Effect of Vanadium Substitution on the Structure and Microwave Dielectric Properties of 5BaO-2Nb₂O₅ Binary Ceramic System

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Some of the contents of this chapter have published in

4.1 Introduction

Recently, microwave communication has witnessed unprecedented growth with wide range of applications such as satellite communications, mobile phones, global positioning systems etc. This wide spread usage of microwave communication systems demands a new family of low temperature co-fired ceramics (LTCC) to realize miniaturized microwave devices suitable for high frequency applications [1]. Basically, ceramic compositions having low dielectric constant ($\varepsilon_r$), relatively high quality factor (Qxf) and nearly zero temperature coefficient of resonant frequency ($\tau_f$) are preferred for microwave LTCC applications. In addition, LTCC technology necessitates the co-firing of both metal electrodes and dielectric materials without inter-diffusion. High temperature sinterable ceramics cannot be co-fired with Ag since the melting temperature of Ag electrode is 961°C [2]. Therefore, the sintering temperature of dielectrics should be lower than the melting temperature of metal electrode. In addition, there should be good chemical compatibility between the LTCC material and the metal electrode [1, 3].

Generally, most of the commercial microwave dielectric materials such as Ba(Mg$^{1/3}$Ta$^{2/3}$)O$_3$, Ba$_5$Nb$_4$O$_{15}$, (Zr,Sn)TiO$_4$, Ba$_2$Ti$_9$O$_{20}$ etc. have good microwave dielectric properties, but they sinter only at elevated temperatures [4-7]. Addition of sintering aids are effective in bringing down the sintering temperature of microwave dielectric ceramics but these additives deteriorate the microwave dielectric properties due to the formation of secondary phases [8-11]. Although Ba(Mg$^{1/3}$Ta$^{2/3}$)O$_3$ is an archetypical high Q material, the sintering temperature of this material is extremely high (<1600°C) and their intrinsic quality factor is governed by the order-disorder effect and microstructural properties [12]. In this context, cation-deficient hexagonal perovskite, Ba$_5$Nb$_4$O$_{15}$ is an attractive microwave ceramic material suitable for tailor making LTCC composition by proper substitution owing to their excellent microwave dielectric properties, good sintering characteristics and ease of phase formation [13].

Ba$_5$Nb$_4$O$_{15}$ ceramic in the A$_5$B$_4$O$_{15}$ family crystallizes in the trigonal space group and it is one of the classic high Q ceramic materials, ideally suited for microwave communication applications. The structure and microwave dielectric
properties of Ba$_5$Nb$_4$O$_{15}$ were studied by many researchers and it is reported that Ba$_5$Nb$_4$O$_{15}$ can be sintered in the temperature range 1400-1450ºC and exhibits a dielectric constant of 39, Q$_{xf}$ value of 23,700 GHz and $\tau_f$ of ~78 ppm/ºC [14, 15]. The microwave dielectric properties of Ba$_5$Nb$_4$O$_{15}$ ceramic were accurately determined using Whispering Gallery Mode (WGM) by Ratheesh et al. [16]. Ba$_5$Nb$_4$O$_{15}$ powders synthesized by molten salt method with NaCl-KCl flux in the 1:1 ratio sintered at 1300ºC for 2h exhibit good microwave dielectric properties with $\varepsilon_r$=39.2, Q$_{xf}$ ~ 27,200 GHz and $\tau_f$ ~ 72 ppm/ºC [17].

Relatively high sintering temperature of ~1400ºC is needed to get dense Ba$_5$Nb$_4$O$_{15}$ ceramics by conventional solid state ceramic route [15], although it was reported that 3wt% B$_2$O$_3$ addition to Ba$_5$Nb$_4$O$_{15}$ reduces the sintering temperature to 925ºC with microwave dielectric properties of $\varepsilon_r$ ~39, Q$_{xf}$ ~18,700 GHz and $\tau_f$ ~ 0 ppm/ºC [18]. Also, the addition of small amount of B$_2$O$_3$ in to Ba$_5$Nb$_4$O$_{15}$- BaNb$_2$O$_6$ mixtures significantly lowers the sintering temperature to 900ºC [19]. The low fired 0.84Ba$_5$Nb$_4$O$_{15}$ - 0.16BaNb$_2$O$_6$ mixture possesses $\varepsilon_r$ ~ 42, Q$_{xf}$ ~19,500 GHz and $\tau_f$ ~ 0 ppm/ºC at microwave frequencies and hence suitable for low temperature co-fired ceramic (LTCC) applications [20]. The effect of tantalum substitution for niobium in the structure and microwave dielectric properties of Ba$_5$Nb$_4$O$_{15}$ ceramic was also reported [15]. Even though tantalum has larger ionic polarizability, Ba$_5$Ta$_4$O$_{15}$ has lower dielectric constant ($\varepsilon_r$=28) than Ba$_5$Nb$_4$O$_{15}$. This is because of the lattice anharmonicity of Ba$_5$Nb$_4$O$_{15}$, which results relatively larger dielectric constant for Ba$_5$Nb$_4$O$_{15}$ ceramic [14, 15]. Recent literature [21] revealed the phase relations and microwave dielectric properties of vanadium modified Ba$_5$Nb$_4$O$_{15}$. It was found that the addition of vanadium reduces the sintering temperature of Ba$_5$Nb$_4$O$_{15}$ from 1450ºC to 1100ºC and Ba$_5$Nb$_{4-x}$V$_x$O$_{15}$ (x=0-1) compositions exhibit Ba$_3$V$_2$O$_8$ as secondary phase and the intensity of the peaks corresponding to Ba$_3$V$_2$O$_8$ phase increases with increasing vanadium content [21]. Recent studies on the crystal structure of single crystal Ba$_2$Cd$_3$V$_4$O$_{15}$ by Mertens et al. prompted us to see whether 5BaO-2V$_2$O$_5$ phase will exist in the BaO-V$_2$O$_5$ binary system [22]. These authors identified the co-existence of (VO$_4$)$^{3-}$ and (V$_2$O$_7$)$^{4+}$ groups (Figure 4.1) together with
BaO$_9$ and BaO$_{12}$ polyhedra in Ba$_2$Cd$_3$V$_4$O$_{15}$, having an orthorhombic crystal structure with $P2_12_12_1$ space group with four number of molecules per unit cell [22].

Even though conventional methods such as low-melting glass addition, chemical processing and additives were found effective in lowering the sintering temperature, but are relatively expensive, time consuming and often deteriorates the microwave dielectric properties [8-10, 17, 23]. However, substitution of low melting oxides in the parent composition can be considered as an effective method for the formation of low fired ceramics [10, 21]. In the present study, Nb$^{5+}$ ions in Ba$_5$Nb$_4$O$_{15}$ is substituted by V$^{5+}$ ions and its structural, microstructural and microwave dielectric properties are investigated in detail.

![Figure 4.1](image_url)  
**Figure 4.1** Linkage of the [Cd(2)Cd(3)O$_8$] zig zag chains by V(3)O$_4$ tetrahedra (close hatching) and V$_2$O$_7$ tetrahedron dough (Black, formed from V (1) and V (2)) [Ref: 22]

### 4.2 Experimental techniques

Ba$_5$Nb$_{4-x}$V$_x$O$_{15}$ (x=0-4) ceramics were prepared by conventional solid state ceramic method. High purity BaCO$_3$ (Sigma Aldrich, 99%), Nb$_2$O$_5$ (Aldrich, 99.9%) and V$_2$O$_5$ (Sigma Aldrich, 99%) were used as starting materials. Stoichiometric amounts of the raw materials were weighed and wet mixed in distilled water for an hour using agate mortar. The resultant slurry was dried at 100°C in hot air oven, then
ground well, and calcined at various temperatures. The calcined powders were ground again and then mixed with 5 wt% polyvinyl alcohol (PVA) as binder and the slurry was dried. The powders were again ground well and then pressed uniaxially in a tungsten carbide (WC) die of about 11 mm diameter by applying a pressure of 250 MPa in a hydraulic hand press. These cylindrical green compacts were sintered in a programmable furnace in the 900-1400°C temperature range for 1h. Ba$_3$V$_2$O$_8$ and Ba$_2$V$_2$O$_7$ ceramics were also prepared through solid state ceramic route and sintered in the 800-1300°C temperature range for 1h. The green pellets were initially fired at a rate of 8°C/min up to 600°C and then at a rate of 10°C/min up to the sintering temperature. An intermediate soaking was given at 600°C for 30 min to expel the binder.

Phase purity of the samples was studied by powder X-ray diffraction (XRD) measurement using CuK$_\alpha$ radiation (Bruker 5005, Germany). The Raman spectra of the ceramic compositions under study were recorded using a Thermo Scientific DXR with Nd:YVO$_4$ DPSS laser of 532 nm. The sintered samples were thermally etched for 30 min at a temperature of about 100°C below the sintering temperature, and the surface morphology was studied using a scanning electron microscope (Carl Zeiss, Model No: EVO18 Research, Germany). The shrinkage behavior of the 5BaO-2V$_2$O$_5$ ceramic was studied in the temperature range 30-900°C using an EXSTAR 6000 model Thermo Mechanical Analyzer (SII Nano technology INC., Japan). The low frequency measurements of the samples were carried out at 1 MHz using an impedance analyzer (Agilent, 4294A, Malaysia). The microwave dielectric properties were measured using a vector network analyzer (Agilent make PNA E8362B, Bayan Lepas, Malaysia). The dielectric constant and the unloaded quality factor of the samples were measured by Hakki and Coleman post resonator [24] and cavity perturbation methods [25] respectively. The temperature coefficient of resonant frequency ($\tau_f$) was measured by noting the variation of TE$_{01\delta}$ mode frequency with temperature in the range of 30-100°C.
4.3 Results and discussion

4.3.1 X-ray diffraction studies

Figure 4.2 shows the X-ray diffraction patterns of Ba$_5$Nb$_{4-x}$V$_x$O$_{15}$ (x=0-4) ceramics (hereafter referred as BN4, BN3V, BN2V2, BNV3 and BV4). Figure 4.2a shows the X-ray diffraction pattern of sintered Ba$_5$Nb$_4$O$_{15}$ ceramic. Ba$_5$Nb$_4$O$_{15}$ crystallizes in the hexagonal system with space group $P\overline{3}m1$ having one formula unit per cell ($Z=1$) [26]. The XRD pattern of Ba$_5$Nb$_4$O$_{15}$ obtained in the present study is exactly matches with the available ICDD pattern (ICDD Card No: 14-0028) and hence indexed on the basis of the hexagonal symmetry of Ba$_5$Nb$_4$O$_{15}$ (indicated by I). The X-ray diffraction patterns of BN3V, BN2V2 and BNV3 obtained in the present study are compared with that of Ba$_5$Nb$_4$O$_{15}$ and those phases that are expected to occur in the solid solution. From Figure 4.2b-d, it can be observed that the intensities of the major diffraction peaks of Ba$_5$Nb$_4$O$_{15}$ phase decrease with increasing vanadium content (x) whereas the diffraction peaks of Ba$_3$V$_2$O$_8$ secondary phase increase steadily. It indicates that Ba$_3$V$_2$O$_8$ is formed as secondary phase as a result of vanadium substitution. Moreover, Figure 4.2b-d shows the occurrence of some weak peaks at 20 angles ~ 28.3º and 29.7º (indicated by ‘o’ in Figure 4.2) clearly shows the presence of BaNb$_2$O$_6$ secondary phase (ICDD Card No: 32-0077) in BN3V, BN2V2 and BNV3 ceramics. This phenomenon has already been observed in B$_2$O$_3$ added Ba$_5$Nb$_4$O$_{15}$ ceramics reported by Kim et al. [18].

Recently, Zhao et al. made a comprehensive effort to study the effect of vanadium substitution on the structure and microwave dielectric properties of Ba$_5$Nb$_{4-x}$V$_x$O$_{15}$ (x=0-1) [21]. The objective of this study was to investigate the phase relations and microwave dielectric properties of vanadium modified Ba$_5$Nb$_4$O$_{15}$ as a function of vanadium content and sintering temperature. In this work, Zhao et al. reported the formation of Ba$_3$V$_2$O$_8$ secondary phase in samples with compositions of x ≥ 0.125 and some weak peaks corresponding to BaNb$_2$O$_6$ secondary phase at x ≥ 0.5. These authors suggested that majority of V$^{5+}$ ions hardly substituted in place of Nb$^{5+}$ ions in Ba$_5$Nb$_4$O$_{15}$ hexagonal perovskite, instead forming another compound.
Ba$_3$V$_2$O$_8$. A hexagonal to orthorhombic phase transition for BaNb$_2$O$_6$ secondary phase is also reported by Zhao et al. [21].

Figure 4.2 X-ray diffraction patterns of Ba$_{3-4x}$Nb$_{4-x}$V$_x$O$_{15}$ (x=0-4) ceramics

The X-ray diffraction patterns of BN3V, BN2V2 and BNV3 ceramics obtained in the present study are also in agreement with the results reported by Zhao et al. Furthermore, it is found that the complete substitution of Nb$^{5+}$ ions by V$^{5+}$ ions in Ba$_5$Nb$_4$O$_{15}$ (at x=4) result Ba$_3$V$_4$O$_{15}$, as a multiphase composition comprising of hexagonal Ba$_3$V$_2$O$_8$ and triclinic Ba$_2$V$_2$O$_7$ (Figure 4.2). In order to understand the phase formation of BV4 composition, stoichiometric amounts of BaCO$_3$ and V$_2$O$_5$ were calcined at different temperatures for 1h (Figure 4.3). The specimen fired at 300ºC and 400ºC exhibited diffraction peaks corresponding to that of BaCO$_3$ and V$_2$O$_5$, indicating that no reaction has taken place between BaCO$_3$ and V$_2$O$_5$ up to 400ºC. The specimen heat treated at 500ºC showed peaks of Ba$_2$V$_2$O$_7$ phase (ICDD Card No: 39-1432), as indicated by arrows in addition to BaCO$_3$ and V$_2$O$_5$. When the calcination temperature exceeds 500ºC, Ba$_3$V$_2$O$_8$ phase was formed due to the reaction of remaining BaCO$_3$ and V$_2$O$_5$ and the peaks are indexed on the basis of ICDD Card No: 29-0211. Both Ba$_3$V$_2$O$_8$ and Ba$_2$V$_2$O$_7$ phases coexist with a small amount of
BaCO$_3$ phase in the specimens fired at 600°C. Furthermore, the specimens fired at temperatures greater than 600°C show the coexistence of both Ba$_3$V$_2$O$_8$ and Ba$_2$V$_2$O$_7$ (ICDD Card No: 29-0211 and 39-1432) phases without the presence of BaCO$_3$ phase. Therefore, it can be inferred that BaCO$_3$ and V$_2$O$_5$ reacted together at temperatures in between 400-500°C and form Ba$_2$V$_2$O$_7$ phase and the reaction of remaining BaCO$_3$ and V$_2$O$_5$ resulted the formation of Ba$_3$V$_2$O$_8$ phase for specimens calcined above 500°C.

In order to further quantify the co-existence of both Ba$_3$V$_2$O$_8$ and Ba$_2$V$_2$O$_7$ phases in BV4, both Ba$_3$V$_2$O$_8$ and Ba$_2$V$_2$O$_7$ powders were individually prepared through conventional solid state ceramic route and calcined at 700°C for 1h. Calcined powders of Ba$_3$V$_2$O$_8$ and Ba$_2$V$_2$O$_7$ were taken stoichiometrically (1:1 ratio), mixed well and sintered at 900°C for 1h. The X-ray diffraction pattern of the sintered Ba$_3$V$_2$O$_8$-Ba$_2$V$_2$O$_7$ composite ceramic is given in Figure 4.4. The sintered Ba$_3$V$_2$O$_8$-Ba$_2$V$_2$O$_7$ mixture do not form single phase material and exactly resembled with the X-ray diffraction pattern of stoichiometrically prepared 5BaO-2V$_2$O$_5$ ceramic (Figure 4.3e). Hence the X-ray diffraction pattern is indexed on the basis of both hexagonal Ba$_3$V$_2$O$_8$ (ICDD Card No: 29-0211) and triclinic Ba$_2$V$_2$O$_7$ (ICDD Card No: 39-1432).

![Figure 4.3 X-ray diffraction patterns of 5BaO-2V$_2$O$_5$ ceramic fired at (a) 300°C (b) 400°C (c) 500°C (d) 600°C and (e) 700°C for 1h](image-url)
Zhang et al. also made an attempt to prepare temperature stable and high Q composite ceramic in low-temperature sinterable BaO-V₂O₅ binary system by cofiring mixtures of phase pure Ba₂V₂O₇ and Ba₃V₂O₈ [27]. They also found the coexistence of Ba₂V₂O₇ and Ba₃V₂O₈ at different sintering temperatures. According to them, the coexistence of Ba₂V₂O₇ and Ba₃V₂O₈ phases might be due to the different crystalline structures of these two phases and the different co-ordination between V⁵⁺, Ba²⁺ and O²⁻ in each crystal structure. Ba₃V₂O₈ has hexagonal structure where the V⁵⁺ ions are located inside tetrahedral [VO₄] units linked by six and ten-fold coordinated Ba²⁺ ions [28]. On the other hand, Ba₂V₂O₇ has triclinic structure with two unique divanadate groups that are repeated by b and c lattice translations to form sheets of divanadate groups parallel to (100) and are linked by four unique Ba²⁺ ions, which lie between themselves [29]. Therefore, the different crystal structures of Ba₂V₂O₇ and Ba₃V₂O₈ hinder the formation of solid solution between these two vanadate ceramics [27]. An attempt has also been made to replace Ba²⁺ with other alkaline earth cations, but all of them exhibited multiphase nature with respective orthovanadate and pyrovanadate analogues.

![X-ray diffraction pattern of Ba₃V₂O₈-Ba₂V₂O₇ mixtures sintered at 900°C for 1h](image)

**Figure 4.4** X-ray diffraction pattern of Ba₃V₂O₈-Ba₂V₂O₇ mixtures sintered at 900°C for 1h
4.3.2 Raman spectroscopic studies

Figure 4.5 shows the Raman spectra of Ba$_5$Nb$_{4-x}$V$_x$O$_{15}$ (x=0-4) ceramics. In the Raman spectrum of BN4 (Figure 4.5a), bands observed at 844 and 770 cm$^{-1}$ are the symmetric stretching vibrations of NbO$_6$ octahedra, whereas asymmetric stretching vibration of NbO$_6$ octahedra is observed at 542 cm$^{-1}$. The vibrational modes observed at 681 cm$^{-1}$ and 439 cm$^{-1}$ are the symmetric and asymmetric bending vibrations of NbO$_6$ octahedra respectively [30]. When the vanadium concentration increased, the intensity of the Nb-O modes reduced considerably. On the other hand, strong vibrational mode is observed at 831 cm$^{-1}$ in BN3V ceramic, which can be ascribed to the symmetric stretching vibration of (VO$_4$)$_3^-$ vibrational units present in Ba$_3$V$_2$O$_8$. On increasing the vanadium concentration, the vibrational modes of Ba$_3$V$_2$O$_8$ become more prominent while the intensity of the vibrational modes of NbO$_6$ octahedra of Ba$_5$Nb$_4$O$_{15}$ reduced. The band assignments of BN4, BN3V, BN2V2, BNV3 and BV4 ceramics are compiled in Table 4.1. In the case of BV4, in addition to the vibrational modes of Ba$_3$V$_2$O$_8$, vibrational modes of Ba$_2$V$_2$O$_7$ are also observed. This result is in accordance with the X-ray diffraction studies of BV4 composition.
In order to study the crystal structure of $5\text{BaO-2V}_2\text{O}_5$ in detail, Laser Raman Spectra of $5\text{BaO-2V}_2\text{O}_5$, $\text{Ba}_3\text{V}_2\text{O}_8$ and $\text{Ba}_2\text{V}_2\text{O}_7$ have been recorded separately and the results are shown in Figure 4.6. It is reported that the structure of $\text{Ba}_2\text{V}_2\text{O}_7$ contains pyrovanadate $(\text{V}_2\text{O}_7)^{4-}$ anions [31] whereas $(\text{VO}_4)^{3-}$ groups are present in the structure of $\text{Ba}_3\text{V}_2\text{O}_8$ [32]. Hence, the internal vibrations of VO$_3$ groups and bridging V-O-V band of the pyrovanadate anions are expected in the Raman spectrum of $\text{Ba}_2\text{V}_2\text{O}_7$.

Strong vibrational modes observed in the Laser Raman spectrum of $\text{Ba}_2\text{V}_2\text{O}_7$ at 888 and 894 cm$^{-1}$ can be attributed to the symmetric stretching vibrations of end VO$_3$ groups. The stretching vibrations of bridging V-O-V bond is observed at 576 cm$^{-1}$ and bending vibrations are observed at 703 and 716 cm$^{-1}$. The vibrational features observed below 270 cm$^{-1}$ are attributed to external modes. On the other hand, vibrations corresponding to $(\text{VO}_4)^{3-}$ molecular groups are seen in the Raman spectrum of $\text{Ba}_3\text{V}_2\text{O}_8$ ceramics. The symmetric stretching vibrations of $(\text{VO}_4)^{3-}$ group is observed at 840 cm$^{-1}$ as a medium intense band. The symmetric and asymmetric bending vibrations are observed at 330 and 384 cm$^{-1}$ respectively (Figure 4.6). Interestingly, the vibrational features of both $(\text{VO}_4)^{3-}$ and $(\text{V}_2\text{O}_7)^{4-}$ groups are seen in the Raman spectrum of $5\text{BaO-2V}_2\text{O}_5$, which is a clear indication of the co-existence of both $\text{Ba}_3\text{V}_2\text{O}_8$ and $\text{Ba}_2\text{V}_2\text{O}_7$ phases. No phases other than $\text{Ba}_3\text{V}_2\text{O}_8$ and $\text{Ba}_2\text{V}_2\text{O}_7$ are seen in the Raman spectrum of $5\text{BaO-2V}_2\text{O}_5$ ceramics and the band assignments are given in Table 4.2.
Table 4.1: Raman mode assignments of BN4, BN3V, BN2V2, BNV3 and BV4 ceramics

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$\nu_s$ – symmetric stretching, $\nu_{as}$ – asymmetric stretching, $\delta$ – asymmetric bending, $\delta_s$ – symmetric bending
Figure 4.6 Raman spectra of (a) BV4 (b) Ba$_3$V$_2$O$_8$ and (c) Ba$_2$V$_2$O$_7$ ceramics
Table 4.2: Raman mode assignments of Ba$_3$V$_2$O$_8$, Ba$_2$V$_2$O$_7$ and BV4 ceramics

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$v_s$ – symmetric stretching, $v_{as}$ – asymmetric stretching, $\delta_{as}$ – asymmetric bending, $\delta_s$ – symmetric bending

4.3.3 Morphological and dielectric studies

Figure 4.7 shows the SEM micrograph of Ba$_5$Nb$_{4-x}$V$_x$O$_{15}$ (x=0-4) ceramics sintered at optimum sintering temperatures. From the SEM pictures, it is clear that Ba$_5$Nb$_4$O$_{15}$ exhibits a well packed microstructure with elongated grains and the grain sizes range between 5-10 $\mu$m. As the vanadium content increases, the homogenous grain morphology changes for x=1 and 2 whereas well defined polygonal grains with average grain size of 1-2 $\mu$m become evident for x=3. It is inferred from the SEM images that the grain size decreases with increasing the vanadium content up to x=3. Dense microstructure with both polygonal and columnar grains are observed for BV4 ceramic with x=4. Polygonal grains having 1 to 3 $\mu$m size and columnar grains having 3-4 $\mu$m size are seen in the backscattered SEM picture of sintered BV4 ceramic. As per Zhang et al., Ba$_3$V$_2$O$_8$ and Ba$_2$V$_2$O$_7$ grains are difficult to distinguish
based on their morphology [27]. In order to further confirm this proposition, EDS analysis of BV4 sample was carried out (Figure 4.7e-g). EDS spot analysis confirms the existence of different types of grains in BV4 ceramic, which are obtained with different atomic% of Ba atoms. EDS mapping also confirms this hypothesis, since larger red grains are seen compared to columnar grains during mapping. The polygonal grains with higher atomic% of Ba could be $\text{Ba}_3\text{V}_2\text{O}_8$ phase rather than $\text{Ba}_2\text{V}_2\text{O}_7$ phase since Ba to V ratio is more (3:1) in former compared to 2:1 in later.

**Figure 4.7** SEM pictures of (a) BN4 (b) BN3V (c) BN2V2 (d) BNV3 (e) backscattered SEM image of BV4 ceramic (f) EDS spot analysis result and (g) EDS mapping of BV4 ceramic sintered at optimum temperature
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The shrinkage behavior of 5BaO-2V₂O₅ ceramic as a function of temperature is shown in Figure 4.8. It is clear from the figure that the shrinkage of BV4 green pellet starts around 600°C.

![Shrinkage behavior of BV4 ceramic](image)

**Figure 4.8** Shrinkage behavior of BV4 ceramic

Table 4.3 shows the sintering temperature, density and dielectric properties of Ba₅Nb₄₋ₓVₓO₁₅ (x=0-4) ceramics sintered in the temperature range 900-1400°C. Among the five compositions studied, BN4, BN3V, BN2V2 and BV4 exhibit microwave dielectric properties, whereas BNV3 did not exhibit microwave dielectric properties. Hence, the dielectric constant of Ba₅Nb₄₋ₓVₓO₁₅ (x=0-4) samples were also measured at 1 MHz. From Table 4.3, it is clear that as the vanadium content increases the sintering temperature, density and dielectric constant of the Ba₅Nb₄₋ₓVₓO₁₅ ceramics decrease and this linear variation of density and dielectric constant of Ba₅Nb₄₋ₓVₓO₁₅ (x=0-4) ceramics at 1 MHz is depicted in Figure 4.9. The decrease in dielectric constant and density can be attributed to the formation of Ba₃V₂O₈ phase having relatively low dielectric constant compared to Ba₅Nb₄O₁₅ ceramic.
Figure 4.9  Variation of density and dielectric constant of \( \text{Ba}_3\text{Nb}_{4-x}\text{V}_x\text{O}_{15} \) ceramics with respect to vanadium content \((x)\) at 1MHz

BV4 ceramic was sintered in the 860-920°C temperature range to obtain optimum density. The variation of density and dielectric constant with sintering temperature of BV4 ceramic is shown in Figure 4.10. The maximum density and dielectric constant of the ceramic are obtained at a sintering temperature of 900°C for 1h. Further increase in temperature, both density and dielectric constant deteriorate. At optimum sintering temperature of 900°C for 1h, BV4 ceramic has an experimental density of 4.52 g/cc. The experimental density values obtained for \( \text{Ba}_2\text{V}_2\text{O}_7 \) and \( \text{Ba}_3\text{V}_2\text{O}_8 \) are 4.17 g/cc at 840°C for 1h and 4.31 g/cc at 1300°C for 1h respectively. The sintering temperature, density, dielectric constant, quality factor and temperature coefficient of resonant frequency of BV4 are compiled in Table 4.3.
Table 4.3: Sintering temperature, density, dielectric constant, quality factor and temperature coefficient of resonant frequency of Ba₅Nb₄₋ₓVₓO₁₅ (x = 0-4), Ba₂V₂O₇ and Ba₃V₂O₈ ceramics

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sintering Temp. (°C)</th>
<th>Density (g/cc)</th>
<th>Low frequency data (Present study)</th>
<th>Microwave frequency data</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td>εᵣ at 1 MHz</td>
<td>tan δ at 1 MHz</td>
<td>εᵣ</td>
</tr>
<tr>
<td>BN4</td>
<td>1400/3h</td>
<td>5.98</td>
<td>42.3</td>
<td>0.002</td>
<td>40</td>
</tr>
<tr>
<td>BN3V</td>
<td>1240/2h</td>
<td>5.3</td>
<td>32.7</td>
<td>0.031</td>
<td>30.5</td>
</tr>
<tr>
<td>BN2V2</td>
<td>1200/2h</td>
<td>5.03</td>
<td>26.3</td>
<td>0.008</td>
<td>23.3</td>
</tr>
<tr>
<td>BNV3</td>
<td>1120/2h</td>
<td>4.94</td>
<td>20.7</td>
<td>0.005</td>
<td>*</td>
</tr>
<tr>
<td>BV4</td>
<td>900/1h</td>
<td>4.52</td>
<td>14.2</td>
<td>0.012</td>
<td>12.1</td>
</tr>
<tr>
<td>Ba₂V₂O₇</td>
<td>840/1h</td>
<td>4.17</td>
<td>11.87</td>
<td>0.055</td>
<td>9.6</td>
</tr>
<tr>
<td>Ba₃V₂O₈</td>
<td>1300/1h</td>
<td>4.31</td>
<td>13.3</td>
<td>0.094</td>
<td>12.3</td>
</tr>
</tbody>
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* No resonance
The dielectric properties of BV4 compacts are measured in the microwave frequency region by Hakki & Coleman post resonator method using a vector network analyzer. At optimum sintering temperature, BV4 ceramics exhibited a dielectric constant of 12.1 and quality factor of ~26,790 GHz. The temperature coefficient of resonant frequency is measured in the 30-100°C range for BV4 ceramics sintered in the 860-920°C temperature range and the average value is found to be ~ 7 ppm/°C. The stoichiometrically weighed and mixed powders of $\text{Ba}_3\text{V}_2\text{O}_8$ and $\text{Ba}_2\text{V}_2\text{O}_7$ ceramics are also well sintered at 900°C for 1h and exhibited a dielectric constant of 11.9 together with a quality factor of ~24,540 GHz and $\tau_f$ of 6 ppm/°C respectively.

![Figure 4.10 Variation of density and dielectric constant with sintering temperature of BV4 ceramic](image)

In the present study, we obtained a dielectric constant of 9.6, unloaded quality factor of 2700 at 11.227983 GHz and $\tau_f = -32$ ppm/°C for $\text{Ba}_2\text{V}_2\text{O}_7$ ceramic and a dielectric constant of 12.3, unloaded quality factor of 4595 at 11.36089 GHz and $\tau_f = 41.6$ ppm/°C for $\text{Ba}_3\text{V}_2\text{O}_8$ ceramic respectively. The above results are reasonably in good agreement with the results reported by other researchers [33, 34]. As in the case of structural features, the microwave dielectric properties of BV4 also show resemblance with that of $\text{Ba}_3\text{V}_2\text{O}_8$. Both BV4 and $\text{Ba}_3\text{V}_2\text{O}_8$ ceramics have almost similar dielectric constant at microwave frequencies whereas the dielectric constant of $\text{Ba}_2\text{V}_2\text{O}_7$ is lower compared to other two compositions.
4.3.4 Compatibility studies

Even though, BV4 ceramic exists as a multiphase composition of Ba$_3$V$_2$O$_8$ and Ba$_2$V$_2$O$_7$ ceramics; it is well sintered at a sintering temperature of 900°C for 1h, and hence falls under the LTCC temperature range. For LTCC applications, BV4 ceramic should have chemical compatibility with silver electrode. Since there are published reports on the microwave dielectric properties and compatibility studies of ceramic composite systems for LTCC applications [35, 36], an attempt has been made to study the chemical compatibility of BV4 ceramic with silver. BV4 ceramic is co-fired with 20 wt% Ag powder at 900°C for 1h and the resultant sample is analyzed using X-ray diffraction and EDS analyses to ascertain the chemical interaction between the electrode material and BV4 composition. The X-ray diffraction pattern of BV4 ceramic co-fired with Ag at optimum sintering temperature of 900°C does not show any secondary phase formation other than Ba$_3$V$_2$O$_8$ and Ba$_2$V$_2$O$_7$ phases as a result of Ag addition (Figure 4.11). The silver peaks are observed separately which are marked with ‘o’ in the X-ray diffraction pattern of the co-fired sample. The planar SEM image of the BV4 ceramic co-fired with Ag powder at 900°C is given in Figures 4.12. The EDS analysis is carried out on both BV4 and Ag grains, which also did not show any chemical interaction between ceramic and metallic powder. Spot 1 in Figure 4.12 shows only the presence of Ag whereas Spot 2 represents the presence of BV4 ceramic without any inter-diffusion of Ag. The X-ray dot mapping of the co-fired BV4 sample is also done to further quantify the non-reactivity of Ag in the host matrix (Figure 4.13). The X-ray dot mapping result clearly shows the isolation of melted Ag particles in deep red color without any inter-diffusion in BV4 grains. Further, EDS line scan of the co-fired sample was carried out (Figure 4.14). From EDS line scan, it is clear that the Ag profile decreases sharply at the interface, which indicates that there is no inter-diffusion of Ag in to the ceramic grains, complementing the XRD and spot analyses results.

Although, the microwave dielectric properties of Ba$_2$V$_2$O$_7$ are previously studied, its chemical compatibility with metal electrode has been not reported yet. Hence, we performed the compatibility studies of barium pyrovanadate with Ag...
powder. $\text{Ba}_2\text{V}_2\text{O}_7$ shows excellent chemical compatibility with Ag and hence can be used for LTCC applications.

Figure 4.11  X-ray diffraction pattern of BV4 ceramic co-fired with 20 wt% Ag powder sintered at 900°C for 1h

Figure 4.12 (a) SEM image of BV4 ceramic co-fired with 20 wt% Ag powder sintered at 900°C for 1h (b) EDS spectrum of Spot 1 (c) EDS spectrum of Spot 2
4.4 Conclusions

The $\text{Ba}_5\text{Nb}_{4-x}\text{V}_x\text{O}_{15}$ ceramics ($x=0-4$) have been prepared through conventional solid state ceramic route. The powder X-ray diffraction studies reveal the existence of $\text{Ba}_3\text{V}_2\text{O}_8$ and $\text{BaNb}_2\text{O}_6$ as secondary phases in BN3V, BN2V2 and BNV3 ceramics, whereas the coexistence of hexagonal $\text{Ba}_3\text{V}_2\text{O}_8$ and triclinic $\text{Ba}_2\text{V}_2\text{O}_7$ phases are found in BV4. Laser Raman studies show that the structural
arrangement of BV4 ceramic is in close agreement with that of hexagonal Ba$_3$V$_2$O$_8$ phase. The SEM pictures of Ba$_5$Nb$_{4-x}$V$_x$O$_{15}$ ($x=0-3$) ceramics show dense microstructures and the grain size decreases with increasing the vanadium content. On the other hand, the SEM picture of BV4 has both polygonal and columnar grains. The sintering temperature, density and dielectric constant of Ba$_5$Nb$_{4-x}$V$_x$O$_{15}$ ($x=0-4$) ceramics decrease with increasing the vanadium content. The BV4 ceramic exhibits low dielectric constant ($\varepsilon_r=12.1$), reasonably good quality factor (Q$_{xf}$=26,790 GHz) and low temperature coefficient of resonant frequency ($\tau_f \sim 7$ ppm/$^\circ$C). The compatibility studies based on X-ray diffraction and EDS analyses confirm the chemical compatibility between BV4 ceramic and Ag powder.
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