

A re-look at critical factors influencing single-phase formation of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ microwave dielectrics

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Abstract. The present study focuses on critical factors limiting single-phase formation of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ (2 : 9). Apart from 2 : 9, other polytitanates that are richer in Ti or Ba could also be prepared as single-phase material without any stabilizing agent through chemical co-precipitation. 2 : 9 is found to be a stoichiometric compound and even 0.5% excess Ti or Ba leads to multiphase formation. Single-phase 2 : 9 could be achieved even through solid-state route without the addition of stabilizing agents using high purity raw materials. The present results do not agree with existing hypotheses viz. diffusion, high surface and nucleation energy, potential barrier, non-stoichiometry etc as critical factors limiting formation of 2 : 9 as single-phase material.

Keywords. Microwave materials; ceramic dielectric resonators; polytitanates; co-precipitation.

1. Introduction

Microwave circuits have been miniaturized owing to the development of dielectric resonators over the past decade. Market potential for dielectric resonators for wireless communication has experienced rapid growth recently (Kim *et al* 1999; Penn and Alford 1999; Cava 2001; Vanderah 2002). The essential characteristics desired for microwave dielectric resonators are high dielectric constant (K) at microwave frequency, high quality factor (Q) and low temperature coefficient of resonant frequency (τ_f). Several ceramic compositions such as $(\text{Zr}, \text{Sn})\text{TiO}_4$, $\text{Ba}(\text{Zn}, \text{Ta})\text{O}_3$, $\text{BaO}-\text{RE}_2\text{O}_3-x\text{TiO}_2$, $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ (2 : 9) etc have been developed for this application (Ezaki *et al* 1993; Kim *et al* 1999; Penn and Alford 1999; Cava 2001; Vanderah 2002; Abdulkhalam *et al* 2004). Among the various potential candidates, 2 : 9 has received much attention in view of its excellent microwave properties such as $K \sim 40$, $\tau_f \sim 2$ ppm/°C and $Q \sim 8000$ at 4 GHz. The structure of 2 : 9 is layered, having a hexagonal close packed arrangement of Ba and O, with Ti occupying the appropriate octahedral sites making up a primitive triclinic unit cell forming six crystal layers (O'Bryan *et al* 1974; Lin and Robert 1999; Wang *et al* 2003).

It can be inferred from the TiO_2 -rich side of the phase-diagram of $\text{BaO}-\text{TiO}_2$ that apart from 2 : 9 many closely related materials such as BaTi_4O_9 (1 : 4), $\text{BaTi}_5\text{O}_{11}$ (1 : 5), $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ (4 : 13), $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ (6 : 17) etc also exist (O'Bryan and Thomson 1974; Ritter *et al* 1986). It is well

recorded in literature that formation of 2 : 9 as a single-phase material is very difficult (O'Bryan and Thomson 1983; Wu and Wang 1988; Wang *et al* 2003). Many theories have been proposed to explain the difficulty of formation of single-phase 2 : 9. Jaakola *et al* (1980) and O'Bryan and Thomson (1983) feel that the formation of 2 : 9 is limited basically by the diffusion of ions. Wu and Wang (1988) argue that it is the thermodynamic factors such as high nucleation energy and surface energy associated with the formation of 2 : 9, which limits its formation and growth as single-phase material. Higher potential energy barrier has been cited as the reason for difficulty of formation of single-phase (Yu *et al* 1994). It has also been proposed that 2 : 9 is a non-stoichiometric material and Ba/Ti ratio influences the phase purity. Wang *et al* (2003) reported that 2 : 9 can accommodate even up to 5.6 wt% of excess TiO_2 . It has also been strongly argued that the presence of 1 : 5 or 2 : 9 at least as a minor phase is necessary at the calcination stage for the formation of 2 : 9 as single phase after sintering (Wu and Wang 1988). It is stated that since 1 : 5 has nearly the same packing density of oxygen as that of 2 : 9, it acts as a precursor for the formation of 2 : 9 during sintering (Wu and Wang 1988).

2 : 9 can be prepared by conventional solid-state route (Negas *et al* 1974; Wu and Wang 1988; Yu *et al* 1994; Lin *et al* 1997; Lin and Robert 1999) and by chemical methodology (Ritter *et al* 1986; Wu and Wang 1988; Lu *et al* 1991; Ptiff 1993; Hari 1997; Chu *et al* 2003). It is extremely difficult to prepare 2 : 9 as a single phase material through solid-state route, as it always ends up with a mixture of phases such as TiO_2 , 1 : 4, 4 : 13, 6 : 17 etc (Negas *et al* 1974; Yu *et al* 1994; Lin *et al* 1997; Lin and

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Robert 1999; Wang *et al* 2003). However, in the presence of stabilizing agents such as Sn^{4+} , Zr^{4+} , Sr^{2+} , Mn^{2+} , BaSnO_3 , B_2O_3 etc, single-phase 2:9 has been achieved through solid-state route (Yu *et al* 1994; Lin and Robert 1999; Wang *et al* 2003). It is recorded in literature that phase pure 2:9 ceramics without any stabilizing agent will result in better material for microwave dielectric applications (Lin *et al* 1997; Lin and Robert 1999). Different chemical methodologies such as sol-gel, co-precipitation etc have also been adopted for the preparation of 2:9 material (Ritter *et al* 1986; Wu and Wang 1988; Lu *et al* 1991; Ptiff 1993; Hari 1997; Chu *et al* 2003). For the present work, we adopted carbonate-gel composite route as well as solid-state synthesis. This paper critically re-examines the factors responsible for the difficulty in formation of 2:9 as a single-phase material. It is observed that the purity of the raw materials seems to be the most important factor influencing formation of single phase 2:9 ceramics.

2. Experimental

The principle of carbonate-gel composite route has been well recorded (Wu and Wang 1988; Hari 1997; Chu *et al*

2003). In this co-precipitation method, the starting materials are BaCl_2 (Merck AR Grade, India), TiOCl_2 (Merck, AR Grade, India), ammonium hydroxide and ammonium carbonate (Merck, AR Grade, India). The TiOCl_2 solution was prepared by gradually adding TiCl_4 into deionized water at about 4°C , with a ratio of TiCl_4 to water being 1:5. The TiOCl_2 and BaCl_2 solutions were mixed together in the desired ratio. Then the mixed solution was slowly added drop wise into a 0.1 M aqueous solution of ammonium carbonate. The co-precipitating solution was kept at pH 9.5 by adding ammonium hydroxide solution slowly into the reaction beaker during the co-precipitation process. After the reaction was complete, the co-precipitated powder was filtered and washed with deionized water 3 times, followed by washing with 99.55% ethanol and filtered twice. The washed powder was dried in an oven and calcined at a temperature of 1100°C for 6 h. The oven dried composite powder, in its reactive form, was taken in steps to 1100°C . The calcined powder was again ground in an agate mortar with isopropyl alcohol as the medium. 5 wt% of polyvinyl alcohol solution was added to the powder and the slurry was dried again. The dried powder was pressed into discs of diameter, ~ 10 mm, by applying a

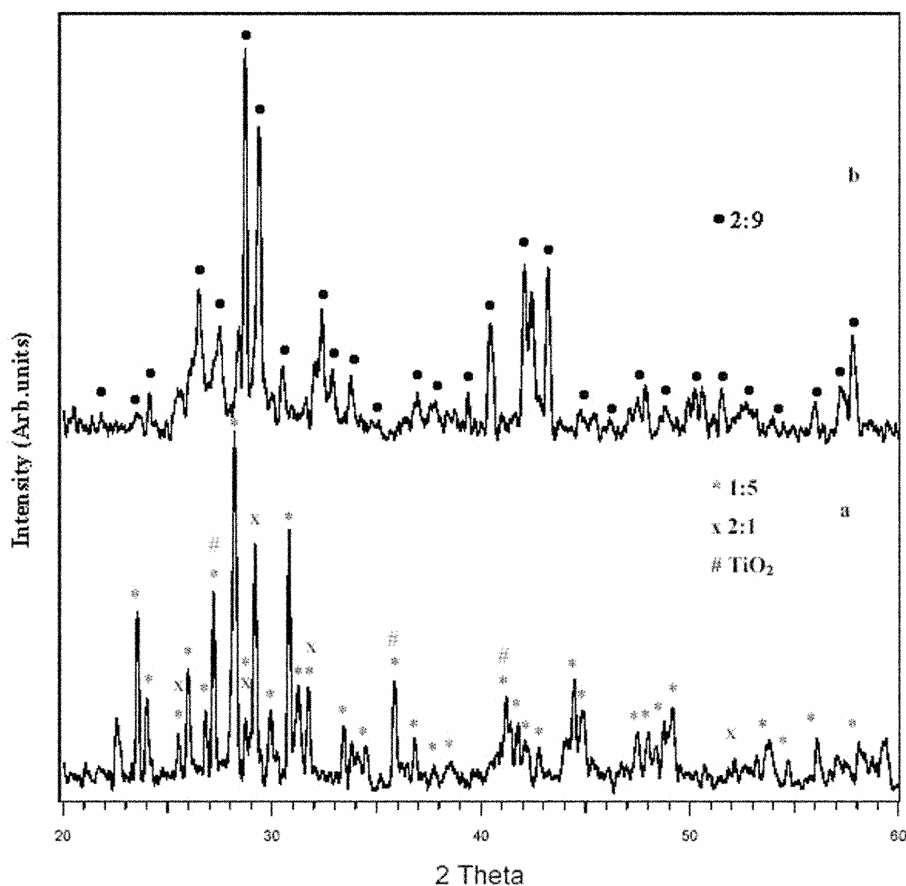


Figure 1. XRD patterns of 2:9 material synthesized through chemical route from stoichiometric Ba/Ti ratio: a. calcined at $1100^\circ\text{C}/6$ h and b. sintered at $1350^\circ\text{C}/3$ h.

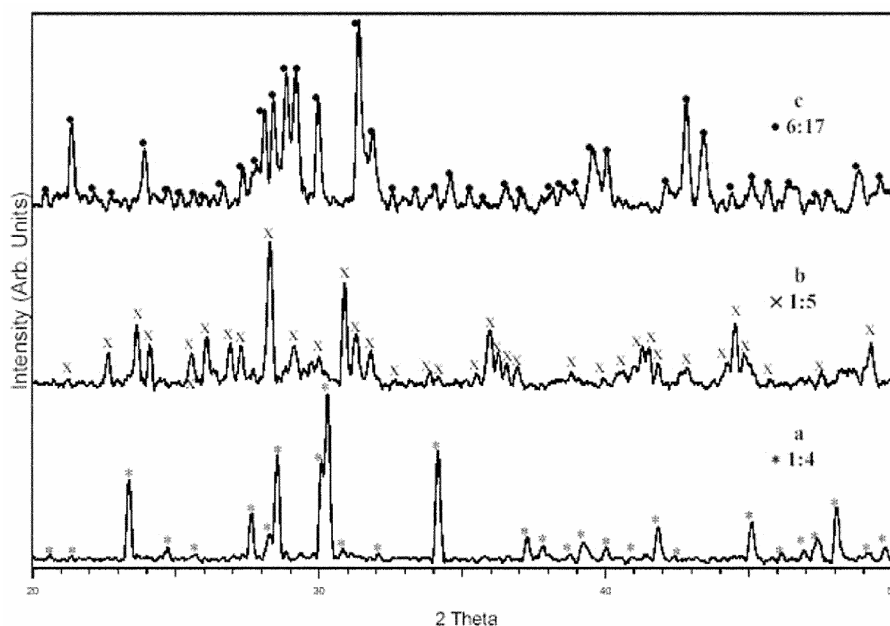


Figure 2. XRD patterns of polytitanates synthesized through chemical route: a. 1 : 4 calcined at 1100°C/6 h, b. 1 : 5 calcined at 1100°C/6 h and c. 6 : 17 sintered at 1350°C/3 h.

Table 1. XRD results of phases formed after calcination and sintering of 2 : 9 ceramics with excess Ti or Ba.

Composition	Phases after calcination	Phases after sintering
Stoichiometric	Major: 1 : 5, 2 : 1 Trace: TiO_2	2 : 9
0.5% Ti excess	Major: 1 : 5, 2 : 1 Trace: TiO_2	2 : 9
1.0% Ti excess	1 : 5, 2 : 1, TiO_2	Major: 2 : 9 Trace: other phases
3.0% Ti excess	1 : 5, 2 : 1, TiO_2	Larger oriented grains of 2 : 9 in 1 : 4 matrix
5.0% Ti excess	1 : 5, 2 : 1, TiO_2	Larger oriented grains of 2 : 9 in 1 : 4 matrix
0.5% Ba excess	1 : 5, 2 : 1, TiO_2	Predominant: 2 : 9 Trace: others, TiO_2
1.0% Ba excess	1 : 5, 2 : 1, TiO_2	2 : 9, 2 : 1, 6 : 17, TiO_2

pressure of ~ 250 MPa. These discs were sintered at different temperatures in the range 1320–1380°C for 4–6 h in air. Samples with 0.5–5 mol% excess Ti and Ba were also prepared. They were also calcined and sintered under similar conditions. Not only 2 : 9, other polytitanates such as 1 : 4, 1 : 5, 4 : 13, 6 : 17 were also prepared by the same method as that of 2 : 9. 2 : 9 was also prepared by solid-state reaction route with $BaCO_3$ and TiO_2 from different sources as starting material, and was calcined and sintered under similar conditions as that of chemical route.

X-ray powder diffraction (XRD) studies were performed with AXS Bruker D5005 diffractometer using $CuK\alpha$ radiation. Scanning electron microscopic (SEM) analysis of the fractured surface under backscattered mode and secondary electron mode was carried out using a Philips

XL-30 microscope. Preliminary dielectric constant measurements were carried out at 1 MHz using a HP 4192A impedance analyser and the temperature coefficient of capacitance was measured between 0 and 100°C.

3. Results and discussion

The XRD patterns of ceramics synthesized through chemical route with a stoichiometric ratio of Ba/Ti without the addition of any stabilizers is shown in figure 1. At the calcination stage, 1 : 5 forms as the major phase along with Ba_2TiO_4 (2 : 1) and traces of TiO_2 . However, 2 : 9 forms as a single-phase material after sintering (figure 1). Our recent results point to the fact that not only 2 : 9 but

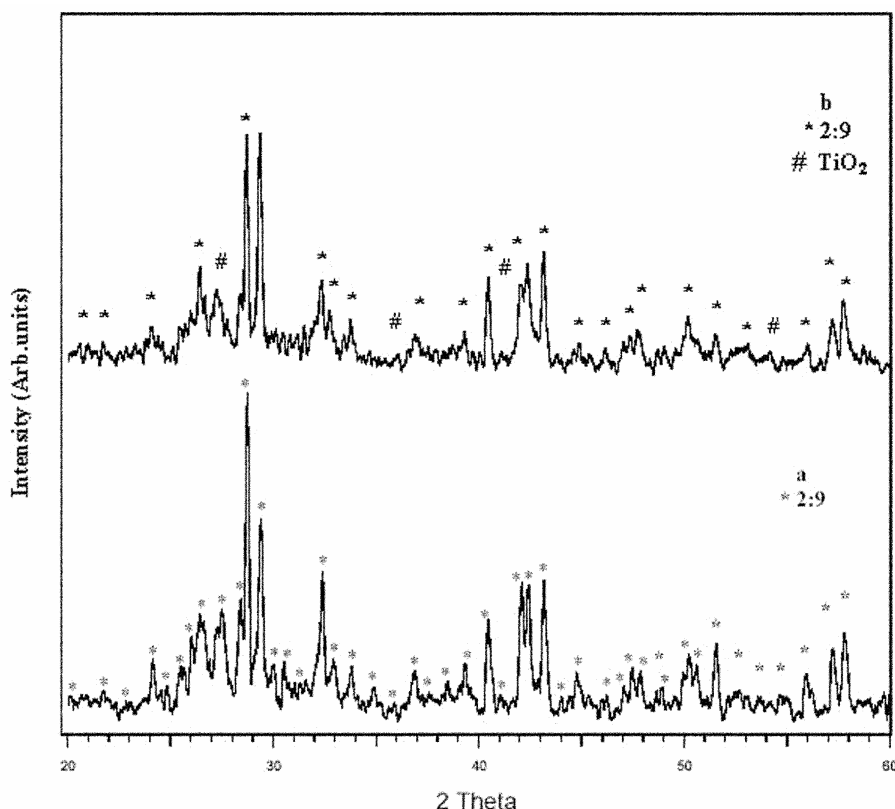


Figure 3. XRD pattern of 2:9 ceramic synthesized through chemical route with a. 0.5% excess TiO_2 and b. 0.5% excess Ba, sintered at $1350^\circ\text{C}/3$ h.

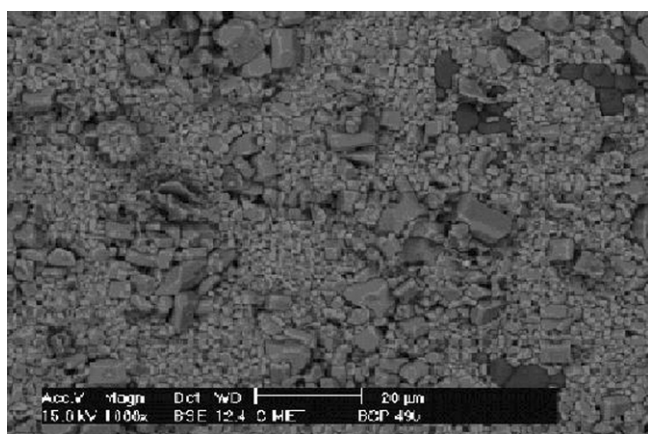


Figure 4. Back scattered image of 2:9 ceramic synthesized through chemical route with 0.5% excess TiO_2 .

also other phases such as 1:4, 1:5, 4:13 and 6:17 could also be prepared as single-phase material through the coprecipitation technique (Raghu *et al* 2007). Single-phase formation of other polytitanates is observed at the calcination stage itself (figure 2). Only in the case of 6:17, single-phase material formed after sintering (figure 2c), i.e. even phases that are richer in Ti or Ba compared to 2:9, forms easily as single-phase material. Hence, diffusion

need not be a critical factor for the difficulty in the formation of single-phase 2:9.

Reports exist that 2:9 is a non-stoichiometric material and it can accommodate up to 5.6 wt% of excess TiO_2 (Wang *et al* 2003). In order to understand the influence of excess Ti or Ba in the phase formation of 2:9, ceramics with varying Ba/Ti ratio close to stoichiometric 2:9 were prepared through chemical route. XRD results of phases formed after calcination and sintering stages are presented in table 1. As can be clearly inferred, XRD results reveal only for stoichiometric compositions and 0.5% Ti excess (figure 3a) single-phase formation after sintering. Even >0.5% excess Ti leads to multi-phase formation. Variation in sintering temperature and time did not produce any noticeable changes in the results. When the excess Ti concentration is $\geq 3.0\%$, large oriented grains along with 1:4 are observed. In the case of Ba excess, even for 0.5% excess Ba, XRD shows multiple phases after sintering (figure 3b). The nature of phases evolved is also reflected in the dielectric properties. Only in the case of stoichiometric and 0.5% Ti excess, the dielectric constant was close to the reported value of ~ 38 . It is well known that the temperature coefficient of resonant frequency (τ_f) is mainly due to the variation of capacitance with temperature (TCC). TCC was measured in a number of samples. Excess Ti and Ba compounds showed very high TCC which

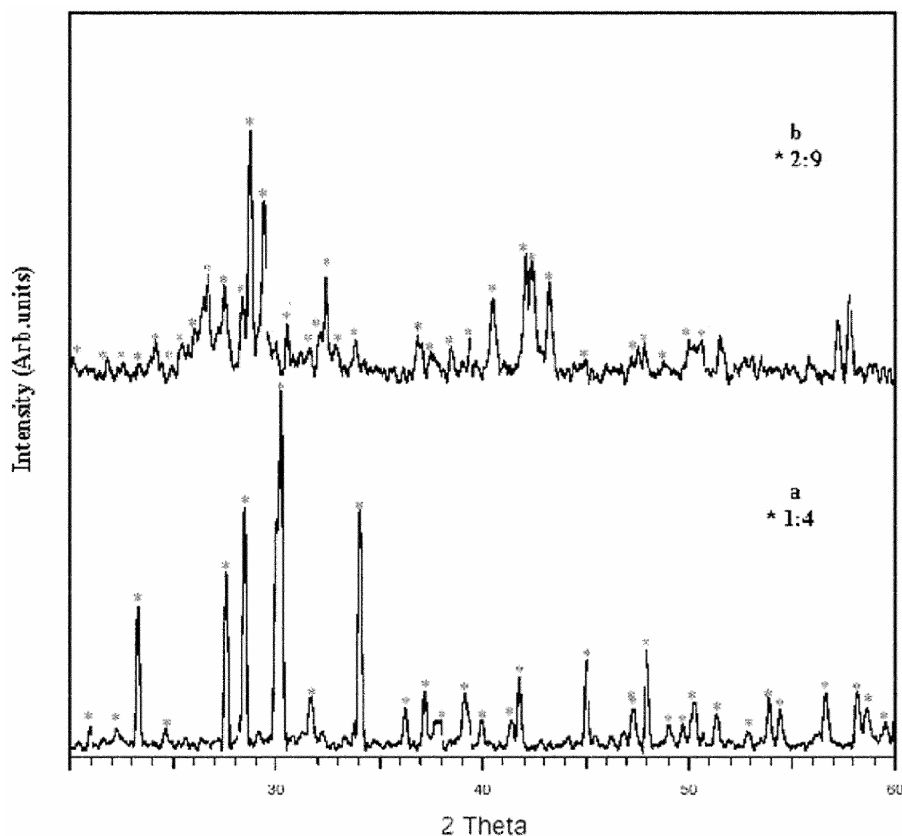


Figure 5. XRD patterns of ceramic synthesized through solid-state route with high purity stoichiometric raw materials: a. calcined at 1100°C/6 h and b. sintered at 1350°C/3 h.

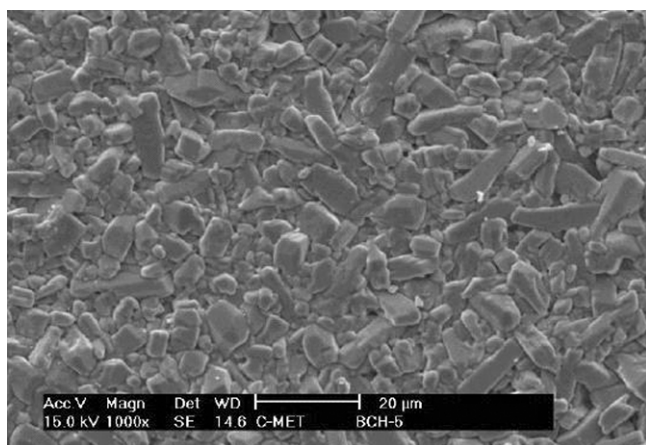


Figure 6. SEM of 2:9 single-phase ceramic synthesized through solid-state route with high purity stoichiometric raw materials.

also indicates clear formation of multi-phase. Increase in TCC could be observed even for 0.5% Ti excess. Even though XRD shows only 2:9 phase for 0.5% Ti excess, SEM reveals multi-phase in the back-scattered mode (fig-

ure 4). These results prove that 2:9 is a stoichiometric material.

In order to further understand why excess Sn^{4+} , Zr^{4+} or Ti^{4+} helps in stabilizing 2:9 phase in the solid-state route, 2:9 ceramics were prepared through solid-state reaction route also starting from $BaCO_3$ and TiO_2 from different sources. Initially, we also observed that single-phase 2:9 forms only when 0.5–1% excess TiO_2 was added. On analysis, it was found that the raw materials, especially, titania contains around 0.8–1% volatile impurities. Hence, we prepared 2:9 by solid-state route starting from stoichiometric proportions of high purity raw materials ($BaCO_3$, 99.98% pure and TiO_2 , 99.99% pure from Sigma Aldrich, India) without addition of any stabilizers. With these high purity raw materials, XRD reveals (figure 5a) the presence of 1:4 phase only, after calcination at 1100°C for 6 h. On further sintering at 1350°C for 3 h, single-phase 2:9 was obtained (figure 5b). SEM micrograph (figure 6) revealed uniform microstructure and did not show presence of any other phase. The distribution of grain size in the ceramic obtained through solid state reaction route could be due to the distribution of particle size in the calcined powder.

It has been reported in the literature that the presence of 1 : 5 or 2 : 9, atleast as a minor phase at the calcination stage, is a must for the formation of 2 : 9 single phase after sintering (Wu and Wang 1988). It was argued that since 1:5 has nearly the same oxygen packing density as that of single-phase 2 : 9, it acts as a precursor for the formation of single-phase 2 : 9. The present results show that even though only 1 : 4 phase formed after calcination, 2 : 9 forms as a single-phase material at the sintering stage. Hence, nucleation and surface energy or barrier height need not be the critical factors for the formation of single phase 2 : 9 ceramics. Our results also prove that even through solid-state route with high purity raw materials it is possible to achieve single-phase 2 : 9 ceramics without adding any stabilizing ion. This highlights the fact that the purity of the raw materials is an important factor in the formation of 2 : 9 as single-phase ceramics, which is also supported by the recent work of Varma *et al* (2004). Microwave characterization of these ceramics will be published shortly.

4. Conclusions

(I) Not only 2 : 9 but also other polytitanates such as 1 : 4, 1 : 5, 6 : 17, 4 : 13 etc form as single-phase material without the addition of stabilizers through chemical co-precipitation route.

(II) Even through solid-state route it is feasible to form single-phase 2 : 9 ceramics without any stabilizers.

(III) Purity of the raw materials is a critical factor in the formation of single-phase 2 : 9 ceramics.

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References

- Abdulkhilam L, Sreemoolanathan H, Ratheesh R, Mohanan P and Sebastian M T 2004 *Mater. Sci. & Engg.* **B107** 264
- Cava R J 2001 *J. Mater. Chem.* **11** 54
- Chu L W, Hsiue G H and Lin I N 2003 *Proceedings of 4th Asian meeting on ferroelectrics (AMF-4)* (Bangalore: IISc) p. 211
- Ezaki K, Baba Y, Takahashi H, Shibata K and Nakano S 1993 *J. Appl. Phys.* **32** 4319
- Hari N S 1997 *Self regulating heater ceramics based on n-BaTiO₃ and its solid solutions*, Ph.D. Thesis, Indian Institute of Science, Bangalore
- Jaakola T, Unsimaki A and Leppavuori S 1980 *Int. J. High Technol. Ceram.* **2** 195
- Kim H T, Nahm S and Byun J D 1999 *J. Am. Ceram. Soc.* **82** 3476
- Lin W Y and Robert Speyer F 1999 *J. Am. Ceram. Soc.* **82** 1207
- Lin W Y, Gerhardt R A and Speyer R F 1997 *Mater. Res. Soc. Symp. Proc.* **453** 501
- Lu H C, Burkhardt L E and Schrader G I 1991 *J. Am. Ceram. Soc.* **74** 968
- Negas T, Roth R S, Parker H S and Minor D 1974 *J. Solid State Chem.* **9** 297
- O'Bryan H M Jr and Thomson J Jr 1974 *J. Am. Ceram. Soc.* **57** 522
- O'Bryan H M and Thomson J 1983 *J. Am. Ceram. Soc.* **66** 66
- O'Bryan H M Jr, Thomson J Jr and Plourde J K 1974 *J. Am. Ceram. Soc.* **57** 450
- Penn S and Alford N 1999 *Handbook of low and high dielectric constant materials and their applications* (ed.) H S Nalwa (New York: Academic Press) **2** p. 493
- Ptuff G 1993 *J. Mater. Sci. Lett.* **12** 32
- Raghu N, Seema A, Dhanya K, Bindu K, Sasidharan K and Unnikrishnan G 2005 *Mater. Res. Bull.* **40** 1408
- Ritter J J, Roth R S and Blendell J E 1986 *J. Am. Ceram. Soc.* **69** 155
- Vanderah T A 2002 *Science* **298** 1182
- Varma M R, Sreemoolanathan H and Chandrasekharan V 2004 *J. Mater. Sci. Mater. Electron.* **15** 345
- Wang S F, Hsu Y F, Ueng T H and Chiang C C 2003 *J. Mater. Res.* **18** 201, 1179
- Wu J M and Wang H W 1988 *J. Am. Ceram. Soc.* **71** 869
- Yu J, Xhao H, Wang J and Xia F 1994 *J. Am. Ceram. Soc.* **77** 1052