Synthesis and dielectric/ferroelectric characteristics of Ta-modified PMN$_{0.6}$ · PZN$_{0.2}$ · PT$_{0.2}$ ceramics

JEE-SU KIM, NAM-KYOUNG KIM*, JIN-HO KIM
Department of Inorganic Materials Engineering, Kyungpook National University, 1370 Sankyuk-Dong, Buk-Gu, Daegu 702-701, Korea
E-mail: nkkim@knu.ac.kr

Ceramic powders of a [Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$]$_{0.6}$ · [Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$]$_{0.2}$ · [PbTiO$_3$]$_{0.2}$ system (with Nb replaced by Ta) were prepared via solid-state reaction routes. The structures developed in the B-site precursor and perovskite systems are discussed. Weak-field low-frequency dielectric characteristics as well as the polarization behavior of the perovskite ceramics are presented. The relaxation modes of the dielectric constant spectra are analyzed in terms of diffuseness parameters. A very high maximum dielectric constant of 37 900 (@1 kHz) was obtained when 1/4 of Nb was replaced by Ta. Internal microstructures of the sintered samples are also reported.

© 2004 Kluwer Academic Publishers

Introduction
Lead magnesium niobate Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ and lead zircon niobate Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN and PZN, respectively) are typical disordered complex-perovskite ferroelectric relaxors, which possess excellent dielectric and related properties [1–3]. Dielectric constant spectra of the two compounds are somewhat broad (diffuse phase transition, DPT). Moreover, the dielectric constant values are rather sensitive to the measurement frequency. In contrast, lead titanate PbTiO$_3$ (PT) is a normal ferroelectric with quite a sharp phase transition (SPT) mode and little dielectric dispersion of frequency dependence.

Unlike PMN, perovskite PZN powders cannot be prepared via conventional solid-state calcination, including a “B-site precursor method” [4]. The method is conceptually identical to the so-called “columbite process” [5, 6], but is a more comprehensive terminology. Thus far, many successful attempts at perovskite formation in PZN have been reported in the literature, but only under very high pressures [7, 8], via mechanochemical reaction routes [9, 10], or by the aid of fluxes for crystal growth [11–13].

In a previous report on a pseudoternary system PMN$_{0.8}$ · PZN$_{0.2}$ · PT$_{0.2}$ [14], the maximum dielectric constant of $x = 0.2$ (i.e., PMN$_{0.6}$ · PZN$_{0.2}$ · PT$_{0.2}$) was rather high, 18 300 (@10 kHz). However, the dielectric maximum temperature of the composition (135 °C) was quite high for practical purposes. In the present study, Ta was systematically substituted for Nb to substantially reduce the dielectric maximum temperatures for potential applications to capacitors. The “B-site precursor method” was employed for powder preparation to suppress the development of pyrochlore, the presence of which (even in small quantities) is reported to be detrimental to dielectric properties [15–17].

Experimental
The starting composition of PMN$_{0.6}$ · PZN$_{0.2}$ · PT$_{0.2}$ (molar basis) can be expressed as Pb(Mg$_{1/3}$ Nb$_{2/3}$)$_{0.6}$ (Zn$_{1/3}$Nb$_{2/3}$)$_{0.2}$Ti$_{0.2}$O$_3$, i.e., Pb(Mg$_{0.6}$Zn$_{0.2}$)$_{1/3}$ (Nb$_{0.8}$)$_{2/3}$Ti$_{0.2}$O$_3$. In the present study, the Nb component was systematically replaced by Ta, yielding overall compositions of Pb(Mg$_{0.6}$Zn$_{0.2}$)$_{1/3}$ (Ta$_{0.8}$Nb$_{0.2}$)$_{2/3}$Ti$_{0.2}$O$_3$. The values of $x$ were 0.0–0.8 at a regular interval of 0.2. The raw materials used were high-purity oxide chemicals of PbO (99.5%), MgO (99.9%), ZnO (99.8%), Ta$_2$O$_5$ (99.9%), Nb$_2$O$_5$ (99.9%), and TiO$_2$ (99.9%). The moisture contents of the raw materials and of the B-site precursor powders were measured and introduced into the batch calculations to maintain the compositions as close to the nominal values as possible.

Powders of the B-site precursor system [(Mg$_{0.6}$- Zn$_{0.2}$)$_{1/3}$ (Ta$_{0.8}$-Nb$_{0.2}$)$_{2/3}$Ti$_{0.2}$O$_2$ (i.e., [Mg$_{0.2}$Zn$_{0.2}$Ti$_{0.2}$Ta$_{0.8}$-1/3]Nb$_{0.2}$/3)]O$_2$] were prepared by weighing the constituent chemicals in the required ratios, wet-milling under alcohol, drying, and reacting at 1100–1200 °C (depending on composition) for 2 h in air. The resulting lumps were milled, dried, and calcined again at the same conditions (to promote phase formation) and studied by X-ray diffractometry (XRD) for phase identification. Appropriate amounts of PbO were added to the B-site precursor powders and the mixtures were wet-milled, dried, and calcined at 800–850 °C for 2 h.

*Author to whom all correspondence should be addressed.

The calcinations were repeated once at 850–900 °C for 2 h, with intermediate milling stages. Prepared powders (with 2 wt% aqueous solution of polyvinyl alcohol added as a binder) were pressed isostatically into pellet-type samples. The powder compacts were fired (heating rate = 300 °C/h) at 1000–1200 °C for 1 h in a multiple-enclosure crucible setup [18], with identical composition powders surrounding the pellets to suppress PbO volatilization at high temperatures. Au was sputtered onto the sintered pellets for electrical contacts. The dielectric constant and loss values were measured under weak-field (∼ 1 Vrms/mm) low-frequency (1–1000 kHz) conditions using an impedance analyzer. Field-dependent polarization responses of the ceramics were monitored using a ferroelectric hysteresis test system. The samples were fractured, Au-coated, and examined using a scanning electron microscope (SEM) to investigate microstructure development.

Results and discussion

Fig. 1(a) shows the XRD results of the B-site precursor system [(Mg$_{1-x}$Zn$_x$)$_{1/3}$/Ti$_{2/3}$O]$_2$. At $x = 0.8$ of [(Mg$_{1-x}$Zn$_x$)$_{1/3}$/Ti$_{2/3}$O]$_2$ (which can be resolved as [(Mg$_{1/3}$Zn$_{2/3}$)$_{1/3}$/Ti$_{2/3}$O]$_2$, columnite was the major structure, along with a smaller fraction of rutile. It has been reported that MgNb$_2$O$_6$ and ZnNb$_2$O$_6$ (both of columnite structures, ICDD Nos. 33-875 and 37-1371) readily formed $\langle$Mg,Zn$\rangle$Nb$_2$O$_6$ columnite solid solution in the entire composition range [19]. Meanwhile, columnite [(Mg,Zn)$_{1/3}$]Nb$_{2/3}$O$_6$ and rutile TiO$_2$ form rutile solid solutions of [(Mg$_{1/3}$Nb$_{2/3}$)$_{1/3}$/Ti$_{2/3}$O]$_2$ and [(Zn$_{1/3}$Nb$_{2/3}$)$_{1/3}$/Ti$_{2/3}$O]$_2$ (ICDD Nos. 40-366 and 39-291). Reflection patterns of the two rutiles are basically identical to that of TiO$_2$ rutile (ICDD No. 21-1276), except for the substantial angular shifts (by the modification of unit cell dimensions) as well as the absence of the (1 1 1) reflection in [(Zn$_{1/3}$Nb$_{2/3}$)$_{1/3}$/Ti$_{2/3}$O]$_2$. For comparison, the respective (weight-averaged) ionic radii of Mg$_{1/3}$Zn$_{2/3}$, Zn$_{1/3}$Nb$_{2/3}$, and Ti are 0.667, 0.673, and 0.6065 mm [20].

When positions as well as intensities of the reflections (especially at high angles) are compared, the rutile developed at $x = 0.8$ seems closer to $\langle$[(Mg,Zn)$_{1/3}$-Nb$_{2/3}$)$_{1/3}$/Ti$_{2/3}$O]$\rangle_2$, a 1:1 mixture between $\langle$[(Mg,Zn)$_{1/3}$]Nb$_{2/3}$O$_2$ and TiO$_2$, rather than to TiO$_2$. Then, the resolved formula of $\langle$[(Mg$_{1/3}$]Nb$_{2/3}$)$_{1/3}$/(Zn$_{1/3}$- Nb$_{2/3}$)$_{1/3}$/Ti$_{2/3}$O]$\rangle_2$ can be modified as $\langle$[(Mg,Zn)$_{1/3}$-Nb$_{2/3}$]$_{1/3}$/Ti$_{2/3}$O]$\rangle_2$, which agrees well with the observed intensity ratio of the two structures. Moreover, mutual dissolution of the $\langle$[(Mg,Zn)$_{1/3}$]Nb$_{2/3}$O$_2$ and $\langle$[(Mg,Zn)$_{1/3}$]Nb$_{2/3}$]Ti$_{2/3}$O$\rangle_2$ components (nominally 60 and 40 mol %, respectively) into each other seemed to have occurred to some extent, as evidenced by the small counter-shifts of the reflection angles; i.e., increasing and decreasing peak positions of the former and latter structures, respectively. Additionally, the shifts were more pronounced (up to a few tenths of a degree at 50–60° 20) in the case of columnite, indicating that the columnite structure took a larger amount of the rutile component into the solid solution formation, as compared with the case of the rutile solid solution taking columnite.

At intermediate compositions, two more rutiles of [(Mg$_{1/3}$]Ta$_{2/3}$]$_{1/3}$/Ti$_{2/3}$O$_2$ and [(Zn$_{1/3}$]Ta$_{2/3}$]$_{1/3}$/Ti$_{2/3}$O$_2$ (ICDD Nos. 40-365 and 39-292) might have additionally formed. However, the two rutiles had undoubtedly formed a solid solution with other rutile constituents. Besides, the rutile reflections shifted to lower 20 values with increasing Ta content. The apparent shifts seemed to have resulted from the nature of $\langle$[(Mg,Zn)$_{1/3}$-Ta$_{2/3}$]$_{1/3}$/Ti$_{2/3}$O$\rangle_2$ rutile taking more fractions of $\langle$Mg,Zn$\rangle$//Ta$_{2/3}$$_2$O$_6$ with larger effective ionic radii, and hence becoming larger as regards the unit cell dimensions. The analysis is consistent with the observation that the intensities of the columnite became smaller with increasing Ta content. Finally, at $x = 0.0$ of [(Mg$_{1/3}$]Ta$_{2/3}$]$_{1/3}$/Ti$_{2/3}$O$_2$ (i.e., $\langle$[(Mg$_{1/3}$]Ta$_{2/3}$]$_{1/3}$/Ti$_{2/3}$O$\rangle_2$, only a tritrite structure (MgTa$_2$O$_6$, ICDD No. 32-631) was identified, whereas reflections of the rutile and columnite structures disappeared completely, indicating that the two remaining components of (Zn$_{1/3}$]Ta$_{2/3}$]$_{1/3}$O$_2$ and TiO$_2$ (nominally 20 mol % each) had dissolved thoroughly into the host solid solution of tritrite. In contrast, the 20 mol % component of TiO$_2$ at $x = 0.8$ was not assimilated into the columnite structure, but rather