

Effects of Cu substitution on microstructures and microwave dielectric properties of $\text{Li}_2\text{ZnSiO}_4$ ceramics

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Abstract. Herein, the influence of Cu^{2+} substitution on the phase composition, bulk density, microstructures, and microwave dielectric properties of $\text{Li}_2\text{Cu}_x\text{Zn}_{1-x}\text{SiO}_4$ ($0 \leq x \leq 0.06$) ceramics prepared by a solid-state reaction were investigated. The results of XRD and mapping showed that Cu^{2+} substitution can avoid the influence of secondary phase on the properties of samples. According to the analysis of bulk density, microstructure and microwave dielectric properties, a proper amount of Cu substitution not only improved the sintering characteristics of $\text{Li}_2\text{Cu}_x\text{Zn}_{1-x}\text{SiO}_4$ ceramics, reduced the densification temperature from 1250 °C to 950 °C, but also increased the $Q \times f$ value. Furthermore, Cu^{2+} substitution also improved the temperature stability of the samples. Particularly, the $\text{Li}_2\text{Cu}_{0.04}\text{Zn}_{0.96}\text{SiO}_4$ ceramics sintered at 950 °C for 5 h possessed excellent microwave dielectric properties: $\epsilon_r = 5.624$, $Q \times f = 12,764$ GHz, and $\tau_f = -77$ ppm/°C, exhibiting a potential for the low temperature co-fired ceramic applications.

1 Introduction

In recent years, the continuous innovation and development of communication technology has brought great convenience to all aspects of human production and social activities. Microwave dielectric ceramic is a kind of dielectric ceramic material which is used in microwave band circuit and realizes specific functions. It has become the key basic material of modern communication technology and the cornerstone of communication technology innovation. Microwave dielectric ceramics have three important parameters: (A) dielectric constant (ϵ_r), which is related to the delay of microwave propagation in materials ($T_d = L\sqrt{\epsilon_r}/c$, where L is the traveling distance of the signal and c is the speed of light) [1]. Low dielectric constant corresponds to short delay time, it is conducive to signal propagation. (B) quality factor ($Q \times f$), which represents the dielectric loss of the material and is related to the reliability and life of the material. (C) the temperature coefficient of the resonant frequency (τ_f), the closer τ_f value is to zero, the better the temperature stability of the resonant frequency of the sample. Low temperature co-fired ceramic (LTCC) is a

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technology used to package passive and active components into multi-layer structures to achieve miniaturization and multi-function. In addition to the above three parameters, it should also meet the requirements of co-firing with silver electrode. Therefore, the sintering temperature of LTCC materials should be lower than the melting point of Ag (961 °C) [2, 3].

Silicate is a typical microwave dielectric ceramic with low dielectric constant, but its high temperature sintering characteristics limit its application in LTCC devices. Compared with other silicate systems, $\text{Li}_2\text{ZnSiO}_4$ and $\text{Li}_2\text{MgSiO}_4$ ceramics have lower sintering temperature ($\text{ST}=1250\text{ }^\circ\text{C}$) [4, 5], which is more conducive to the research of low temperature modification. The research on low temperature sintering of $\text{Li}_2\text{MgSiO}_4$ has been reported, but the low temperature characteristics of $\text{Li}_2\text{ZnSiO}_4$ have not been systematically studied. Generally, there are three methods to reduce the sintering temperature of ceramics: using superfine raw materials, adding sintering additives or ion substitution. The high cost of using superfine raw materials is not conducive to industrial mass production. Adding sintering additives is a common method to reduce sintering temperature, but it is easy to introduce impurities or increase dielectric loss. Compared with the former two methods, the substitution of ions with similar radius and lower sintering temperature can avoid the formation of secondary phase and realize low temperature sintering.

According to the previous research, Cu^{2+} can reduce the sintering temperature to a certain extent [6, 7], and the radius of Cu^{2+} is close to that of Zn^{2+} [8]. Therefore, Cu^{2+} ions are used to replace Zn^{2+} ions to adjust the sintering characteristics of $\text{Li}_2\text{ZnSiO}_4$ ceramics to achieve low-temperature sintering. In addition, the effects of Cu substitution on the phase, microstructures and microwave dielectric properties of the samples were analyzed by XRD and scanning electron microscopy (SEM).

2 Experimental and methods

The $\text{Li}_2\text{Cu}_x\text{Zn}_{1-x}\text{SiO}_4$ ($0 \leq x \leq 0.06$) ceramics were fabricated using the solid - state reaction process. High - purity starting materials of Li_2CO_3 (99%), CuO (99%), ZnO (99%), and SiO_2 (99%) were weighed according to the desired molar ratio. The raw materials were mixed and ball-milled for 6 h in a nylon container, using distilled water and ZrO_2 balls as the grinding medium. The processed powders were calcined at 925°C in an alumina crucible for 5 h. The calcined powders were re-milled and then dried. After that, the powders with 12 wt% PVA as a binder were pressed into pellets with 12 mm-diameter and about 6 mm height under a pressure of 10 MPa. All pellets sintered at 925, 950, 975 and 1000°C for 5 h, respectively.

The crystal phases of the ceramics were characterized by X-ray diffraction analysis with $\text{Cu K}\alpha$ radiation. The microstructure, energy-dispersive spectra (EDS), back-scattered electron (BSE), and mapping images were observed via scanning electron microscopy. The bulk density of the samples was measured using an Archimedes method. Microwave dielectric properties were measured through a Hakki–Coleman dielectric resonator method and a cavity method. The τ_f values were measured in the temperature ranging from $25\text{ }^\circ\text{C}$ to 85°C based on the following equation:

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \times 10^6 \text{ (ppm/}^\circ\text{C)},$$

where f_1 and f_2 represent the resonant frequencies at temperatures 25°C and $85\text{ }^\circ\text{C}$ respectively.

3 Results and discussions

The bulk densities of $\text{Li}_2\text{Cu}_x\text{Zn}_{1-x}\text{SiO}_4$ ($0 \leq x \leq 0.06$) ceramics sintered at different temperatures are shown in Fig.1. It is obvious that with the increase of Cu^{2+} substitution, the bulk densities of the samples increase first and then decrease, which indicates that the bulk densities depend strongly on the content of Cu. When the sintering temperature increases from 925°C to 1000°C , the bulk density values of all specimens increase approaching to a maximum value at 950°C , indicating that 950°C is the optimal temperature of the $\text{Li}_2\text{Cu}_x\text{Zn}_{1-x}\text{SiO}_4$ ceramics. Therefore, we select the samples sintered at 950°C for further investigation in detail.

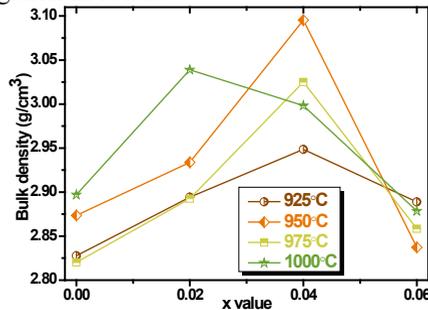


Fig. 1. The bulk densities of $\text{Li}_2\text{Cu}_x\text{Zn}_{1-x}\text{SiO}_4$ ($0 \leq x \leq 0.06$) ceramics sintered at different temperatures.

The XRD patterns of $\text{Li}_2\text{Cu}_x\text{Zn}_{1-x}\text{SiO}_4$ ($0 \leq x \leq 0.06$) ceramics sintered at 950°C for 5 h are shown in Fig.2. The patterns of all the samples match well with the monoclinic $\text{Li}_2\text{ZnSiO}_4$ phase (ICSD#8237), and no secondary phase existed. Obviously, no phase containing Cu^{2+} was observed, indicating that Cu^{2+} entered the lattice and formed a solid solution in $\text{Li}_2\text{Cu}_x\text{Zn}_{1-x}\text{SiO}_4$ ceramics, which is mainly due to the similar ionic radius of Cu^{2+} (0.73 \AA , CN=6) and Zn^{2+} (0.74 \AA , CN=6) [8].

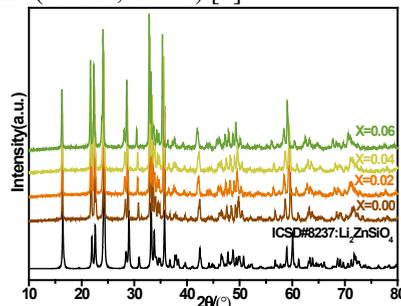


Fig. 2. The XRD patterns of $\text{Li}_2\text{Cu}_x\text{Zn}_{1-x}\text{SiO}_4$ ($0 \leq x \leq 0.06$) ceramics sintered at 950°C for 5 h.

The microstructure of $\text{Li}_2\text{Cu}_x\text{Zn}_{1-x}\text{SiO}_4$ ($0 \leq x \leq 0.06$) ceramics sintered at 950°C for 5 h was characterized by SEM, as shown in Fig. 3 (a-d). Obviously, the grains of the samples not substituted by Cu^{2+} are small and heterogeneous, accompanied by the existence of pores. With the increase of substitution amount, the grain size increases and the porosity decreases. When $x = 0.04$, dense and uniform microstructure is obtained. With the further increase in x value, the grain boundary blurs and the pores reappear, which indicates that excessive substitution is not conducive to the further densification of the samples. The analysis of BSE and EDS surface scanning of $\text{Li}_2\text{Cu}_{0.04}\text{Zn}_{0.96}\text{SiO}_4$ ceramics is shown in Fig. 3 (e). It can be observed that there is only one kind of grain in the sample, and the element content ratio is close to $\text{Li}_2\text{Cu}_{0.04}\text{Zn}_{0.96}\text{SiO}_4$. In addition, the mapping image shows that the

distribution of Cu is similar to that of Zn. These results further prove that Cu^{2+} substitution does not produce secondary phase and forms a solid solution [9], which is consistent with XRD results.

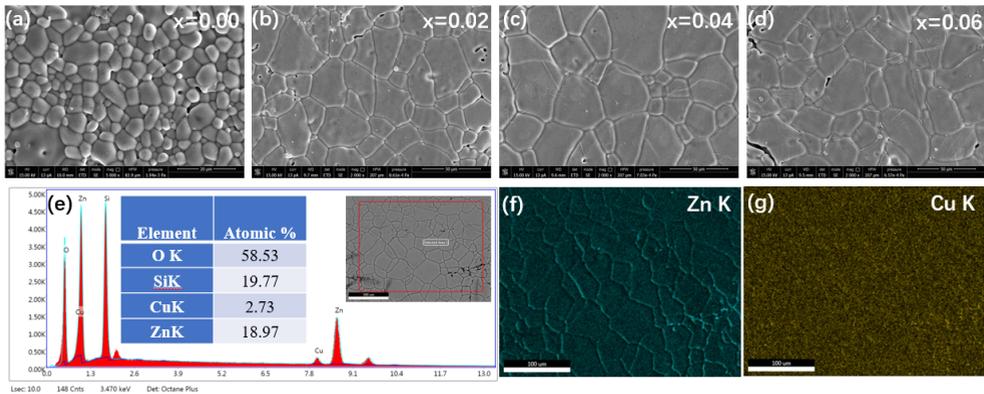


Fig. 3. (a-d) Microstructure of $\text{Li}_2\text{Cu}_x\text{Zn}_{1-x}\text{SiO}_4$ ($0 \leq x \leq 0.06$) ceramics sintered at 950°C for 5 h; (e) The analysis of BSE and EDS surface scanning of $\text{Li}_2\text{Cu}_{0.04}\text{Zn}_{0.96}\text{SiO}_4$ ceramics; (f-g) The distributions of Cu and Zn elements in $\text{Li}_2\text{Cu}_{0.04}\text{Zn}_{0.96}\text{SiO}_4$ ceramics.

The relative permittivity of $\text{Li}_2\text{Cu}_x\text{Zn}_{1-x}\text{SiO}_4$ ($0 \leq x \leq 0.06$) ceramics sintered at different temperatures is present in Fig.4(a). The ϵ_r values of the samples at different sintering temperatures present a similar trend, which first increases and then decreases with the increase of Cu substitution. Generally, the ϵ_r value of microwave ceramics is affected by both external factors (bulk density and secondary phase) and internal factors (molecular polarizability) [3]. There is no secondary phase in this study, so the effect of secondary phase can be ignored. According to Fig. 4(a) and Fig. 1, the dielectric constant and bulk density show the same trend at each temperature, indicating that bulk density as an external factor has an obvious effect on the ϵ_r value of $\text{Li}_2\text{Cu}_x\text{Zn}_{1-x}\text{SiO}_4$ ceramics. In addition, the molecular polarizability is also one of the factors that affect the ϵ_r value. Because the ion polarizability of Cu^{2+} (2.11\AA^3) is higher than that of Zn^{2+} (2.01\AA^3) [10], the molecular polarizability increases with the increase of Cu substitution, which result in the initial increase of the ϵ_r value.

The variations in $Q \times f$ value of $\text{Li}_2\text{Cu}_x\text{Zn}_{1-x}\text{SiO}_4$ ($0 \leq x \leq 0.06$) ceramics sintered at different temperatures are display in Fig.4(b). As we all know, the $Q \times f$ value is closely related to the dielectric loss, which can be separated into intrinsic loss and extrinsic loss [11]. In the study, the extrinsic loss mainly includes microstructures and bulk density. As shown in Fig.4(b), with the increase of Cu substitution, $Q \times f$ value increases first and then decreases. When $x = 0.04$ and sintering temperature is 950°C , the optimal value is obtained, which is consistent with the bulk density and indicates that the influence of bulk density on the $Q \times f$ value can be not neglected. Furthermore, the microstructures present that the samples sintered at 950°C are densified with the increase in x value. When $x = 0.04$, the sample has the most uniform and dense microstructure, which has the least defects, the lowest porosity and the smallest external loss, result in the optimal $Q \times f$ value. The subsequent decrease of $Q \times f$ value is due to the over burn caused by excessive substitution, which increases the porosity, decreases the bulk density and increases the dielectric loss.

The τ_f value is a parameter representing the temperature stability about resonance frequency of microwave dielectric ceramic. The closer it is to zero, the better the temperature stability. The τ_f values of $\text{Li}_2\text{Cu}_x\text{Zn}_{1-x}\text{SiO}_4$ ($0 \leq x \leq 0.06$) ceramics sintered at 950°C are shown in Fig.4(c). It is gratifying that with the increase of x value, the τ_f value increase gradually, indicating that Cu substitution optimizes the temperature stability of the

sample to a certain extent. According to the research of Lai et al. [7], the change of temperature coefficient of resonant frequency may be caused by the substitution of Cu^{2+} for Zn^{2+} , which affects the interaction between cation and anion, resulting in the change of bond length, structural order and polyhedral properties.

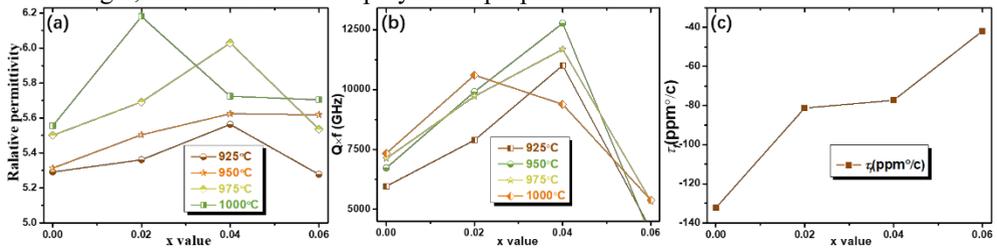


Fig. 4 (a) ϵ_r values of $\text{Li}_2\text{Cu}_x\text{Zn}_{1-x}\text{SiO}_4$ ($0 \leq x \leq 0.06$) ceramics sintered at different temperatures; (b) The variations in $Q \times f$ value of $\text{Li}_2\text{Cu}_x\text{Zn}_{1-x}\text{SiO}_4$ ($0 \leq x \leq 0.06$) ceramics sintered at different temperatures; (c) τ_f values of $\text{Li}_2\text{Cu}_x\text{Zn}_{1-x}\text{SiO}_4$ ($0 \leq x \leq 0.06$) ceramics sintered at 950 °C for 5 h.

4 Conclusion

In this study, $\text{Li}_2\text{Cu}_x\text{Zn}_{1-x}\text{SiO}_4$ ($0 \leq x \leq 0.06$) ceramic samples were prepared by solid state reaction method, and the effects of Cu substitution on the phase and microstructure of the samples were analyzed by XRD and SEM. In general, the appropriate amount of Cu substitution is beneficial to reduce the sintering temperature and obtain compact microstructure. When $x = 0.04$, the sample has a relatively dense and uniform microstructure, and the dielectric loss is the lowest. In addition, Cu^{2+} substitution also improves the temperature stability of the samples to a certain extent. The $\text{Li}_2\text{Cu}_{0.04}\text{Zn}_{0.96}\text{SiO}_4$ ceramics sintered at 950 °C have satisfactory properties: $\epsilon_r = 5.624$, $Q \times f = 12,764$ GHz, and $\tau_f = -77$ ppm/°C, which presents a potential for the low temperature co-fired ceramic applications.

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