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New vanadium based $Ba_3MV_4O_{15}$ (M=Ti and Zr) high Q ceramics for LTCC applications

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Abstract

Low-temperature sinterable $Ba_3TiV_4O_{15}$ and $Ba_3ZrV_4O_{15}$ ceramics have been prepared through conventional solid state ceramic route. Phase purity of the materials has been studied using powder X-ray diffraction technique. The microwave dielectric properties of the materials were studied by Hakki and Coleman post resonator technique and resonant cavity methods respectively using a Vector Network Analyzer. Both $Ba_3TiV_4O_{15}$ and $Ba_3ZrV_4O_{15}$ ceramics exhibited low dielectric constant and comparatively high unloaded quality factor. At optimum sintering temperature of 800 °C, the temperature coefficient of resonant frequency of $Ba_3TiV_4O_{15}$ and $Ba_3ZrV_4O_{15}$ ceramics are 10 ppm/°C and −102 ppm/°C respectively. Both compositions exhibited good chemical compatibility with silver and aluminum electrodes.

Keywords: A. Solid state reaction; A. Sintering; B. X-ray methods; C. Dielectric properties

1. Introduction

Wireless communication system witnessed a phenomenal growth both in terms of technology and utility for the past few decades. Low temperature co-fired ceramic (LTCC) materials have been extensively used to reduce the size of wireless communication systems such as band pass filters, cellular phones, antenna duplexers, etc. [1–4]. Because of its high conductivity and low cost, silver is commonly used as the electrode material in LTCC materials, which is having a melting point of 961 °C. Therefore the processing temperature of LTCC base material should be less than 950 °C and it should have chemical compatibility with the metal electrodes [5]. But most of the ceramics having good microwave dielectric properties sinter at relatively higher temperatures, which restricts their wider use in LTCC applications [6–8].

Often glass or other additives such as Bi_2O_3, CuO, TeO_2 etc. are used to reduce the sintering temperature of microwave ceramic materials for co-firing with Ag or Al [9–13]. The addition of low melting oxides can reduce the sintering temperature of the ceramics [14–17]. However this approach is not preferred, since it deteriorates the microwave dielectric properties of the host material, especially the quality factor. Ota et al. reported that the addition of 0.5 wt% of B_2O_3 in $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}(x=2/3)$ ceramics reduces the sintering temperature from 1733 K to 1473 K, which in turn reduces the dielectric constant and the quality factor as well [18]. Therefore, the search for novel low sintering ceramic materials is the only approach to cater the large requirement of low temperature co-fired ceramic materials. Umemura et al. reported that $Mg_3(VO_4)_4$ ceramic which sinters at 950 °C/50 h possesses a dielectric constant of 9.1, *Qf* of 64,142 GHz, and τ_f value of −93.2 ppm/°C together with chemical compatibility with Ag electrodes [19]. Wang et al. reported that $Zn(Nb_{0.95}V_{0.025})_2O_{5.875}$ sintered at 1000 °C is having ε_r of 23.8, *Qf* of 64,000 GHz and τ_f of −50 ppm/°C and the material exhibited good chemical compatibility with metal electrodes [20].

Only a few literatures are available on the structure and microwave dielectric properties of V_2O_5 ceramic systems. From the available reports, it is clear that V_2O_5 based

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ceramics are good candidate materials for LTCC applications. In the present study, new vanadate compositions such as $Ba_3TiV_4O_{15}$ (BTV) and $Ba_3ZrV_4O_{15}$ (BZV) ceramics have been prepared and its microwave dielectric properties and chemical compatibility with silver and aluminum metal electrodes have been judiciously studied.

2. Experimental procedure

The $Ba_3TiV_4O_{15}$ and $Ba_3ZrV_4O_{15}$ ceramics have been prepared through conventional solid state ceramic route. The starting materials were $BaCO_3$ (99%, Sigma Aldrich), V_2O_5 (98%, Himedia), ZrO_2 (99%, Sigma Aldrich) and TiO_2 (99%, Sigma Aldrich). The stoichiometric proportions of the raw materials were weighed and wet mixed in distilled water for about an hour and then dried. For BTV ceramics 11.8404 g of $BaCO_3$, 1.598 g of TiO_2 and 7.2752 g of V_2O_5 were accurately weighed and mixed in an agate mortar using distilled water and 2.4644 g of ZrO_2 was used instead of TiO_2 for the preparation of BZV ceramics. The resultant slurry was dried and calcinated at 700 °C for 2 h in a programmable SiC furnace. After calcination, 5 wt% polyvinyl alcohol (PVA) solution was added to the powder and the slurry was dried. The powder was again ground well and then pressed in tungsten carbide die of 11 mm diameter. Cylindrical compacts were made under a pressure of 250 Mpa. These compacts were sintered at different temperatures in the range 760°–820 °C for 2 h.The density of the sintered compacts was determined using dimensional method. The phase purity and the structural behavior of the samples were determined using M/s Brucker 5005 model powder X-ray diffractometer. The dielectric constant and the unloaded quality factor of the sintered sample were studied using Hakki and Coleman [21] and resonant cavity method [22] respectively, using a vector network analyzer (Agilent, E8362B, Malaysia). The temperature coefficient of resonant frequency (τ_f) was measured in the temperature range 30°–100 °C.

3. Result and discussion

The powder X-ray diffraction (XRD) patterns of BTV and BZV ceramics are shown in Figs. 1 and 2 respectively. The XRD pattern of BTV is compared with that of standard JCPDS file no. 36-1488 and it exactly matches with that of the standard pattern. BTV ceramics have an orthorhombic crystal structure with space group *Pnma* (62). The lattice parameters of BTV ceramic is calculated as $a=32.434$, $b=7.2466$, and $c=5.522$ Å and the values are in good agreement with the JCPDS data.

Slight shifting of peak positions to the lower 2θ angles and splitting of the peaks at (8 1 0) and (6 1 1) planes can be attributed to the higher ionic radius of Zr^{4+} in place of Ti^{4+} in BZV ceramic (Fig. 2) [23–24]. The calculated lattice parameters of BZV ceramic are $a=31.958$, $b=7.8049$ and $c=6.591$ Å which are comparable with the lattice parameters of BTV ceramics. From these results, it can be inferred that the crystal structure of BZV is isomorphous with that of BTV ceramics.

The BTV and BZV ceramics were sintered at different temperature in the range 760–820 °C. The variation of density and dielectric constant with sintering temperature of BTV and BZV ceramics are shown in Fig. 3(a and b) respectively. The maximum density and dielectric constant of the ceramics are obtained at a sintering temperature of 800 °C for 2 h for both the compositions. Further increase in temperature deteriorates the density and dielectric constant, which may be due to the decomposition of some of the constituents in the ceramics. BTV ceramics exhibited a maximum density of 3.74 g/cm^3 and a dielectric constant of 13.6 at optimum sintering temperature (800 °C) where as BZV ceramics has a maximum density of 3.59 g/cm^3 together with a dielectric constant of 10.7. The variation of *Qf* values of BTV and BZV ceramics with sintering temperature is shown in Fig. 4. As a function of density, the *Qf* values of both BTV and BZV ceramics show an increasing trend (Fig. 4). The maximum *Qf* value of BTV

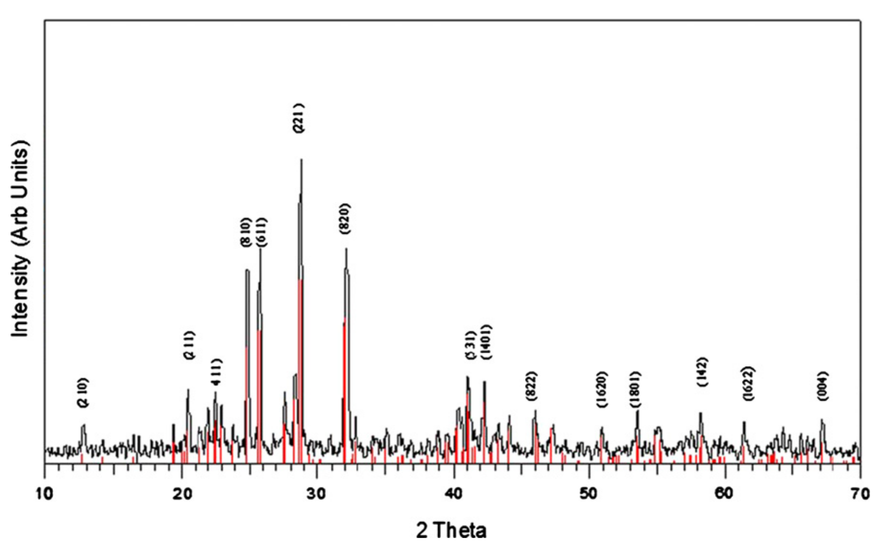

Fig. 1. Powder X-ray diffraction patterns of BTV ceramics.

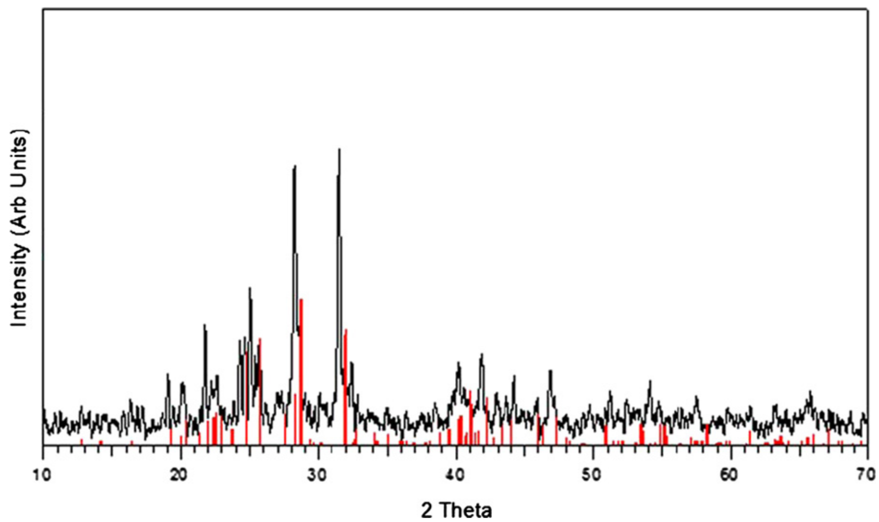

Fig. 2. Powder X-ray diffraction patterns of BZV ceramics.

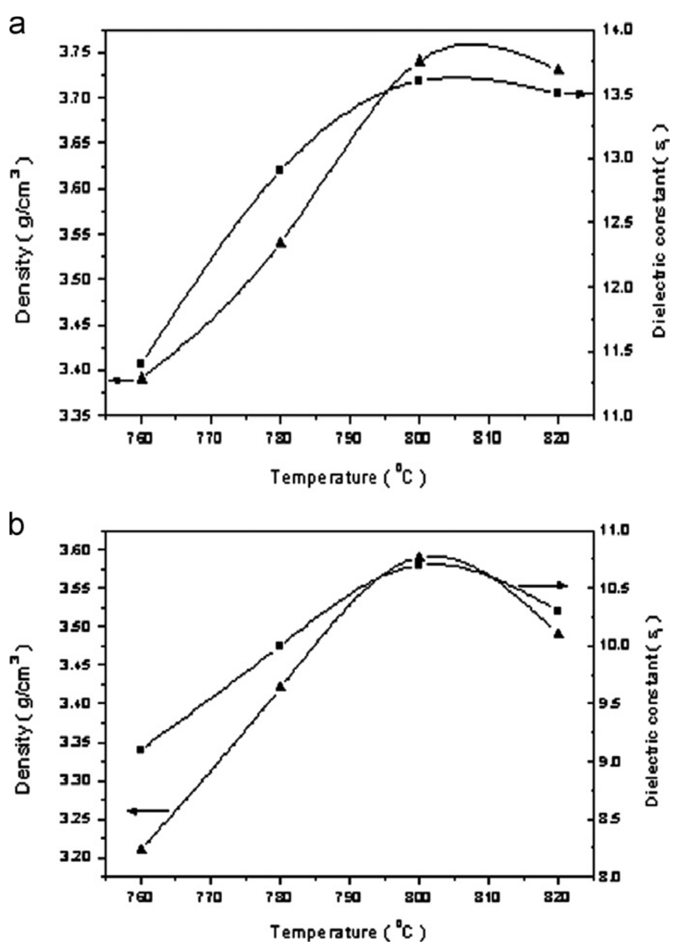

Fig. 3. (a) Variation of density and dielectric constant of BTV ceramics with sintering temperature and (b) variation of density and dielectric constant of BZV ceramics with sintering temperature.

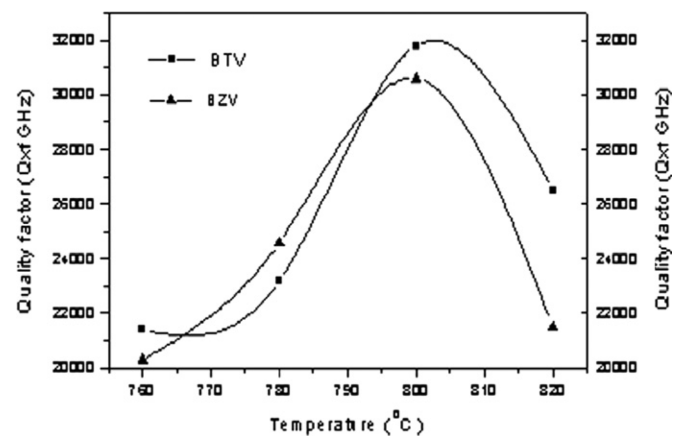

Fig. 4. Variation of Quality factor of BTV and BZV ceramics with sintering temperature.

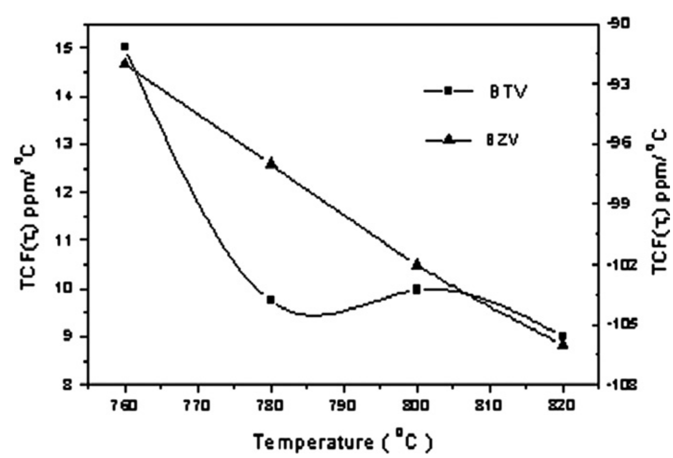

Fig. 5. Variation of temperature coefficient of resonant frequency (τ_f) of BTV and BZV ceramics with sintering temperature.

and BZV ceramics are 31,800 and 30,600 respectively at an optimum sintering temperature of 800 °C for 2 h. Fig. 5 shows the variation of temperature coefficient of resonant frequency (τ_f) of BTV and BZV ceramics with respect to sintering temperature. For BTV ceramics, τ_f varies from 8 to 15 ppm/°C where as for BZV it varies from -92 to -106 ppm/°C. At optimum sintering temperature, BTV and BZV have τ_f values of 10 ppm/°C and -102 ppm/°C respectively.

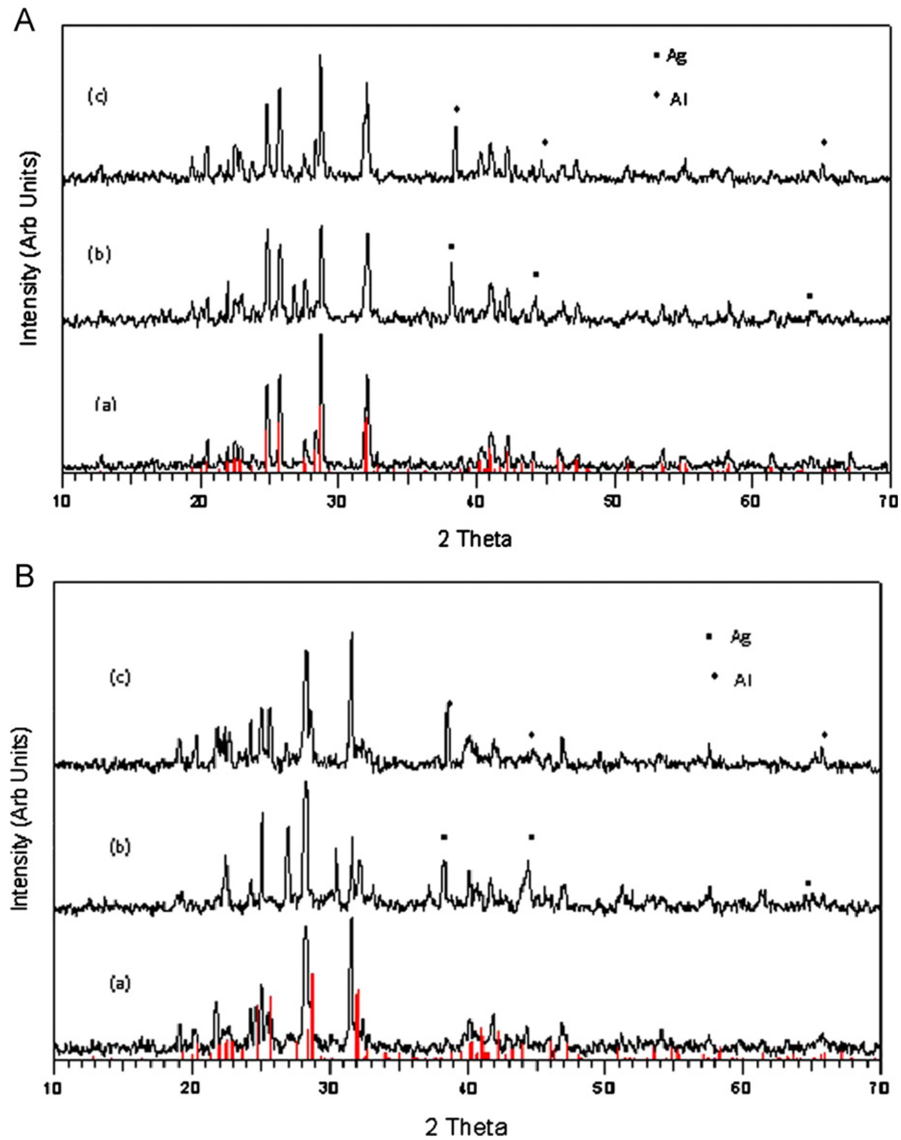

Fig. 6. (A) XRD patterns of (a) BTV ceramics; (b) BTV+20 wt% Ag; and (c) BTV+20 wt% Al. (B) XRD patterns of (a) BZV ceramics; (b) BZV+20 wt% Ag; and (c) BZV+20 wt% Al.

From the above results, it can be inferred that temperature stable microwave ceramic system can be tailor made by making a solid solution of $Ba_3Ti_{1-x}Zr_xV_4O_{15}$ ceramics.

In order to study the chemical compatibility of BTV and BZV ceramics with metal electrodes such as silver and aluminum, 20 wt% of Ag and Al were separately added to each of these ceramics and sintered at 780 °C for 2 h in a SiC furnace. The resultant XRD patterns are shown in Fig. 6(A and B) respectively. Silver and aluminum peaks are marked with * and ● in the XRD patterns. Since no additional peaks are observed in the XRD patterns which indicates good chemical compatibility of BTV and BZV ceramics with silver and aluminum. It is clear from the present study that both BTV and BZV ceramics have low sintering temperature, excellent microwave dielectric properties and good chemical compatibility with both Ag and Al electrodes. Therefore, BTV and BZV ceramic systems can be used as a suitable candidate for LTCC applications.

4. Conclusions

Phase pure $Ba_3TiV_4O_{15}$ and $Ba_3ZrV_4O_{15}$ ceramics were prepared by solid state ceramic method. XRD analysis shows that these ceramics have an orthorhombic crystal structure. At optimum sintering temperature of 800 °C, BTV ceramic exhibits a dielectric constant of 13.6, unloaded quality factor of 3700 at 8.6225 GHz and temperature coefficient of resonant frequency of 10 ppm/°C. Slight variation in dielectric properties was observed while replacing Ti^{4+} with Zr^{4+}. BZV ceramic possesses a dielectric constant 10.7, unloaded quality factor of 3600 at 8.5114 GHz and temperature coefficient of resonant frequency −102 ppm/°C respectively.

X-ray diffraction studies reveal excellent chemical compatibility of BTV and BZV ceramics with silver and aluminum electrodes, which make them promising candidate for LTCC applications.

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