



SYNTHESIS AND DIELECTRIC PROPERTIES OF VANADATE BASED CERAMICS

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Abstract

Low temperature co-firable ceramics (LTCC) possessing good microwave dielectric properties have been widely investigated due to the necessity for miniaturization of devices in order to reduce the size of wireless communication system. The LTCC is widely used for substrate, semiconductor package, passive integrated device and module applications in wireless communication. Low temperature sinterable Ba₂V₂O₇ and BaZnV₂O₇ ceramics has been prepared through solid-state ceramic technique. The phase purity and crystal structure of the prepared ceramic materials are studied using X-ray diffraction analysis. The Ba₂V₂O₇ compound has a triclinic structure with $a = 13.571(3) \text{ \AA}$, $b = 7.320(2) \text{ \AA}$, $c = 7.306(2) \text{ \AA}$. Ba₂V₂O₇ and BaZnV₂O₇ ceramics sintered at 750°C exhibited a dense microstructure with a relative permittivity (ϵ_r) of 9.8 and 7.9 and dielectric loss ($\tan \delta$) 0.014 and 0.0025 respectively. Thus due to low dielectric constant and low dielectric loss it is obvious that the prepared ceramics are promising materials for low temperature co fired ceramic applications.

Keywords: *vanadates, relative permittivity, dielectric properties, ltcc*

INTRODUCTION

The low temperature co-fired ceramic technology has been generating considerable interest due to its advantages. This technology combines many thin LTCC modules and has been widely used in microwave modules such as filters, resonators and capacitors. Because of the development of LTCC technology, there is an emerging progress in the wireless communication system such as mobile phones, global positioning systems, patch antennas, etc^{1,2,3,4}. In the case of LTCC technology, the dielectrics are needed to co-fired with electrode metal with high conductivity such as silver. Therefore, the

layers of ceramic and conducting electrode resulting in multi layer

sintering temperature of the dielectric should lower than the melting point of silver. By the addition of sintering aid such as B₂O₃, V₂O₅ and CuO, we can effectively reducing the sintering temperature of microwave dielectric ceramics³.

In general situation the characteristics of the ceramics are low dielectric constant to increase the signal speed, for increase the frequency selectivity it should have high quality factor and has a stable temperature

coefficient of resonant frequency for the stability of the resonant frequency against temperature fluctuations⁴. But the selected material become easily available, nontoxic and also cost effective. LTCC application mainly used in the field of substrates, semiconductor packages, passive integrated devices, electronic devices, telecommunication etc.

The substrate material for microwave integrated circuits should have a low dielectric constant (ϵ_r), a high quality factor ($Q \times f$) and a near zero temperature coefficient of resonance frequency (ζ_f).³ For the application to low temperature co-fired ceramic multilayer devices, they should be sorted at below 900°C. Recently, we reported that $X_2V_2O_7$ ($X = \text{Mg, Ba, Sr, Ca}$) ceramics have a low sintering temperature and has good microwave dielectric properties^{5,6}. We can reduce the sintering temperature of the Barium Vanadate ceramics by the addition of any impurity with low melting point such as Zinc. So we can analyze the change in dielectric properties and structure of the ceramics with the addition of Zinc in Barium Vanadate ceramic⁸⁻¹¹.

2 EXPERIMENTAL

The $\text{Ba}_2\text{V}_2\text{O}_7$ and BaZnV_2O_7 samples are prepared via solid state method. In this study, the high purity materials such as BaCO_3 , ZnO and V_2O_5 are starting materials. The purity of the raw materials are BaCO_3 (>99%, Sigma-Alorich), ZnO (99.9%, Sigma-Alorich) and V_2O_5 (99.2%, Alfa Aesar). The stoichiometric ratios of the raw materials are weighed and mixed in an agate mortar with distilled water as the grinding medium. The resultant mixture is dried and calcined at a temperature of temperature are 650°C/4h and 625°C/4h for $\text{Ba}_2\text{V}_2\text{O}_7$ and BaZnV_2O_7

respectively. For calcination, the heating and cooling rates are 10°C and 5°C respectively. After calcining, the powder is ground well and polyvinyl alcohol (PVA) is added as binder. The binder helps in increasing the mechanical strength of the sample. Then the powdered sample is made into cylindrical shaped pellets with diameters 14mm and 12mm. The calcined powder is pressed in a tungsten carbide die at 50KN pressure. These pellets were sintered in the range 700-750°C for 2h in a furnace with heating and cooling rate at 10°C and 5°C respectively. Diameter, height and mass of the sintered pellet is measured and the density is found out using dimension method. The crystalline phase of the samples are identified by using the X-ray powder diffraction (XRPD). The microwave dielectric properties of the samples were measured by using LCR meter.

3 RESULTS AND DISCUSSIONS

3.1 X- RAY ANALYSIS

Fig.1 shows the XRD pattern of $\text{Ba}_2\text{V}_2\text{O}_7$ and BaZnV_2O_7 ceramics calcined at 750°C. The powder patterns are indexed and are comparable with ICDD file card numbers 76-0612 for $\text{Ba}_2\text{V}_2\text{O}_7$ ceramic and 46-0759 for BaZnV_2O_7 ceramic respectively. The d values of our sample seem to be matching with the standard value. The $\text{Ba}_2\text{V}_2\text{O}_7$ ceramic is anorthic with lattice parameters $a = 13.57$, $b = 7.32$, $c = 7.306$ and $\alpha = 90.090$, $\beta = 99.480$, $\gamma = 87.320$. The BaZnV_2O_7 ceramic is orthorhombic with lattice parameters $a = 13.04$, $b = 5.570$, $c = 7.558$.

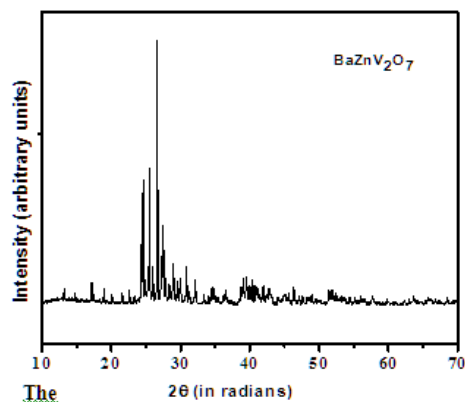
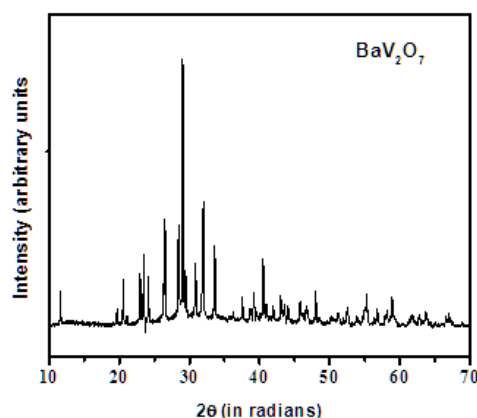


Fig. 1 The XRD pattern of $\text{Ba}_2\text{V}_2\text{O}_7$ and BaZnV_2O_7

3.2 DENSITY VARIATION OF $\text{Ba}_2\text{V}_2\text{O}_7$ AND BaZnV_2O_7 WITH TEMPERATURE

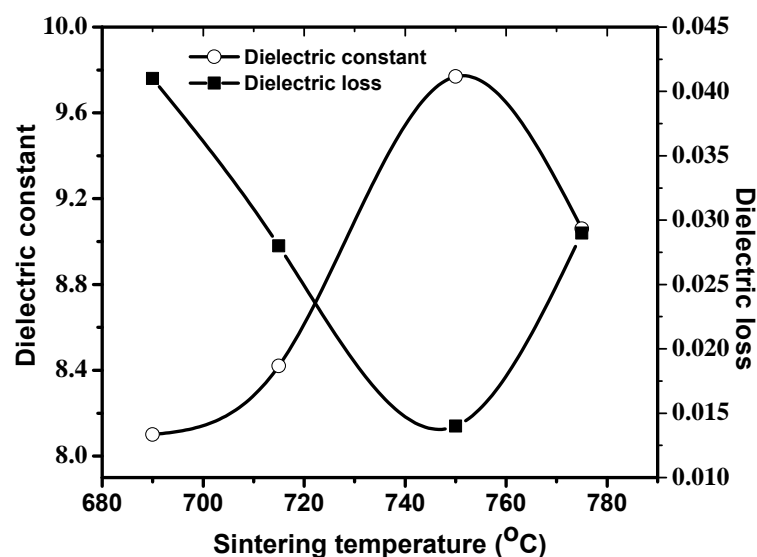
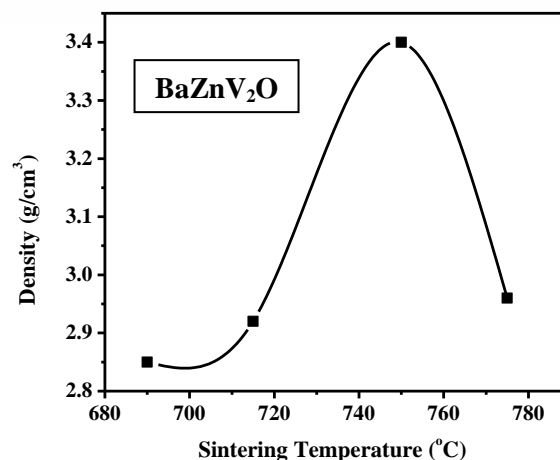
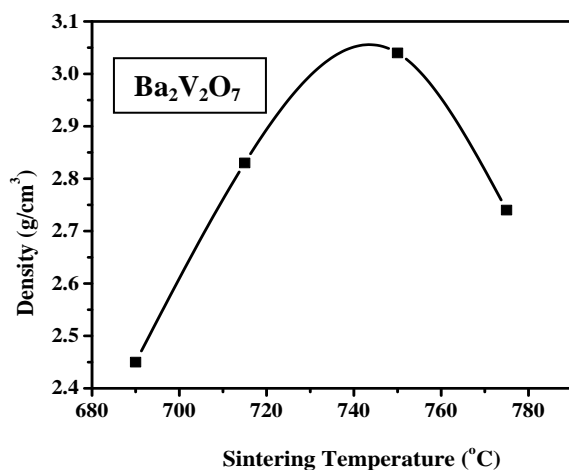


Fig. 2 Variation of density with temperature in $\text{Ba}_2\text{V}_2\text{O}_7$ and BaZnV_2O_7 .

The density varies with sintering temperature. The density increases with sintering temperature reaches a maximum value and then decreases. The decrease in density may be due to any defects or additional phases. This increase in density may be due to the high density of zinc

3.3 DIELECTRIC STUDIES

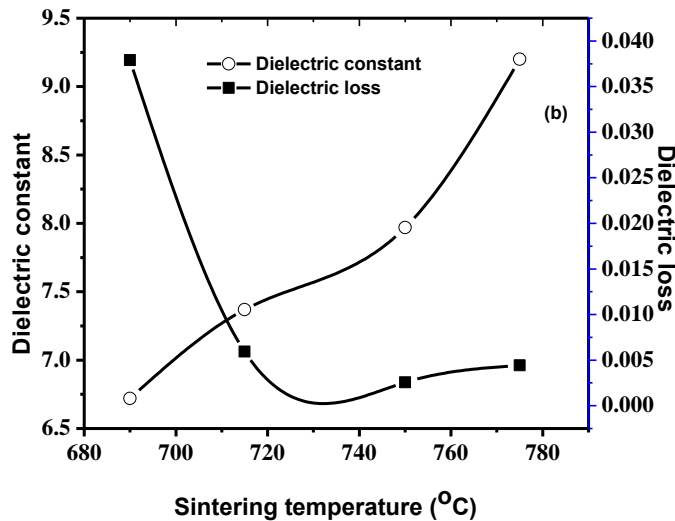


Fig.3 Variation of dielectric constant and dielectric loss with temperature in (a) Ba₂V₂O₇ and (b) BaZnV₂O₇ ceramic at 1 MHz

The variation of dielectric constant and dielectric loss with sintering temperature at 1 MHz is shown in figure 3(a) and (b). It can be seen that dielectric constant increases with sintering temperature. The increase of the dielectric constant is attributed to improved densification of the ceramic.¹² It can be seen that dielectric loss decreases with sintering temperature, reaches a minimum and then increases. The optimized dielectric constant and dielectric loss are 9.77 and 0.014 for Ba₂V₂O₇ ceramic and 7.97 and 0.0026 for BaZnV₂O₇ respectively.

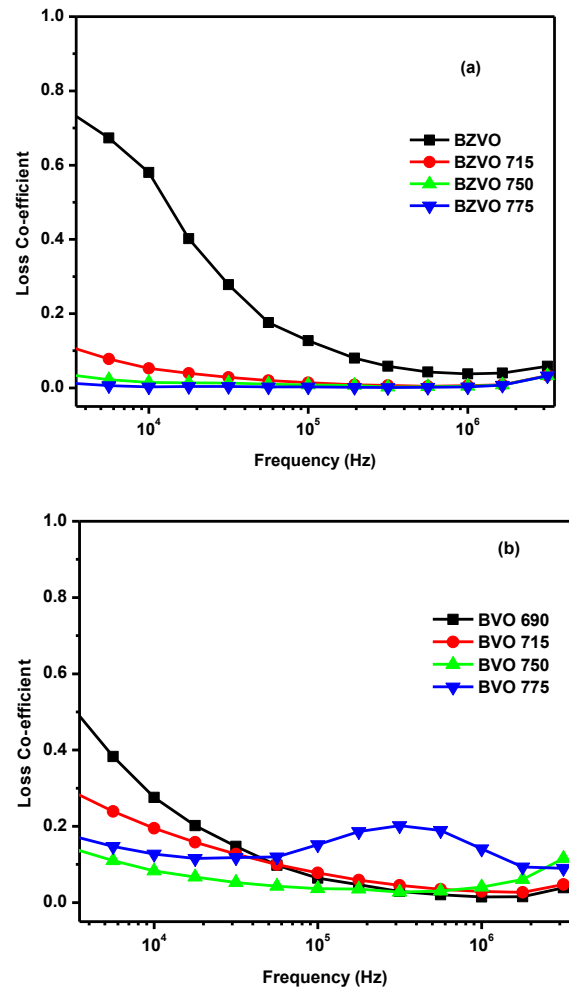


Fig. 4 Variation of dielectric loss with frequency In (a) Ba₂V₂O₇ and (b) BaZnV₂O₇

Fig. 4(a)-(b) shows the variation of dielectric loss with frequency in Ba₂V₂O₇ and BaZnV₂O₇ respectively. For both Ba₂V₂O₇ and BaZnV₂O₇ ceramics in the lower frequency range the dielectric constant decreases with frequency and remains constant for all sintering temperatures. It is believed that a decrease in the dipolar polarization of the matrix and the accumulation of charges results in a large scale field distortion.¹³ Above 100 kHz, the changes become smaller.¹⁴ The dielectric loss shows

a sharp decrease with frequency up to 1 MHz and thereafter the decrease is small and gradual. This means the extent of interfacial polarization is substantially augmented as the frequency is gradually reduced yielding quite a high value of loss at each composition. It is known that both relative permittivity and dielectric loss depend on electronic, ionic, dipole-orientation and space charge polarizations. At lower frequencies interfacial polarization pronounces thus increasing the dielectric loss and dielectric constant¹⁵.

4 CONCLUSIONS

The phase composition of the ceramic prepared is identified using X-ray diffraction method. The $\text{Ba}_2\text{V}_2\text{O}_7$ and BaZnV_2O_7 ceramic are single phase ceramics. The optimized dielectric constant and dielectric loss are 9.77 and 0.014 for $\text{Ba}_2\text{V}_2\text{O}_7$ ceramic and 7.97 and 0.0026 for $\text{Ba}_2\text{V}_2\text{O}_7$ respectively at 1 MHz. It is obvious that prepared ceramics due to low dielectric constant and low dielectric loss and low sintering temperature are promising materials for LTCC substrate applications.

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