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Influence of ZrO_2 and SnO_2 on the synthesis of $Ba_2Ti_9O_{20}$ powders

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Abstract

The effects of ZrO_2 and SnO_2 dopants on the microstructure evolution of $Ba_2Ti_9O_{20}$ were studied. The dopants facilitated the formation of phase-pure $Ba_2Ti_9O_{20}$. At 1150 °C, there was more $Ba_2Ti_9O_{20}$ phase for the doped sample. For the composition without dopants the $Ba_2Ti_9O_{20}$ phase decomposed easily into $BaTi_4O_9$ phase at the high temperature, and more $BaTi_4O_9$ phase was observed at 1350 °C than at 1250 °C. ZrO_2 and SnO_2 could promote and stabilize $Ba_2Ti_9O_{20}$ phase. $BaTi_5O_{11}$ and $BaTi_4O_9$ were intermediate phases before the formation of $Ba_2Ti_9O_{20}$.

Keywords: $Ba_2Ti_9O_{20}$ ceramics; Crystallization; Stability

1. Introduction

The development of dielectric resonators for telecommunications has experienced rapid growth in the past. A variety of applications that use relatively low-cost ceramics have been developed for various applications such as personal communication systems, global positions systems and cellular systems.

Several microwave dielectric materials have been studied recently. Among these, $Ba_2Ti_9O_{20}$ has received great attention for its good microwave properties, good quality factor, high dielectric constant, and low temperature coefficient [1,2]. O'Bryan and Thomson [3] mentioned that the realization of such dielectric ceramics of the polytitanate type required a severe control on component stoichiometry in order to obtain the desired phases. Phase-pure $Ba_2Ti_9O_{20}$ could be formed at 1400 °C, but when the temperature cooled down, the second phase would be produced. In order to stabilize $Ba_2Ti_9O_{20}$ phase, Pfaff [4] synthesized $Ba_2Ti_9O_{20}$ with peroxide route, Ritter et al. [5] obtained the desired phase by alkoxide precursor. The processes are difficult to control in these works. Fang et al. [6] prepared phase-pure $Ba_2Ti_9O_{20}$ by the reaction of $BaTi_4O_9$ with TiO_2, but how to prepare phase-pure $BaTi_4O_9$ is still a problem. In this experiment two factors, which benefit to form stable $Ba_2Ti_9O_{20}$ phase, are considered: lowering the sintering temperature and doping in the BaO–TiO_2 compositions. Based these, ZrO_2 and SnO_2 were doped together and the influencing on the formation and crystallization of $Ba_2Ti_9O_{20}$ phase was studied in this paper.

2. Experimental

The polytitanate dielectric ceramic materials based on $Ba_2Ti_9O_{20}$ were obtained by using reagent-grade titanium dioxide and barium carbonate (purity 99.9%) as starting materials. The undoped group was made according to the compound stoichiometry (Ba:Ti = 2:9 in molar ratio), called A sample, and the another group was doped by ZrO_2 0.5 mol% and SnO_2 0.5 mol%, called B sample. Both groups were mixed and ground by planet mill having agate balls as grinding bodies and using deionized water as grinding medium.

After drying, the batches were pressed into pellets of 17.5 mm in diameter and approximately 2.5 mm in thickness. These pellets were calcined at a temperature between 1050 and 1350 °C in the air atmosphere for the duration of 4 h.

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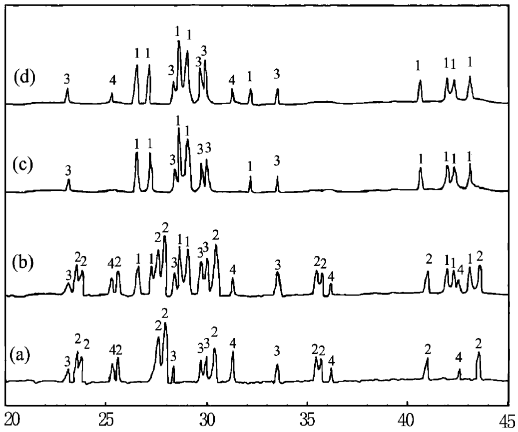

Fig. 1. XRD patterns of undoped $Ba_2Ti_9O_{20}$ powders at 1050–1350 °C for 4 h. 1–$Ba_2Ti_9O_{20}$, 2–$BaTi_5O_{11}$, 3–$BaTi_4O_9$, 4–TiO_2. (a) 1050 °C, (b) 1150 °C, (c) 1200 °C, (d) 1350 °C.

Crystallization of the two groups of calcined samples was also investigated by X-ray diffraction (XRD) patterns (Model: D/Max-3B, Cu Kα radiation, Rigaku Japan). The formed intermediate phases were studied at the calcining temperatures of 1050–1350 °C. The microstructure was then examined using scanning electronic microscope (SEM Model: JSM-35CF).

3. Results and discussion

The XRD patterns of the two groups of $Ba_2Ti_9O_{20}$ calcined at various temperatures were showed in Figs. 1 and 2, and the phase analyses were summarized in Tables 1 and 2. As various calcining temperatures were used, various phases were observed. The volume fraction of each phase was roughly determined via the ratio of the most-intense XRD peak heights of itself to the sum of the most-intense peak heights of TiO_2 and barium polytitanate. Because of the limit of XRD precision, when the fraction is lower than 5%, the phase will not exist in the XRD patterns.

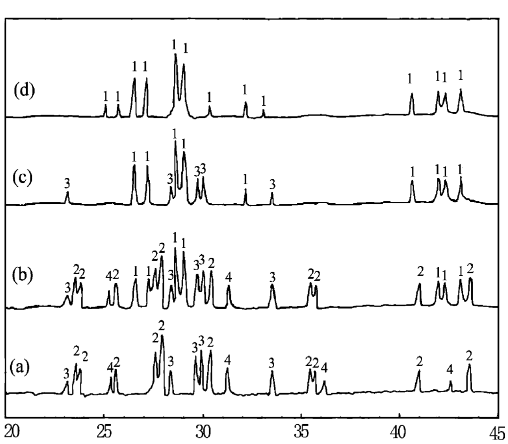

Fig. 2. XRD patterns of $Ba_2Ti_9O_{20}$ powders doped with ZrO_2 and SnO_2 at 1050–1350 °C for 4 h. 1–$Ba_2Ti_9O_{20}$, 2–$BaTi_5O_{11}$, 3–$BaTi_4O_9$, 4–TiO_2. (a) 1050 °C, (b) 1150 °C, (c) 1200 °C, (d) 1350 °C.

Table 1
The barium polytitanate phases of calcined no-doped $Ba_2Ti_9O_{20}$ powders

Temperature (°C)	$BaTi_5O_{11}$ (%)	$BaTi_4O_9$ (%)	$Ba_2Ti_9O_{20}$ (%)	TiO_2 (%)
1050	52	22	0	26
1150	38	21	30	11
1200	0	32	68	0
1250	0	25	75	0
1350	0	37	52	11

In the two groups of samples, $BaTi_5O_{11}$ and $BaTi_4O_9$ formed first at 1050 °C, and $BaTi_5O_{11}$ was dominating phase. By contrast, we found that the B sample doped with ZrO_2 and SnO_2 formed $Ba_2Ti_9O_{20}$ more than A sample at 1150 °C. The result of this present study is different from many other papers [7,8], which considered that $BaTi_5O_{11}$ was never observed when using the solid-state reaction. This study confirmed that the $BaTi_5O_{11}$ phase can be gained, but it is apt to be decomposed into $BaTi_4O_9$ above 1050 °C or react with $BaTi_4O_9$ into $Ba_2Ti_9O_{20}$. This can be seen by comparing Figs. 1a and 2a with Figs. 1b and 2b. The phases of ZrO_2 and SnO_2 were not found in Fig. 2. So it is postulated that $BaTi_4O_9$ and $BaTi_5O_{11}$ have a high solubility for Zr^{4+} and Sn^{4+} replacement of Ti^{4+} cations. The ion radius of the Zr^{4+} and Sn^{4+} are larger than Ti^{4+}. The dilation of the $BaTi_4O_9$ and $BaTi_5O_{11}$ unit cell because of the replacement of Ti^{4+} seems to facilitate the formation of $Ba_2Ti_9O_{20}$ at a temperature of 1150 °C. Further raising the calcining temperature to 1200 °C, the intermediate phases $BaTi_5O_{11}$ almost consume down. At 1250 °C, the dominating phase was $Ba_2Ti_9O_{20}$, there were less other barium polytitanate phases. For the undoped A sample there was more $BaTi_4O_9$ phases at 1350 °C than at 1250 °C. But there was only phase-pure $Ba_2Ti_9O_{20}$ for the doped B sample at 1350 °C (Fig. 2d). This implied that ZrO_2 and SnO_2 could promote the forming of $Ba_2Ti_9O_{20}$ at under 1400 °C and stabilize $Ba_2Ti_9O_{20}$ phase.

The crystal structure of $Ba_2Ti_9O_{20}$ is made up of six crystal-structured layers, having a hexagonal, close-packed arrangement of Ba and O, with Ti occupying the appropriate octahedral sites [9]. When layer-structured $Ba_2Ti_9O_{20}$ crystallize, stress often arises along the crystal-structured layers because of the structural factor. The stress then shoots these crystals into an unstable high-energy state, resulting in a high potential–energy barrier, and the nucleation and growth of the layer-structured crystals are hindered. Con-

Table 2
The phases of calcined $Ba_2Ti_9O_{20}$ powders doped with ZrO_2 and SnO_2

Temperature (°C)	$BaTi_5O_{11}$ (%)	$BaTi_4O_9$ (%)	$Ba_2Ti_9O_{20}$ (%)	TiO_2 (%)
1050	47	32	0	21
1150	31	19	36	14
1200	0	30	70	0
1250	0	14	86	0
1350	0	0	100	0

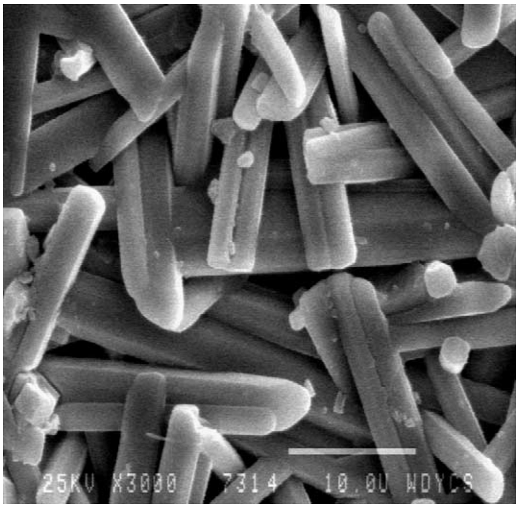

Fig. 3. SEM of the sample doped with ZrO_2 and SnO_2 calcined at 1350 °C.

Fig. 4. SEM of the undoped sample calcined at 1350 °C.

sequently, until enough energy has been accumulated to surmount the high potential–energy barrier, no layer-structured crystals can form. The defects coming from larger Zr^{4+} and Sn^{4+} replacement of Ti^{4+} cations can decrease the stress in the formation of $Ba_2Ti_9O_{20}$ grains, and improve $Ba_2Ti_9O_{20}$ to crystallize. Further investigating is still going on.

Figs. 3 and 4 are the SEM micrographs of the two groups of specimens calcined at 1350 °C. Fig. 3 showed that almost all crystals were bar-shape, and Fig. 4 showed that there were crystals of both bar-shape and little square-shape. It indicated that there were $Ba_2Ti_9O_{20}$ and other phases in the undoped A sample, and only $Ba_2Ti_9O_{20}$ phase in the B sampled doped with ZrO_2 and SnO_2. This just proved the conclusion got by XRD. So the reaction sequence for the undoped sample calcined from 1050 to 1350 °C was gained as follows:

$$BaTi_5O_{11} \rightarrow BaTi_4O_9 + TiO_2 \quad (1)$$

$$BaTi_5O_{11} + BaTi_4O_9 \rightarrow Ba_2Ti_9O_{20} \quad (2)$$

$$Ba_2Ti_9O_{20} \rightarrow 2BaTi_4O_9 + TiO_2 \quad (3)$$

For B sample, the reaction procedure (3) did not exist. ZrO_2 and SnO_2 dopants stabilized $Ba_2Ti_9O_{20}$ phase and prevented its decomposition. When the calcined temperature was 1400 °C, the A and B samples were melted down. So the temperature of calcining and sintering $Ba_2Ti_9O_{20}$ ceramic should not exceed 1400 °C.

4. Conclusion

The $Ba_2Ti_9O_{20}$ doped with ZrO_2 and SnO_2 could form phase-pure $Ba_2Ti_9O_{20}$. At 1150 °C there was more $Ba_2Ti_9O_{20}$ phase for the doped sample. At high temperature $Ba_2Ti_9O_{20}$ phase declined to decompose into $BaTi_4O_9$ for undoped composition and more $BaTi_4O_9$ phase was observed at 1350 °C than at 1250 °C. The $Ba_2Ti_9O_{20}$ phase doped with ZrO_2 and SnO_2 existed stably. ZrO_2 and SnO_2 were helpful to improve and stabilize $Ba_2Ti_9O_{20}$ phase.

Acknowledgements

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