BaTi_5O_{11}$ and $BaTi(BO_3)_2$, and the $BaTi(BO_3)_2$ phase become more obvious with the increasing of LBS [8]. To further verify the result, XRD patterns of Ba-Zn-Ti +5 wt% LBS sintered at 750 °C to 850 °C were also measured (Fig. 3). The formation of $BaTi_5O_{11}$ and $BaTi(BO_3)_2$ could be observed at about 800 °C, and is more obvious with higher temperature. Combining with the wetting behavior of LBS and Ba-Zn-Ti [8], it is believed that the liquid phase formed from LBS even invisible to the naked eye. The liquid phase reacted with the Ba-Zn-Ti and caused the formation of $BaTi_5O_{11}$ and $BaTi(BO_3)_2$..

The SEM images of the polished surfaces of Ba-Zn-Ti +5 wt% LBS sintered at 750–900 °C (a~e) are exhibited in Fig. 4, corresponding to the different shrinkage as shown in Fig. 1. The sample sintered at 750 °C (a) and 800 °C (b) shows a less compact microstructure with many pores, and there is almost no shrinkage of ceramic at the temperature range. The sample becomes more compact with the temperature increasing from 850 °C (c) to 900 °C (e), while the obvious shrinkage could be observed at the same time. The abnormal grain growth caused by the increasing of $BaTi(BO_3)_2$ [8] could be observed and become more obvious with the increasing sintered temperature. These results are consistent with the XRD results, the Ba-Zn-Ti reacted with the liquid phase caused by LBS and formed $BaTi_5O_{11}$ and $BaTi(BO_3)_2$..

As a comparison, the differential scanning calorimetry (DSC) analyses of Ba-Zn-Ti and Ba-Zn-Ti+5 wt% LBS were also preformed in Fig. 5. There is no obvious exothermic or endothermic peak observed with the pure Ba-Zn-Ti. However, the exothermic peak around 790 °C

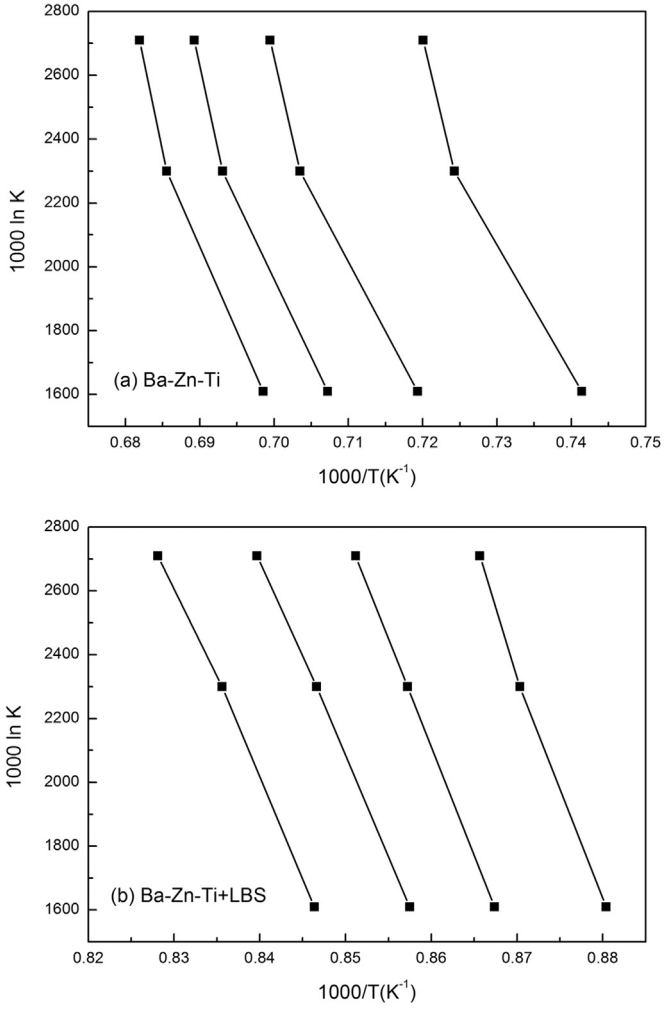

Fig. 2. The sintering rate (1000 ln k) plotted against the inverse of temperature (1000/T) for specific shrinkage values for (a) Ba-Zn-Ti and (b) Ba-Zn-Ti+LBS.

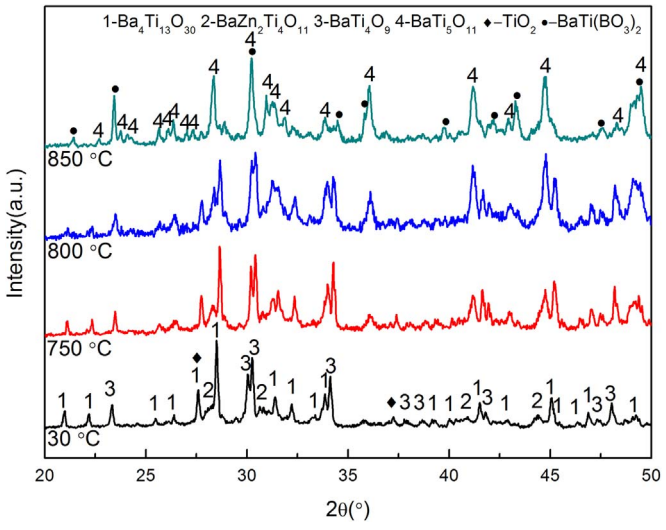

Fig. 3. The XRD patterns of Ba-Zn-Ti +5 wt% LBS sintered at 750–850 °C..

was observed with LBS added. It is believed to be the reaction exothermal of Ba-Zn-Ti and LBS..

All the results explain the mechanism of the low-temperature sintering of the Ba-Zn-Ti ceramic with LBS. The following relationship [12] describes the rate of reagent conversion, where G is the degree of