MICROSTRUCTURE AND DIELECTRIC PROPERTIES OF $BaTiO_3$–Nb_2O_5–$Zn_{0.8}Mg_{0.2}TiO_3$ TERNARY SYSTEM

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Ceramics of $BaTiO_3$–Nb_2O_5–$Zn_{0.8}Mg_{0.2}TiO_3$(ZMT) composition were prepared by solid state reaction. The influence of Nb_2O_5 and ZMT addition on phase transition, microstructure, temperature-capacitance change (TCC), temperature dependence of permittivity and Curie temperature (Tc) have been studied profoundly. With only 1 mol% Nb doping, a single perovskite phase has been observed. Nevertheless, when Nb amount exceeded 2 mol%, a secondary phase of $BaTiNb_4O_{13}$ was observed. The SEM and XRD analysis showed that the solubility of ZMT in $BaTiO_3$ with 1 mol% Nb is < 4 mol%. It was observed that for a fixed amount of ZMT dopant increasing the amount of Nb content decreased the room temperature dielectric constant and shifted the Tc to higher temperatures. Finally, a new dielectric sintered in air atmosphere at intermediate temperature (1180°C) was obtained with large permittivity, low dissipation factor and high resistivity, meeting EIA X8R specification.

INTRODUCTION

In recent years, multilayer ceramic capacitors (MLCs) have been used for automotive application, such as the engine electronic control unite (ECU), programmed fuel injection (PGMFI), and antilock brake system (ABS). Electronic parts in the control module for automotive uses are required to be excellent in circuit temperature stability, and satisfaction of the X7R($\Delta C/C$ = ±15% or less at -55 to +125°C) characteristic is not good enough to be used in an electronic apparatus of an automobile which is used in the above-mentioned harsh environments. Therefore, much attention has been paid to MLCs satisfying X8R specification (-55 to 150°C, $\Delta C/C_{25°C}$ = ±15% or less). [1, 2]

As a temperature-compensation capacitor material superior in temperature characteristic, there are generally known $(Sr,Ca)(Ti,Zr)O_3$ based compositions, $Ca(Ti,Zr)O_3$ based compositions, Nd_2O_3–$2TiO_2$ based compositions, and so on. But these compositions have extremely low specific permittivities (generally 100 or less), it is practically impossible to manufacture a capacitor having a large capacitance. To create dielectric ceramic composition having a high permittivity and a smooth capacitance-temperature characteristic, compositions comprised of $BaTiO_3$ as a main component plus Nb_2O_5–Co_3O_4, Nb_2O_5–ZnO, Bi_2O_3–TiO_2, PbO–TiO_2, etc. are known. However, although these $BaTiO_3$ based high-permittivity materials can satisfy the EIA standard X8R characteristic when they are modified by $CaZrO_3$ (or $SrZrO_3$, $BaZrO_3$), existing powders still suffer from significant limitations, such as high sintering temperature(generally more than 1250°C), high dielectric loss, low resistivity, hazardous heavy metals, etc. Accordingly, there is a need for research of an excellent system for X8R MLCs.

The dielectric properties of ternary system $BaTiO_3$–Nb_2O_5–ZMT have not been reported to our knowledge. In this work, a dielectric ceramic based on $BaTiO_3$–Nb_2O_5–ZMT system, with a flat capacitance-temperature characteristics and a low sintering temperature, was prepared using a conventional ball-milled method. $BaSiO_3$ was added to improve the sinterability. The influence of the Nb and ZMT amount on the microstructure and dielectric properties of $BaTiO_3$–Nb_2O_5–ZMT ternary system was also studied.

EXPERIMENTAL

Preparation of $Zn_{0.8}Mg_{0.2}TiO_3$

$Zn_{1-x}Mg_xTiO_3$ is a useful microwave dielectric with low sintering temperature and promising microwave properties.[3] $ZnTiO_3$ has a perovskite type oxide structure and could be an useful candidate for microwave materials, but the preparation of pure $ZnTiO_3$ from a mixture of ZnO and TiO_2 has not been successful because the compound decomposes into Zn_2TiO_4(cubic) and rutile at about 945°C as follows [4, 5]:

$2ZnTiO_3$ (hexagonal) $\xrightarrow{\geq 945°C}$ Zn_2TiO_4 (cubic + TiO_2 (rutile)

$MgTiO_3$ can depress the above reaction and favor the formation of hexagonal single-phase $Zn_{1-x}Mg_xTiO_3$ by a conventional solid-state reaction.[3] The characterization of $Zn_{1-x}Mg_xTiO_3$ was later clarified by Yee-Shin Chang.[6]

The $Zn_{0.8}Mg_{0.2}TiO_3$ composition used in our experiment was prepared using the conventional solid-state reaction, reagent-grade ZnO, rutile TiO_2, and MgO powders were used. After ball milling for 18 h, the mixed powders were sintered at 900°C for 2 h. The heating rate was about 10°C/min.

Preparation of BT ceramics

Submicrometer size hydrothermal $BaTiO_3$ powders and Nb_2O_5 (1~4 mol%), ZMT (1~4 mol%) and the sintering aid $BaSiO_3$ (1 mol%), were used as starting materials. The mixed powders were ball-milled in deionized water for 8 hours. The prepared ceramic powders were pressed in disk form (10 mm in diameter and 1 mm in thickness) by mixing ceramic powders with 3wt.% of polyvinyl alcohol (PVA) binder, and then the disks were finally fired at 1180°C for 2 hours in air.

Characterization

After samples were fired at 800°C with Ag electrodes on both surfaces, dielectric properties of samples were measured from -55°C to 150°C with an impedance analyzer LCR(HP4284A) at 1 KHz and 1V rms. Insulation Resistance was measured at room temperature on a megohmmeter (HM2672A) under 100V DC.

Phase identification of the sintered specimens was performed using X-ray diffractometry (XRD) (Philips X'Pert, Netherlands), and their microstructures were examined using scanning electron microscope (SEM) (Hitachi S-530, Japan). A differential thermal analysis (DSC) (NETZSCH STA 449C, Germany) was used to determine the Curie temperature of the specimens.

RESULTS AND DISCUSSION

XRD results for the samples of Nb concentration ranging from 1 to 4 mol% are shown in Figure 1. A single perovskite phase is observed when dielectric composites contain only 1 mol% Nb. However, the secondary phase is observed when Nb amount just exceeds 2 mol%, which is proved to be $BaTiNb4O_{13}$. It has been, therefore, assumed that the solubility of Nb in $BaTiO_3$ with 1 mol% ZMT is < 2 mol%. The solubility limit of Nb in $BaTiO_3$ at 1300°C in air is 5 mol% as suggested by Kowalski et al. [7] It was confirmed that the occupation of Nb ions on Ti site in the BT lattice produces the Ti segregation out of the grains.[8] This phenomenon is responsible for the secondary phases formation. Therefore, it is considered that the extra Ti in the ZMT dopant strongly influenced on the solubility of Nb in $BaTiO_3$ matrix. Figure 2 shows the X-ray diffraction patterns of the various ZMT doped $BaTiO_3$ ceramics. It can be seen that the secondary phase were hardly to be detected even 3 mol% of ZMT were added to BT. As the ZMT concentration increased to 4 mol%, a new phase of $ZnTiNb_2O_8$ formed. This indicated the solubility of ZMT in $BaTiO_3$ with 1 mol% Nb is < 4 mol%. A scanning electron micrograph for the samples with various ZMT doped $BaTiO_3$ ceramics fired at 1180°C are shown in Figure 3. As can be seen from Figure 3c, the existence of a secondary phase was found in the 3 mol% ZMT-doped sample, and the volume of the secondary phase increased with ZMT doping amount (Figure 3d). It was assumed that the comparatively low concentration of the secondary phase, which has been identified in Figure 3c, cause it difficult to detected by X-ray diffraction as shown in Figure 2.

Figure 4 depicts the temperature-capacitance characteristics of samples with different ZMT concentrations. As it shows, $BaTiO_3$ ceramics doped with 1 mol% Nb and 1 mol% ZMT resulted in a sharp dielectric peak at Curie point around 125°C, cause it exceeded range of the X8R window. However, further addition of ZMT

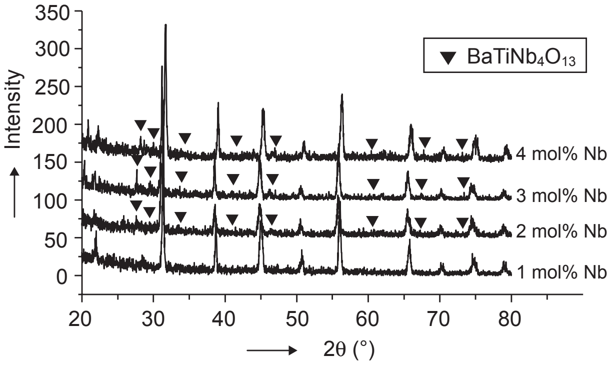


Figure 1. XRD patterns of $BaTiO_3$ with 1 mol% ZMT and various amounts of Nb.

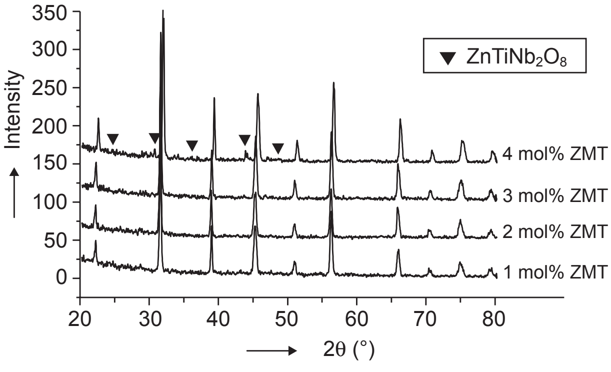


Figure 2. XRD patterns of $BaTiO_3$ with 1 mol% Nb and various amounts of ZMT.

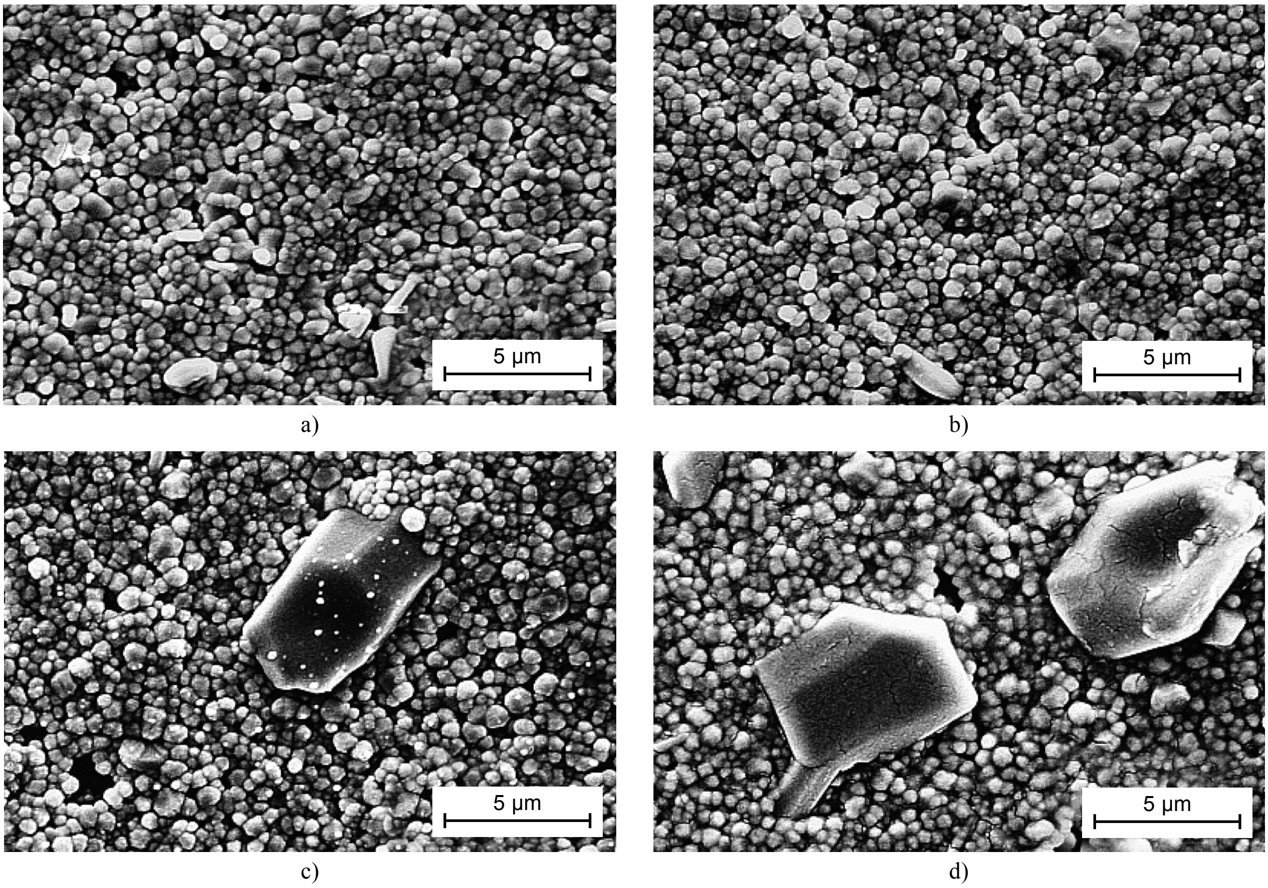
greater than 1 mol% significantly depressed the temperature-capacitance characteristics at 150°C ($TCC_{150°C}$), which is still incompatible with X8R materials. The result indicates that the TCC curve of BT ceramics can't be tailored by controlling the amount of ZMT in the dielectric materials.

Figure 5 depicts the TCC of dielectric materials with different Nb concentrations. For the sample with 1 mol% Nb, although the TCC at a low temperature side was comparatively gently to satisfy the X8R specification, its capacitance variation is still out of range of the X8R window. The high temperature peak of TCC (at Tc) exhibited a continuous decrease and X8R specification was satisfied when the amount of Nb was exceeded 2 mol%. The cubic-to-tetragonal transition temperatures Tc of various Nb amounts doped $BaTiO_3$ ceramics were measured using DSC. The effect of Nb amount on Tc is illustrates in Figure 6. Tc shifting toward high temperatures indicated that the ferroelectric phase became stable at high temperature [9] and it's considered to be very helpful to improve the temperature stability of the dielectrics at high temperatures. The doping effect on the Curie temperature of $BaTiO_3$ has been extensively researched and it has been apparent that Tc relates to tetragonality [10, 11] and internal stress [12, 13].

Figure 6 also shows the dielectric constant at room temperature of Nb-doped $BaTiO_3$ ceramics. The value of dielectric constant at room temperature declined from 2352 to 1736 as volume of Nb increased to 4 mol%, and a nearly linear relationship is demonstrated. This phenomenon was due to the increase of paraelectric phase in the so-called grain core and grain shell structures.[14] For the sample with 2 mol% Nb and 1 mol% ZMT that was sintered at 1180°C, the permittivity, dielectric loss, and resistivity at room temperature are 2004, 0.84 % and $1.4\times10^{12}\Omega\cdot$cm, respectively. This ceramic material is very promising for preparation of X8R MLCs, which can be sintered at intermediate temperature with large capacitance.

CONCLUSIONS

The effects of Nb and ZMT amount on the microstructure and the dielectric properties of ZMT-doped $BaTiO_3$ system were investigated. XRD analysis revealed that the solubility of Nb in $BaTiO_3$ with 1 mol% ZMT is < 2 mol% and a second phase of $BaTiNb_4O_{13}$ was detected in the samples when more than 2 mol% Nb were doped. The SEM and XRD observation indicated that the solubility of ZMT in $BaTiO_3$ with 1 mol% Nb is



a) b)

c) d)

Figure 3. SEM micrographs of $BaTiO_3$ with 1 mol% Nb and various amounts of Nb. (a) 1 mol% ZMT, (b) 2 mol% ZMT, (c) 3 mol% ZMT, and (d) 4 mol% ZMT.

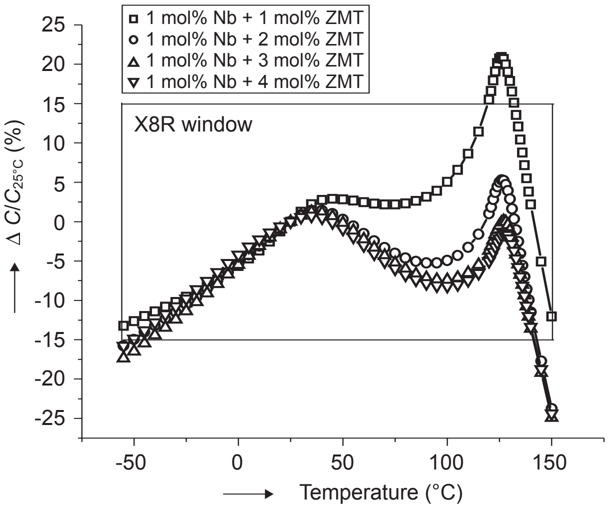


Figure 4. Temperature dependence of capacitance variation for $BaTiO_3$ with 1mol% Nb and 1-4 mol% ZMT.

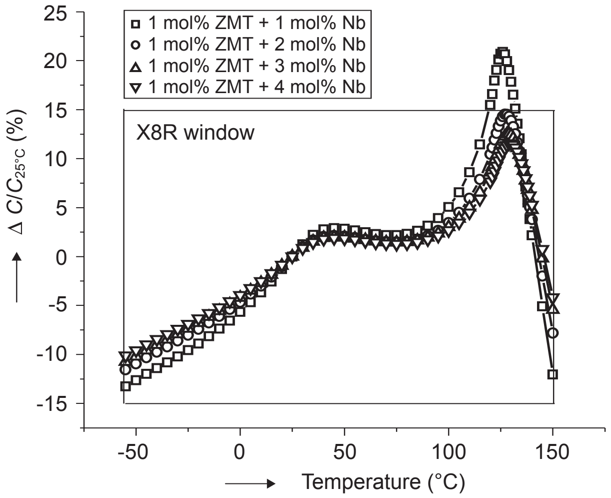


Figure 5. Temperature dependence of capacitance variation for $BaTiO_3$ with 1.0 mol% ZMT and 1-4 mol% Nb.

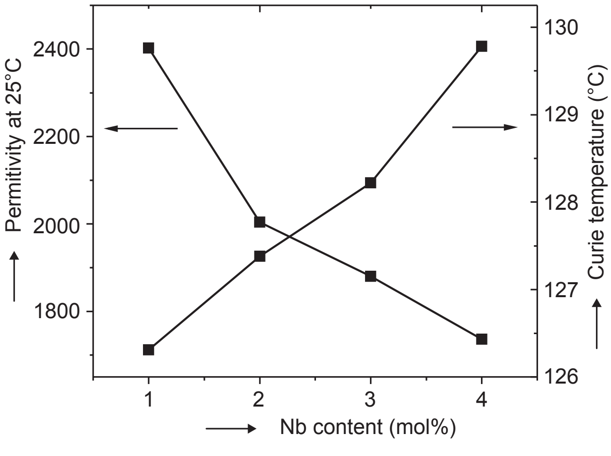


Figure 6. Permittivity and Curie temperature versus Nb amount for $BaTiO_3$ with 1.0 mol% ZMT.

< 4 mol%. The permittivity of samples decreased with increasing Nb concentrations, whereas the Curie temperature was shifted to higher temperatures. We can adjust the dosage of Nb_2O_5–$Zn_{0.8}Mg_{0.2}TiO_3$ dopants to develop the environmental friendly $BaTiO_3$-based X8R dielectric materials with high performance (low sintering temperature, large permittivity, low dissipation factor and high resistivity).

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MIKROSTRUKTURA A DIELEKTRICKÉ VLASTNOSTI TERNÁRNÍ SOUSTAVY $BaTiO_3$–Nb_2O_5–$Zn_{0.8}Mg_{0.2}TiO_3$

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Reakcí v pevném skupenství byly připraveny keramické hmoty sestávající z $BaTiO_3$–Nb_2O_5–$Zn_{0.8}Mg_{0.2}TiO_3$ (ZMT). Důkladně byl zkoumán vliv přídavku Nb_2O_5 a ZMT na fázový přechod, mikrostrukturu, změnu teploty-kapacitance (TCC), teplotní závislosti permitivity a Curieova teplota (T_c). Po přidání pouze 1 mol% Nb vznikla jedna fáze perovskitu. Nicméně když množství Nb přesáhlo 2 mol%, byla pozorována sekundární fáze $BaTiNb_4O_{13}$. Analýza SEM a XRD ukázala, že rozpustnost ZMT v $BaTiO_3$ s 1 mol% Nb je < 4 mol%. Bylo pozorováno, že v případě neměnného přídavku ZMT a zvyšujícího se množství obsahu Nb došlo ke snížení dielektrické konstanty při teplotě místnosti a posunutí T_c k vyšším teplotám. Nakonec byl v atmosféře vzduchu při střední teplotě (1180°C) získán nový dielektrický slinutý produkt s velkou permitivitou, nízkým disipačním faktorem a vysokým měrným odporem, který splňuje specifikaci EIA X8R.