

Synthesis of barium titanate-barium magnesium niobate solid solution by a mixed-oxide method

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In the present study, the phase formation characteristics of the $(1-x)\text{BaTiO}_3\text{-}x\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (or $(1-x)\text{BT-xBMN}$) system were examined as a function of processing conditions. Various preparation techniques and processing parameters are investigated in all samples. Phase formation and microstructural evolution are examined via X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. From the results, it can be seen that complete solid solutions in the BT-BMN system was obtained. The optimum calcination temperature of the powder in this system increases with increasing BMN content. Additionally, the average particle size also increases with increasing BMN content. The larger particle size of BT-BMN powders may relate to the higher optimum calcination temperature for each composition.

Key words: BaTiO_3 , $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, Perovskite, Solid solution.

Introduction

Since the discovery of the dielectric properties of barium titanate (BT), this material has been mainly applied for many electronic devices such as thermistors, protective sensors, self-controlled heaters and multilayer ceramic capacitors (MLCC) [1, 2] due to its excellent dielectric constant. However, the industrial requirements of these applications need properties that conform to standard variations with temperature and frequency. The finding of materials working over a wide range of temperature and frequency has been the subject of extensive study since the 1950s. Therefore, the initial properties of barium titanate must be modified by incorporating many doping compounds. Additions to barium titanate and their effects on properties of this ceramic are then the topic of much research nowadays, especially the dielectric properties which give rise to this interest. Furthermore, presently, demand for non-lead materials increases since lead can harm both human health and the environment. In the literature, it is well known that the electrical properties of barium titanate can be normally controlled by two approaches. Microstructural modification is one approach [3]. Another approach used utilizes additives to form new phases [4]. Numerous studies have been carried out on the solid solutions between barium titanate and the oxide groups such as lead zirconate titanate-barium titanate (PZT-BT) and bismuth sodium titanate-barium titanate (BNT-BT) systems, and a small amount of study has been made of the

synthesis or the phase formation of the solid solution between barium titanate and barium magnesium niobate (BT-BMN).

Barium magnesium niobate (BMN) is a microwave dielectric ceramic which exhibits a high dielectric constant (ϵ_r), a high quality factor (Q), a small temperature coefficient (τ_f) and a low dielectric losses ($\tan\delta$). BMN is widely applied in microwave communication systems, such as communication satellites, radar detectors and dielectric resonators [5-7]. Weill *et al.* [8, 9] prepared the $\text{BaTiO}_3\text{-BaM}_{1/3}\text{N}_{2/3}\text{O}_3$ system, where $M = \text{Co}$ or Mg and $N = \text{Nb}$ or Ta , by a chemical route. Their results showed that a high dielectric constant can be obtained in a 4 mol% BMN-doped BT ceramic. Moreover, Munpakdee *et al.* [10, 11] have been discovered that BT doped with 2 mol% of BMN exhibited the highest dielectric constant which was prepared by a high-temperature solid-solution method. So far, there have been only a few studies on the BT-BMN system, systematic investigation of this system is still required for a better understanding of the phase development in BT-BMN solid solutions. Thus, in the present study, the phase formation characteristics of the $(1-x)\text{BaTiO}_3\text{-}x\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (or $(1-x)\text{BT-xBMN}$) system were examined as a function of processing conditions. Various preparation techniques and the effects of processing parameters are applied in all samples. The relationships among these experimental results are discussed.

Experimental

$(1-x)\text{BaTiO}_3\text{-}x\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (or $(1-x)\text{BT-xBMN}$), where $x = 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09$ and 0.10 , powders were prepared by the classical mixed-oxide method. Reagent grades of BaCO_3 (Fluka, > 98.5% purity), TiO_2 (Riedel, > 99% purity), MgO and Nb_2O_5 (Aldrich, > 99% purity) were used as raw materials

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for this system. BaTiO_3 (BT) powder was firstly prepared by mixing BaCO_3 and TiO_2 precursors together via a ball milling technique for 24 h in ethanol using alumina balls. The mixtures were then dried and calcined at 1200°C for 2 h in air in order to obtain a pure BT phase. $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (BMN) powder was also prepared by mixing BaCO_3 , MgO and Nb_2O_5 precursors together via a ball milling technique for 24 h in ethanol using alumina balls. The mixtures were dried and calcined at 1300°C for 4 h in air in order to obtain a pure BMN phase. After that, the $(1-x)\text{BT}-x\text{BMN}$ powders were formulated from the BT and BMN powders by processing with a similar mixed-oxide procedure. The reactions of uncalcined BT-BMN powder, taking place during heat treatment, were investigated by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) using a heating rate of $10\text{ K}\cdot\text{minute}^{-1}$ in air from room temperature to 1250°C . According to the DTA results, each composition was calcined in air for 4 h in the temperature range of $1200\text{--}1300^\circ\text{C}$. All the powder processing is shown schematically in Fig. 1. The phase formation process was followed by X-ray diffraction analysis (XRD) in order to obtain single phase $(1-x)\text{BT}-x\text{BMN}$ powders. The lattice parameters of all powders were then determined using Cohen's least squares method [12]. Morphology of powders was also observed using scanning electron microscopy (SEM).

Results and Discussion

The TG-DTA results for the BT-BMN precursors prepared by the mixed-oxide method are shown in Fig. 2. In the temperature range from room temperature to $\sim 1250^\circ\text{C}$, the sample shows many exothermic and endothermic peaks

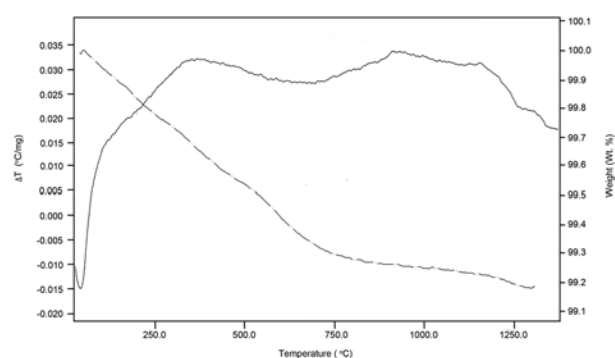


Fig. 2. TG-DTA curves for the mixture of BaTiO_3 - $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ powders.

in the DTA curves. The first peak is found at $\sim 120^\circ\text{C}$ which can be attributed to the decomposition of the organic species originating from the milling process [13, 14]. Corresponding to the continuous decrease in specimen weight, by increasing the temperature up to $\sim 800^\circ\text{C}$, the solid-state reaction between BaTiO_3 and $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ might occur. The broad exothermic characteristic present in the DTA curve represents this reaction, which has a maximum at $\sim 400^\circ\text{C}$. No further significant weight loss was observed for temperatures above 800°C in the TGA curve. However, several DTA peaks are observed at $\sim 900\text{--}1250^\circ\text{C}$. There is no obvious interpretation of these peaks, although it is likely to correspond to a phase transition reported in similar systems by other workers [15, 16]. These data were used to define the range of calcination temperatures for XRD investigations.

XRD patterns of the calcined powders having nominal composition $(1-x)\text{BT}-x\text{BMN}$ ($0.0 \leq x \leq 0.1$) are analyzed and shown in Fig. 3. The two end members, i.e. BaTiO_3 and $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, were found to have a tetragonal structure which matched with JCPDS file no. 76-0744

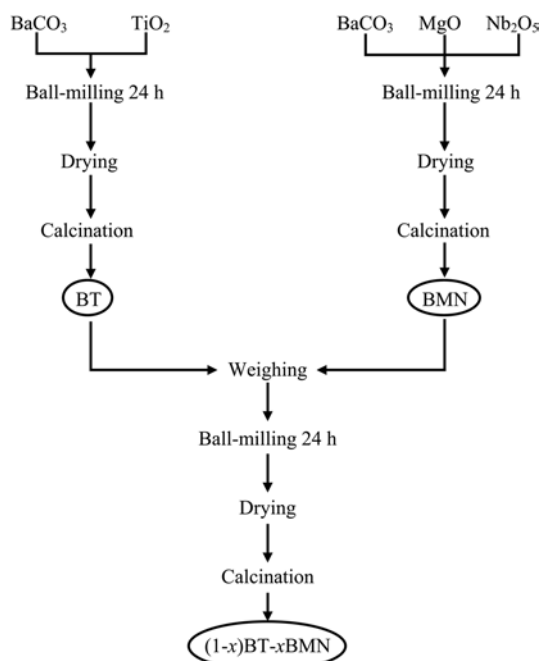


Fig. 1. Preparation route for the $(1-x)\text{BT}-x\text{BMN}$ powders.

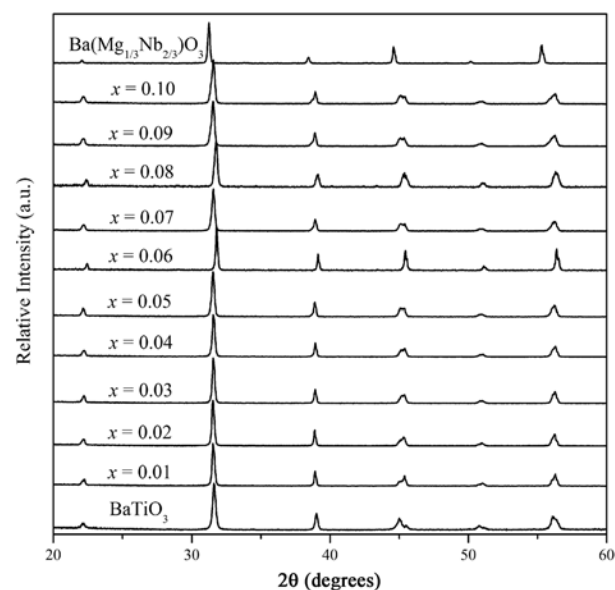


Fig. 3. Room temperature XRD patterns of the $(1-x)\text{BT}-x\text{BMN}$ powders after being calcined at their optimum conditions.

and an hexagonal structure which matched with JCPDS file no. 17-0173, respectively. In the latter patterns, some workers [17, 18] have reported that the secondary phase, $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$, was always found in the Nb-doped BaTiO_3 system. However, in this study, it is seen that all compositions in the series $(1-x)\text{BaTiO}_3$ - $x\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ form complete solid solutions with a perovskite structure without any secondary phases. The crystal structures of the samples are found to be tetragonal for all compositions. This observation indicates that the use of high purity BT and BMN precursors at optimum firing temperatures can effectively enhance the yield of the perovskite phase. Moreover, increasing the BMN content (x) gradually leads to a lower lattice volume as indicated by the XRD peak shifts towards higher angles (or lower d values) [12]. The cell parameters of the solid solutions were calculated and are given in Table 1. From the result, the a - and c -values seem to decrease with an increase of x . The gradually decrease of the parameters satisfies Vegard's law, therefore the perovskite BT-BMN system is confirmed as developing complete solid solubility. Furthermore, the broadening and splitting of (200)/(002) and (211) peaks demonstrate the formation of the tetragonal phase. The variation of the optimum calcination temperature, where only a single phase of perovskite was detected, as a function of BMN content is also given in Table 1. A continuous increase in the optimum calcination temperature with increasing BMN content could be ascribed to the nature of the BMN powder prepared by a solid state reaction, which required higher energy to form a single phase than that of BT (optimum calcination temperature of BMN is 1300 °C whereas that of BT is 1200 °C).

Fig. 4 shows the morphological evolution of BT-BMN powders as a function of their composition. In general, the particles are agglomerated and basically irregular in shape with a substantial variation in particle sizes. The smallest and the biggest particle sizes of powders were estimated from SEM micrographs and are listed in Table 1. From the results, it is seen that average particle size increases with increasing BMN content. The larger particle size of BT-BMN powders may relate to a higher optimum calcination temperature for each composition. It is interesting to point out that average particle size tends to increase with calcination temperature. This observation may be attributed

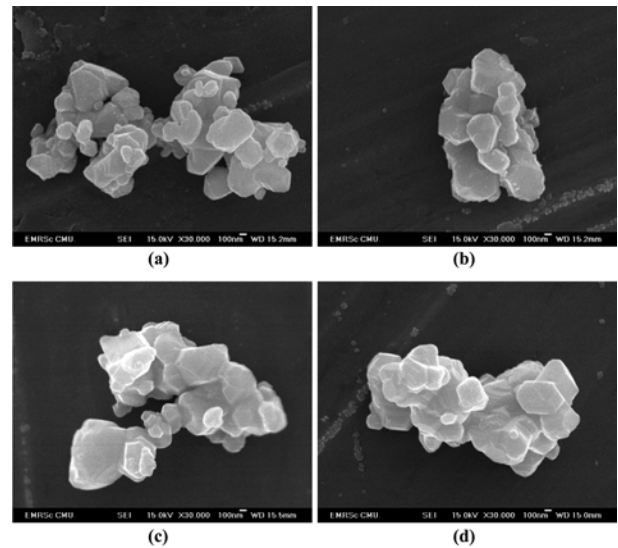


Fig. 4. SEM micrographs of $(1-x)\text{BT}$ - $x\text{BMN}$ powders: (a) 0.99BT-0.01BMN, (b) 0.97BT-0.03BMN, (c) 0.95BT-0.05BMN and (d) 0.93BT-0.07BMN.

to the occurrence of hard agglomeration with strong inter-particle bonds within each aggregate resulting from the firing process.

Conclusions

Complete solid solution of $(1-x)\text{BT}$ - $x\text{BMN}$, where x changes from 0.0 to 0.1 at regular intervals of 0.01, powders were successfully prepared by the classical mixed-oxide method. The effect of calcination conditions on the phase formation and microstructural evolution of this system was investigated via an X-ray diffractometer (XRD) and a scanning electron microscope (SEM), respectively. From the results, it can be concluded that the optimum calcination temperature of powder in this system increases with increasing BMN content. The cell parameters of the solid solutions were calculated from the XRD data and found to decrease with increasing BMN content, satisfying Vegard's law and confirming the development of complete solid solubility. Moreover, the average particle size also increases with increasing BMN content. The larger particle size of BT-BMN powders may relate to the higher optimum calcination temperature for each composition.

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Table 1. Characteristics of $(1-x)\text{BT}$ - $x\text{BMN}$ powders

BMN content (x)	Calcination temperature (°C)	Lattice parameters (nm)		Particle size range (nm)
		a	c	
0.01	1200	0.3993	0.4027	83-700
0.02	1200	0.4000	0.4020	100-833
0.03	1300	0.3993	0.4011	200-883
0.04	1300	0.3993	0.4015	210-921
0.05	1300	0.4000	0.4020	236-883
0.06	1300	0.3978	0.3988	184-710
0.07	1300	0.3991	0.4016	315-1000
0.08	1300	0.3983	0.4001	447-1789
0.09	1300	0.3996	0.4018	450-1950
0.10	1300	0.3993	0.4016	520-2010

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