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ScienceDirect
Ceramics International 38S (2012) S187–S190
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Relations on synthesis, crystal structure and microwave dielectric properties of $SrZnP_2O_7$ ceramics

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Available online 4 May 2011

Abstract

Different experimental conditions were applied to investigate the optimum sintering properties of $SrZnP_2O_7$ ceramics, and its crystal structure and microstructure were investigated by X-ray powder diffraction and scanning electron microscope, respectively. The microwave dielectric properties were measured using a network analyzer. In calcination process, $SrZnP_2O_7$ powders were synthesized at different temperatures. The sintering characterizations and electric properties of the $SrZnP_2O_7$ ceramics prepared from the different calcined $SrZnP_2O_7$ powders were studied systematically. Better microwave dielectric properties can be obtained when using well calcined powders and optimum sintering conditions.

Keywords: A. Powders: solid state reaction; B. X-ray methods; C. Dielectric properties; E. Substrates

1. Introduction

Recently, many investigations for microwave dielectric materials have been focused on the applications of integrated multilayer millimeter-wave band devices. For this application, it is necessary to use low temperature co-fired ceramics (LTCC) technology, which offers significant benefits over other established packaging technologies for high density, high RF, and digital applications requiring hermetical packaging and good thermal managements. For the LTCC application using at the millimeter-wave band, dielectric ceramics must have a high quality factor (Q) to reduce the dielectric loss ($Q = 1/\tan\delta$) significantly, a low dielectric constant (ε) to shorten the time for electric signal transmission, and zero temperature coefficient of resonant frequency (τ_f) to provide stability at various operating temperatures. Moreover, the dielectric ceramics should be sintered at temperatures below the melting point of the metal electrode, such as Cu (1064 °C), because the dielectric ceramics and electrodes should be co-fired simultaneously [1].

In a series of earlier reports, phosphate ceramics with different kinds of cations and crystal structures were reported, and all kinds of them have a low dielectric constant around 10. In these phosphates, complex pyrophosphate compounds, such as $CaZnP_2O_7$ and $SrZnP_2O_7$, exhibit many merits for LTCC applications [1]. But the synthesis characteristics and relations of synthesis conditions and sintering properties of these systems were hardly characterized, due to scarce reports of crystal structures. In this paper, we focus on the relations between synthesizing conditions and microwave dielectric properties of $SrZnP_2O_7$ ceramics with monoclinic crystal structure. The effects of different crystal structures and temperatures of calcination on the sintering and microwave dielectric properties were discussed.

2. Experimental

$SrZnP_2O_7$ powders were prepared using a conventional solid-state reaction method. High purity $SrCO_3$ (99.0%), ZnO (99.5%) and $NH_4H_2PO_4$ (99.90%) were used as raw materials. Stoichiometric mixtures of starting materials were homogenized by ball-milling with ZrO_2 balls in acetone for 24 h, and then calcined at 850–900 °C for 2 h to investigate the formation process of $SrZnP_2O_7$ phase. The calcined powders were then milled again, dried and sieved. PVA (9 wt.%) was added into sieved powders and was granulated, and then uniaxially pressed

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0272-8842/$36.00
doi:10.1016/j.ceramint.2011.04.080

into pellets with a diameter of 16 mm. The compacts were sintered at a temperature range from 900 °C to 980 °C in order to investigate the sintering behaviors.

The phase constituents of the calcined and sintered samples were identified by X-ray powder diffraction (XRPD, Bruker D8 Advance, Bruker Corporation, Germany). The bulk density of the sintered specimens was identified by Archimedes's method. The microstructure of sintered samples was characterized by scanning electron microscopy (SEM, JSM-6360LV, JEOL Ltd., Japan). The microwave dielectric properties of the sintered samples were measured at a frequency range of 10–11 GHz by using a network analyzer (Hewlett Packard, Agilent E8363A PNA Series, USA). The dielectric constant was measured according Hakki-Coleman method using the TE011 resonant mode [2], and the temperature coefficient of resonant frequency (τ_f) was measured in the temperature range of 25–85 °C.

3. Results and discussion

Fig. 1 shows the unit cell structure of $SrZnP_2O_7$ designed by the Diamond v3.1.1a software. Compared with the structure unit cell of α-$Sr_2P_2O_7$ [3], $SrZnP_2O_7$ can be treated as a derivative of substitution. 4 Sr^{2+} atoms were substituted by 4 Zn^{2+} atoms, in which [ZnO_5] pyramids formed and connected with [P_2O_7] groups to form a 3D-network by sharing the oxygen at the vetex of polyhedra, and the Sr^{2+} ions locate at the dodecahedra formed in the Zn–P–O network. Although continuous substitution of Zn^{2+} for Sr^{2+} was not expected due to the different coordination behavior with oxygen, the special compound, $SrZnP_2O_7$, can be formed, which has the similar atom spatial distribution with α-$Sr_2P_2O_7$ in crystal structure [4].

Fig. 2(a) shows the X-ray diffraction (XRD) patterns of $SrZnP_2O_7$ powders calcined at different temperatures. The powders are a mixed phase with a major phase of $SrZnP_2O_7$, and a small amount of $Sr_2P_2O_7$ and $Zn_2P_2O_7$, when a low calcination temperature was applied at 850 °C. The lowest temperature for synthesizing pure $SrZnP_2O_7$ phase is at 880 °C. When the synthesizing temperatures were lower than 880 °C, the trace phase of $Sr_2P_2O_7$ and $Zn_2P_2O_7$ were existed, which means the solid-state reaction were not completed. The indices in Fig. 2 are results calculated by the Diamond Software [5]. Fig. 2(b) shows the XRD patterns of $SrZnP_2O_7$ ceramics sintered at different temperatures. It shows that the ceramics are almost the same phase constitution with well calcined powders prepared at relative high temperatures (880 °C or 900 °C). A series of $SrZnP_2O_7$ ceramics shows similar patterns when the $SrZnP_2O_7$ powders calcined at low temperature (850 °C), and the ceramics sintered at lower temperature (920 °C); however, the ceramics sintered at higher temperature show obvious changes in the relative intensities of diffraction peaks. Very low bulk densities were observed for these ceramics, and the microwave dielectric properties were deteriorated, which are resulted from unusual grain growth and appearance of cracks both incurred by partial melting [6].

Fig. 3 shows the SEM photographs of $SrZnP_2O_7$ ceramics sintered at different temperatures. Relative dense structure can be obtained for the samples calcined at low temperature (850 °C) and sintered at 920 °C, but some small pores scattered in the grain boundaries can be observed (Fig. 3(a)), which indicated that the ceramics could not reach the maximum density at this experimental condition. This situation can be improved when the powders calcined at high temperature (880 °C) was used, as shown in Fig. 3(b), the number of pores in

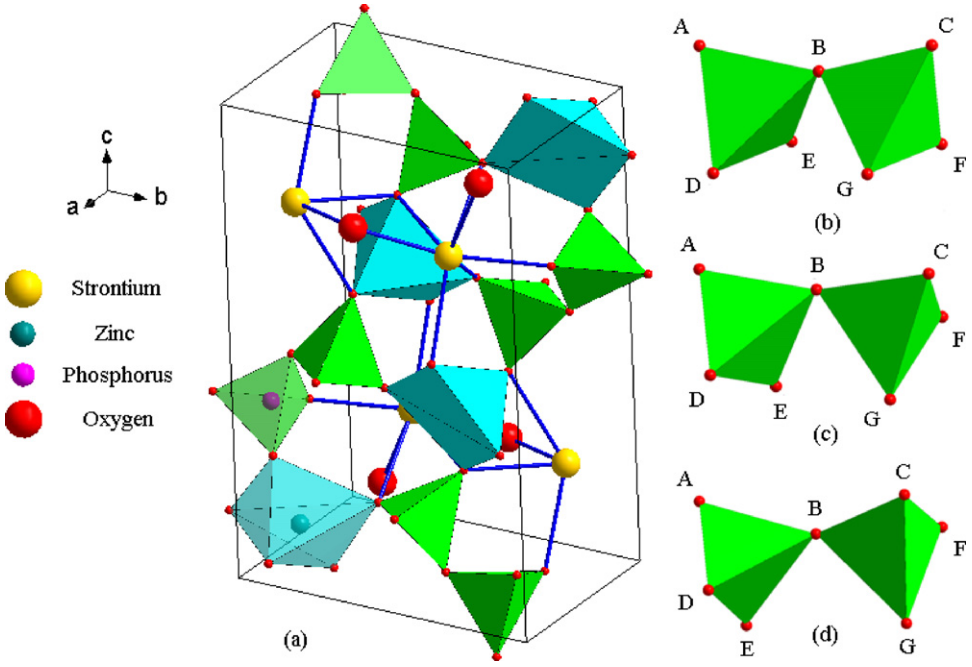

Fig. 1. The crystal structure of $SrZnP_2O_7$ and representative $P_4O_7^{4-}$ groups in relative compounds, where (a) crystal structure of $SrZnP_2O_7$; (b), (c) and (d) representative $P_4O_7^{4-}$ groups in α-$Sr_2P_2O_7$, $SrZnP_2O_7$ and α-$Zn_2P_2O_7$, respectively.

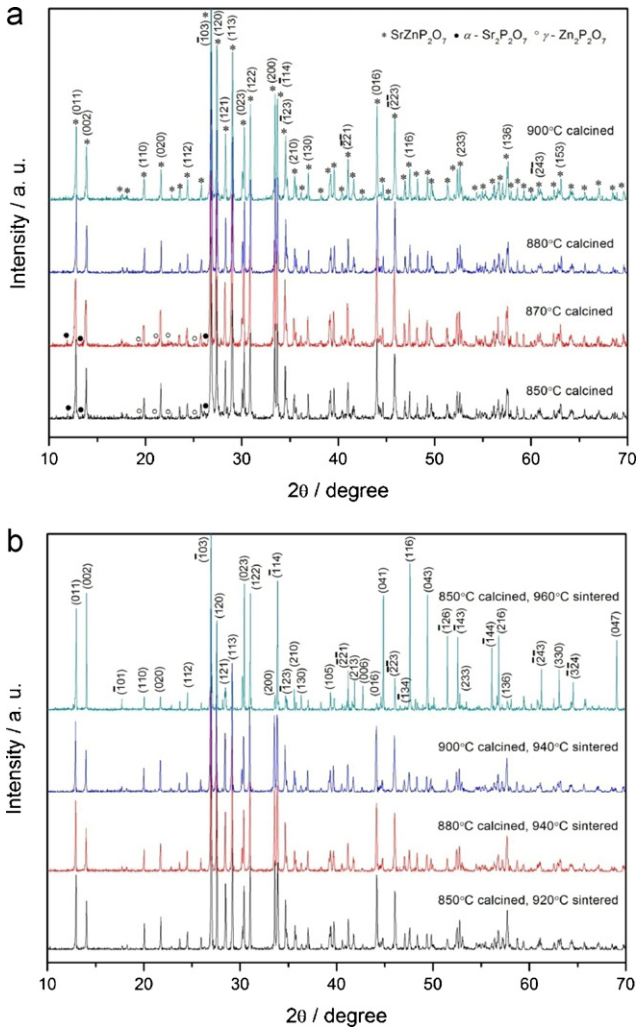

Fig. 2. XRD patterns of $SrZnP_2O_7$ powders and ceramics, where (a) powders calcined at different temperatures; (b) ceramics prepared at different conditions.

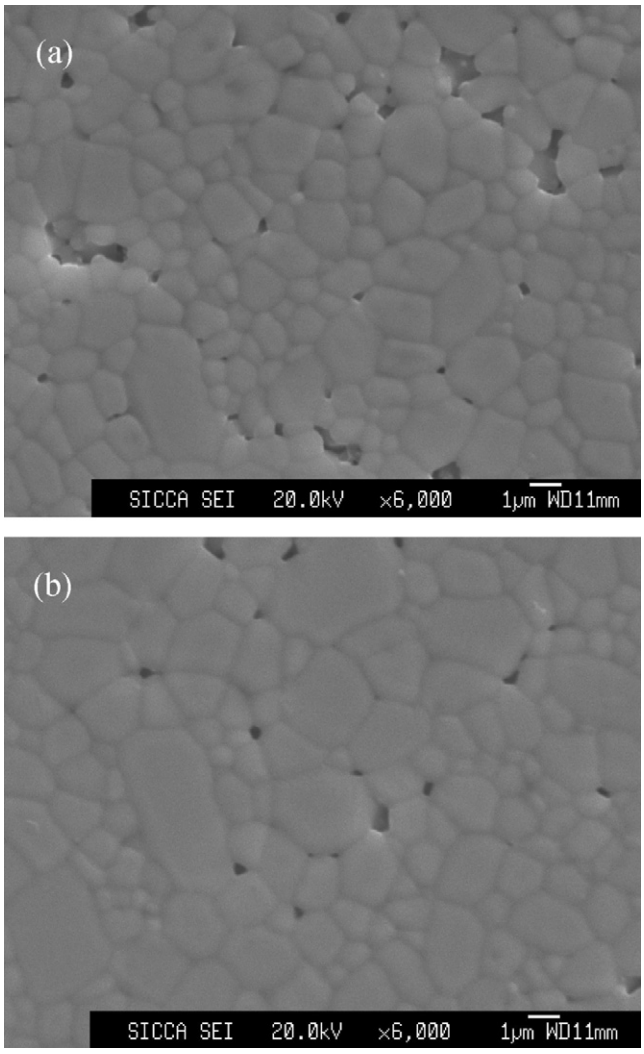

Fig. 3. SEM micrographs of $SrZnP_2O_7$ ceramics, where (a) calcined at 850 °C and sintered at 920 °C; (b) calcined at 880 °C and sintered at 940 °C.

this sample decreased, and higher values of the bulk density were achieved (Fig. 4). Fig. 4 shows the density values of $SrZnP_2O_7$ ceramics sintered at different temperatures. The bulk density values increased with sintering temperature before 930 °C for all samples prepared from powders calcined at different temperatures. For the ceramics from powders calcined at low temperature (850 °C), the density values decreased obviously when sintered at high temperatures; however, there was no obvious decrease for the ceramics from the powders calcined at high temperature, and sintered at high temperatures. The theoretical density of $SrZnP_2O_7$ compound (3.90 g/cm^3) was calculated from the Diamond Software. For the ceramics from the powders calcined at 880 °C, sintered at 960 °C for 2 h, a maximum bulk density (3.70 g/cm^3) with a relative density (95%) was obtained.

The dielectric constant of $SrZnP_2O_7$ ceramics is also shown in Fig. 4 when it sintered at different temperatures. It shows almost the same trends as the density values. When a high sintering temperature applied, the dielectric constant values decreased for the samples from the powders calcined at low temperature, and there were no obvious changes for the samples from the powders calcined at high temperatures. Larger permittivity values, 6.98–7.02 can be achieved for samples from powders calcined at high temperature in pre-reaction process (880 °C).

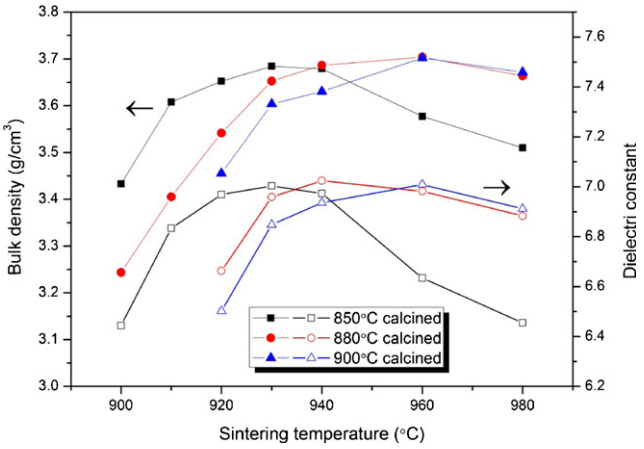

Fig. 4. Density (solid symbols: ■ ● ▲) and dielectric constant (open symbols: □ △ ○) values of $SrZnP_2O_7$ ceramics prepared at different conditions.

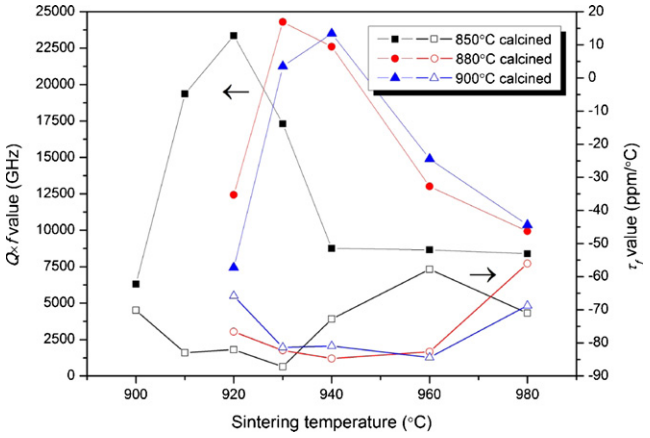

Fig. 5. Quality factor (solid symbols: ■ ● ▲) and τ_f (open symbols: □ △ ○) values of $SrZnP_2O_7$ ceramics prepared at different conditions.

Fig. 5 shows the quality factor values of $SrZnP_2O_7$ ceramics prepared at different conditions. It shows similar trends as the density values. For samples from powders calcined at all temperatures, the $Q \times f$ values can reach a maximum value higher than 22,500 GHz when proper sintering temperatures applied. But, when powders calcined at lower temperatures, the $Q \times f$ values decreased rapidly when high sintering temperature were applied.

In general, the temperature coefficient of resonant frequency (τ_f) is an integrated character of thermal properties including capacitance (τ_ε) and macroscopic geometric shapes (α_L). Fig. 5 also shows the τ_f values of $SrZnP_2O_7$ ceramics prepared at different conditions. It shows that for the samples from the $SrZnP_2O_7$ powders calcined at low temperature, clear rules with increase of sintering temperature cannot be obtained due to unusual grain growth at higher sintering temperature. This situation can be improved when powders calcined at higher temperatures, the stable τ_f values can be obtained at the sintering temperature range of 930–960 °C, with an average τ_f value of −82 ppm/°C.

The phase transformation at low temperature for pyrophosphates is typically caused by the existence of stagger configuration [7]. But $SrZnP_2O_7$ has no phase transformations whereas the anion group $P_4O_7^{4-}$ shows stagger configuration in it [4]. Fig. 1 also shows the $P_4O_7^{4-}$ anion group extracted from α-$Sr_2P_2O_7$, $SrZnP_2O_7$ and α-$Zn_2P_2O_7$, which represent the typical construction of $P_4O_7^{4-}$ in three compounds above. For comparison a series of parameters of angle can be applied to evaluate the relatively stagger degree of two polyhedra in the $P_4O_7^{4-}$ anion group. As shown in Table 1, enhanced stagger degree can be observed from α-$Sr_2P_2O_7$ to $SrZnP_2O_7$, and finally α-$Zn_2P_2O_7$. In $SrZnP_2O_7$, although anion group of $P_4O_7^{4-}$ has a twisted angle values causing stagger configuration, the values are not as large as α-$Zn_2P_2O_7$, which leads to configuration near to an eclipsed one. Maybe for this reason, $SrZnP_2O_7$ has no phase transformation, which leads to smaller absolute values of τ_f, unlike other typical compounds with stagger configuration [1].

Table 1
A series of angle degree values to evaluate the relative twisting extent of two polyhedra in the $P_4O_7^{4-}$ group.

Annotation of angles[a]	α-$Sr_2P_2O_7$	$SrZnP_2O_7$	α-$Zn_2P_2O_7$[b]	
∠ABC	158.33	163.71	140.53 (1)	153.29 (2)
∠DBG	76.23	80.90	96.63 (1)	96.01 (2)
∠EBF	76.23	82.64	112.83 (1)	96.01 (2)

[a] The angles annotated by the first column refer to the definition of "backbone" in Ref. [7], while other parts of $P_4O_7^{4-}$ group located at nearly identical side of the backbone line ABC.

[b] In α-$Zn_2P_2O_7$ unit cell, there are two kinds of $P_4O_7^{4-}$ groups with different spacial configurations, which are annotated by superscript (1) and (2). The kind of (1) showed in Fig. 1(d) has double numbers of kind (2).

4. Conclusions

Pure $SrZnP_2O_7$ powders were synthesized at a low temperature of 880 °C, the ceramics sintered at 940 °C with stable sintering capability and good microwave dielectric properties were achieved: $\varepsilon = 7.02$, $Q \times f = 23{,}000$ GHz and $\tau_f = -84.7$ ppm/°C. No phase transformation occurred at low temperature range due to small twisting angles of two polyhedra in $P_4O_7^{4-}$ groups of $SrZnP_2O_7$.

Acknowledgements

This work was supported by the 973-Project (2009 CB613305), NSFC (50932007), STCSM (08JC1420500), GDSTC (2009A090100006).

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