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Dielectric and Electrical Properties of Ce,Mn:SBN

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ABSTRACT

Temperature and frequency dependence of dielectric and electrical properties was investigated in cerium and manganese doped $Sr_{0.6}Ba_{0.4}Nb_2O_6$(60SBN) ceramic system. Structural deformation of 60SBN by dopants did not appeared. 1350°C-10 h sintered specimen had higher densification than 1250°C-10 h sintered one, to which dielectric properties are related. That the feature of dielectric maxima peaks was typical Diffusive Phase Transition (DPT), it was explained by "random-field Ising model". Even though 60SBN has large dielectric loss at high frequency above 100 kHz, it is desirable for optical applications because of low dielectric loss at low frequency. From Arrhenius plot of temperature, the activation energy was calculated to 0.45~0.49 eV.

Key words : Ce,Mn:SBN, Relaxor ferroelectrics, Diffusive phase transition, Random field Ising model, Arrhenius plot

1. Introduction

Relaxor ferroelectrics are characterized by a significant frequency dependence of their peak permittivity, persistence of the local polarization far above the phase transition temperature T_C, and absence of macroscopic spontaneous polarization and structural symmetry breaking after zero-field cooling. Relaxor ferroelectric behavior occurs dominantly in lead based perovskite structures of $A(B_1B_2)O_3$ compositions, e.g. $PbMg_{1/3}Nb_{2/3}O_3$(PMN).[1)] Similar features are also observed on Tungsten-Bronze (TB) structure materials such as $A_xBa_{1-x}Nb_2O_6$ (A=Sr, Pb).[2)] The tungsten-bronze ferroelectric material strontium-barium niobate $Sr_xBa_{1-x}Nb_2O_6$(SBN) is a interesting material due to the variety of its potential applications, particularly in the areas of pyroelectricity, piezoelectricity, electro-optics, photorefractive optics and non-linear optics.[3-6)]

The nature of the relaxor phase transition can only be found out having detailed knowledge of the influence of internal charge carriers and electric fields in the paraelectric and ferroelectric regime.[7,8)] This influence is of paramount importance for the "random field Ising model," which has been put forward to explain the relaxor behavior of SBN.[9)]

It was known that Ce ion could improve the optical properties of SBN.[10)] When doped with cerium ion it decreases linearly with the doping concentration, and for concentrations of about 2 mol% and more the transition temperature drops below room temperature. The effect of the CeO_2 dopant on the defect structure and sintering behavior of SBN was investigated.[12)] They were found that the cerium dopant would increase the sintering temperature and the activation energy of the SBN ceramics which were sintered in air. The polarization reversal depends strongly on frequency, temperature, dark conductivity, and doping concentration. This so-called electrical aging is attributed to electric pinning centers that hinder the domain-wall motion. The existence of pinning centers on the basis of the quenched random-field model for Ce-doped SBN was discussed.[12)] In optical applications, the photorefractive properties can be enhanced by doping with polyvalent ions like Ce, which increases the photorefraction, or Mn which additionally extends the response into the red spectral region.

The purpose of this study is investigation of dielectrical and electrical behavior of the Ce-, Mn-doped SBN. We discussed on the dopant influence on frequency and temperature in cerium-, manganese-doped SBN.

2. Experimental

High-purity powder of $SrCO_3$ (99.99%, Alfa Aesar), $BaCO_3$ (99.999%, CERAC), Nb_2O_5 (99.999%, H.C. Starck), CeO_2 (99.9%, High-Purity Cemicals), and MnO_2 (99.999%, ACROS ORGANICS) were used as starting material. The mixture having appropriate molar ratio for 0.1 mol% CeO_2, and 0.01 mol% MnO_2 doped $Sr_{0.6}Ba_{0.4}Nb_2O_6$ were wet-ball mixed. Mixing was preformed with ethyl alcohol for 24 h, using zirconia balls. The mixed slurry were dried, pressed, and calcined at 1150°C for 5 h. The phases in the calcined powder was identified by XRD (Rigaku Geigerflex X-Ray Diffractometer) using a CuKα radiation at 30 kV and 20 mA, and was identified by comparing spectra with standard data in

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JCPDS file index (39-0265). Single phase calcined powder was re-pressed in a mold of 10 mm in-diameter under a uniaxial pressure, and the pressed discs were sintered at 1250, 1350°C for 10 h, respectively.

Sintered specimens were ground and polished using 0.3 μm-Al_2O_3 powder. In order to observe the surface of Ce,Mn:SBN, polished specimens were thermally etched at 1000°C for 1 h and chemically etched at HF : HNO_3=1 : 3 acid solution for several hours at room temperature. Surfaces of specimens were gold-coated for SEM analysis (HITACHI S-3000H, Japan).

For dielectric properties and electrical conductivity measurements, polished discs were made electrode with silver paste (Dae-Joo, DS-0081IE) and were heat-treated at 400°C for 1 h. The frequency and temperature dependence of dielectric and electrical properties were estimated from room temperature to 150°C, using a Hioki 3532 LCR HiTester at 50 Hz~5 MHz. Heating and cooling rate of specimens were 0.2°C/min.

3. Results and Discussion

H. Lee *et al.*[13] and Q. Huang *et al.*[14] reported that during the synthesis of $Sr_xBa_{1-x}Nb_2O_6$, four intermediate phases, i.e., $Ba_5Nb_4O_{15}$, $Sr_5Nb_4O_{15}$, $SrNb_2O_6$, and $BaNb_2O_6$ were developed and $Sr_xBa_{1-x}Nb_2O_6$ phase which was synthesized by the reaction between $SrNb_2O_6$, and $BaNb_2O_6$ appeared at 900~1000°C. $Sr_xBa_{1-x}Nb_2O_6$ (x=0.6) was the only crystalline phase in calcined specimens at above 1150°C.

1250°C or 1350°C sintered Ce,Mn:60SBN were of SBN-single phase with the tetragonal tungsten-bronze structure, which was confirmed by X-ray diffraction analysis (Fig. 1). The Miller indices of the main peaks are represented in Fig. 1 showing a single phase material, and same structure to the undoped SBN. Incorporation of cerium and manganese into the lattice might lead to a deformation of the SBN structure because of the difference of ionic valance and ionic size. We see that there is basically no shift of peaks with the small amount of dopants and the sintering condition. The fact suggests that incorporations of Ce and Mn in certain crystallographic sites of the SBN structure occurs completely in the 1250°C or 1350°C sintering process. The integral intensity of some peaks increases in different way with the increase of the sintering temperature, suggesting a possible selective location of the ions at certain crystallographic sites of the structure.[15]

In sintered ceramics, diffusion path of the rate-limiting species related to porosity or densification were usually considered as one of two limiting cases, i.e. lattice and grain boundary.[11] It is common that both the lattice diffusion and the grain boundary diffusion can contribute to mass transport in the system. In sintering SBN ceramics, the rate-limiting species was suggested as the niobium ion.[16,17] If grain size is fine and the temperature is not high, the apparent diffusion rate is determined by grain boundary diffusion rate of Nb ion in SBN. However, if temperature is high enough to have a significant condition of lattice diffusion, both lattice diffusion and grain boundary diffusion of Nb ions would contribute to apparent diffusion rate.[18,19] Surface morphology of specimens sintered at 1250°C and 1350°C respectively are shown in Fig. 2. For the specimen sintered at 1350°C, the porosity is lower than that of 1250°C one. Formation of abnor-

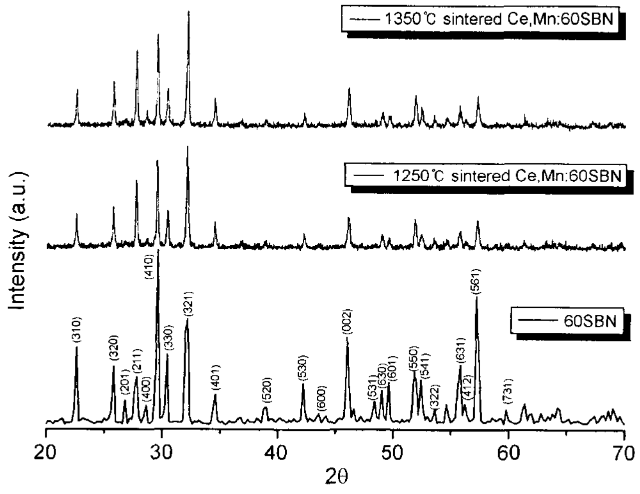
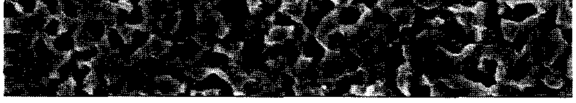
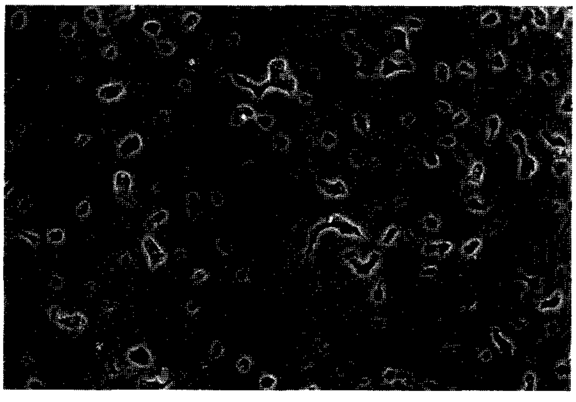


Fig. 1. XRD spectra of Ce,Mn:60SBN sintered at 1350°C, at 1250°C and 60SBN.



(a) 1250℃-10 h sintered



(b) 1350℃-10 h sintered

Fig. 2. Microstructure of Ce,Mn:60SBN for different sintering conditions.

mal spatial morphology affects densification. However, the second phase were not detected, ever when CeO_2 and MnO_2 doped. Because Nb ion has been suggested as a rate-limiting species during sintering of SBN ceramics,[16] the certain of Nb vacancies would lead to the increase of the densification. At present, structural instabilities such as low densification or high porosity have no relation to Ce and Mn dopants. As a mention of above discussion, dopants only affects its optical and electro-optical properties.[20,21]

Temperature dependence of dielectric constants of Ce, Mn:SBN is shown in Fig. 3. The phase transition in SBN is of relaxor-type, i.e., it is "smeared" or "diffused". To explain this situation of the conventional transition behavior, a "random-field Ising model" as a consequence of structural and compositional inhomogeneity was introduced. When the temperature is lowered below the transition, domains become more and more cooperative, until a ferroelectric state is reached.[12] However, transition behavior in the ceramics system with grains having inhomogeneities of structure or composition would be wider than the crystalline system with grains having comparative homogeneities. Inhomogeneity makes that transitional behavior for temperature appears as widespread curve of dielectric constants in wide temperature region.

The dielectric maxima peaks shift to higher temperature with increasing frequency (Fig. 3), that is similar to what is observed in typical Diffusive Phase Transition (DPT) ferroelectrics. In case of 1350°C sintered specimen, weakly dielectric dispersion in lower dielectric constant appears in the low temperature. Dielectric dispersion in low temperature usually is common facts in normal relaxor. But the curve in Fig. 3(b) does not look to be normal relaxor behavior. Specimens with a more uniform distribution of grain size had sharper dielectric maxima.[13,22] There is not significant difference for curves between 1250°C sintered specimen and 1350°C one shown in Fig. 3(a), (b), but the curve of 1350°C sintered specimen will be regarded more uniform distribution. In other words, the decrease of the porosity increases permittivity. F. Guerrero *et al.*[15] and Y. Sato *et al.*[23] have shown similar results.

Fig. 4 illustrates the frequency dependence of the dielectric constants and losses of Ce,Mn:SBN ceramics. Both 1250°C and 1350°C sintered specimens had almost same frequency dependence of the dielectric constants and losses, but at high frequency above 100 kHz dielectric losses increase significantly.[24,25] Ce,Mn:SBN such as $Sr_{0.6}Ba_{0.4}Nb_2O_6$(60SBN) and $Sr_{0.75}Ba_{0.25}Nb_2O_6$(75SBN) is in a fair way to used optical applications. Because low dielectric losses are desirable for electro-optics devices applications.

Temperature dependences of conductivity for cerium and manganese doped 60SBN ceramics is plotted in Fig. 5. The

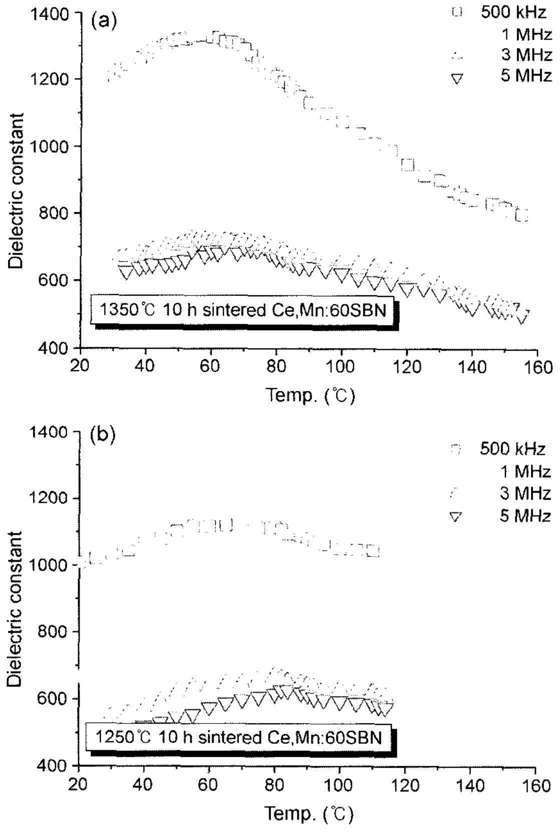


Fig. 3. Temperature dependence of dielectric constants of Ce, Mn:60SBN sintered at (a) 1350°C-10 h and (b) 1250°C-10 h.

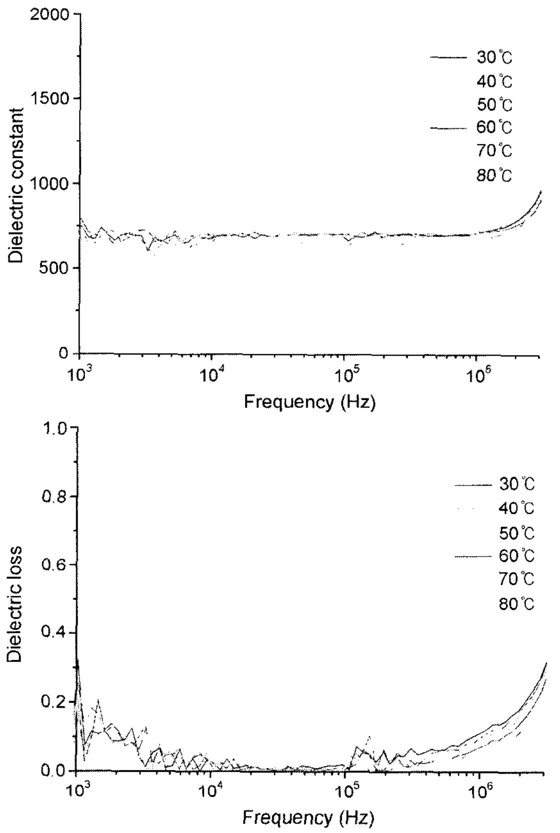


Fig. 4. Frequency dependence of dielectric constants and losses of Ce,Mn:60SBN (1350°C sintered specimen).

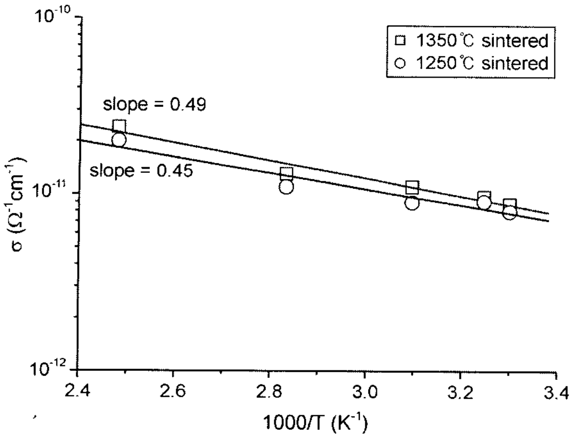


Fig. 5. Temperature dependence of conductivity for Ce,Mn: 60SBN sintered at 1350°C and at 1250°C respectively.

temperature-conductivity curves can be divided into several segments and in each of them (T) is fitted by the function

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

with various values of the pre-exponential term (σ_0) and activation energy (E_a). For temperature under 150°C, the activation energy value indicate about 0.45~0.49 eV. Numerical values over this temperature range are not always available but it is evident from $\log \sigma = f(1/T)$ plots that the slope angles differ by a large factor.

Conductivity and activation energy are greatly affected by temperature and the environment atmosphere in the heat treatment process. These are affected also by heat treatment temperature. At a very low temperatures a stretched-exponential function has to be used for the description of the polaron decay. Due to a tunneling process at low temperatures, the activation energy of the Nb^{4+} polaron cannot be determined.[26,27)] However, in case of Ce-doped SBN sintered at higher temperature, higher mobility of these polarons may reduce the concentration of the polarons that are close to an iron trap, i.e., the polarons are distribute more homogeneously over the crystal and move farther away from the deep donors than at lower temperature.

In this study, electrical charge carrier transport is considered to carry out by the strain field induced thermal fluctuation and the weak Nb^{4+} polaron. Although the activation energy of ceramic system is affected by electric frequency, cerium and manganese in $Sr_{0.6}Ba_{0.4}Nb_2O_6$ has comparatively higher values. If cerium and manganese doped SBN can be obtained by single crystal, for applications such as optically gated holographic storage in SBN, the results obtained in this study seem to be very helpful.

4. Conclusions

At sintering temperature of both 1250°C-10 h and 1350°C-10 h only SBN phase was appeared. Porosity affects dielectric properties of Ce,Mn:SBN ceramics having single phase. Dielectric behavior for temperature was observed as Diffusive Phase Transition (DPT). Dielectric constants are almost equal at all frequency region, but dielectric dispersion was appeared at high frequency of above 100 kHz. A small amount of CeO_2 and MnO_2 dopants have no influences on the structural and compositional homogeneity. Dielectric dispersion at high frequency and low dielectric loss give to advantage for optical applications. In temperature dependence of conductivity of Ce,Mn:SBN, the activation energy was calculate to 0.45~0.49 eV.

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