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Substitutional behavior and dielectric property of $x(Na_{0.5}K_{0.5})NbO_3–(1-x)$ $BaTiO_3$ using x-ray absorption fine structure spectroscopy

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Abstract

The doping effect of $(Na_{0.5}K_{0.5})NbO_3$ (NKN) on the dielectric properties of $BaTiO_3$ have been investigated through the local atomic structure analyses. The dielectric constant of a specimen with $x = 0.05$ was about 105% higher than that of pure $BaTiO_3$. Through Ti *K*-edge x-ray absorption near edge structure (XANES) spectroscopy, it could be determined that the improved dielectric properties are due to the donor substitution by Nb-doping in the B-site. An increase in the XANES intensities with x indicates an increase in degree of hybridization, relating to the donor level, which leads to an increase in conduction electrons. Thus, the enhancement of the dielectric properties is attributed to the increased polarization interaction between the conduction electrons and the relaxation mode. The polarization of the electrons is confirmed by the comparative analysis of bond length data between Ti–O and Nb–O, derived from Ti and Nb *K*-edge extended x-ray absorption fine structure (EXAFS) spectroscopy.

Keywords: C. Dielectric property; $(Na_{0.5}K_{0.5})NbO_3–BaTiO_3$; Donor substitution; Relaxation mode; X-ray absorption fine structure

1. Introduction

The ongoing development of mobile electronic devices has resulted in demands for higher capacitance and further miniaturization for multilayer ceramic capacitors (MLCCs) [1,2]. The electrical properties of basic ferroelectric materials such as $BaTiO_3$ are commonly enhanced by additive doping strategies [2–4]. A chief effect of many doping strategies is the development of relaxor ferroelectric behavior, where a dispersed ferroelectric phase transition occurring over a broad temperature range is obtained instead of a single sharp phase transition at the Curie point. This effect enables the maintenance of a high and stable dielectric constant in doped $BaTiO_3$ even down to room temperature [5]. Among relaxor dopant candidates for $BaTiO_3$, $(Na_{0.5}K_{0.5})NbO_3$ (NKN) has received particular recent attention as an alternative to the previous rare-earth additives because of its excellent dielectric and insulation resistance properties [2,6,7].

When NKN is added in $BaTiO_3$, substitution of Na^+/K^+ (ionic radii=0.97 Å/1.33 Å) on the Ba^{2+} site (1.34 Å) and substitution of Nb^{5+} (0.69 Å) on the Ti^{4+} site (0.68 Å) is achieved. This substitution improves the temperature stability of the dielectric constant by minimizing the amount of change in the tetragonality. The Na^+/K^+ and Nb^{5+} dopants also act as acceptors and donors, respectively, which results in an enhancement of the electrical properties of these dielectrics [8]. Especially in the case of B-site doping, the substitution of Nb^{5+} on the Ti^{4+} site creates conduction electrons. The generated free electrons could be non-randomly distributed within each cluster of off-center Ti^{4+} ions, which increases the local dipole moment of each local cluster. This free conduction electron behavior, through the mutual interaction with the dielectric relaxation mode in Nb-doped $BaTiO_3$, contributes to the improved dielectric properties and temperature stability [9,10]. Additionally, when Na^+ or K^+ ions are substituted for Ba ions, oxygen vacancies are generated to compensate for the

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loss of charge (oxygen vacancy compensation). They combined with $Na_{Ba}^{'}$ or $K_{Ba}^{'}$ to form defect dipole pairs, which help suppress domain wall migration, therefore decreasing the dielectric loss and improving the insulation resistance [8].

In this study, we apply Ti and Nb *K*-edge x-ray absorption fine structure (XAFS) analysis to understand in detail the mechanisms that contribute to the variation in dielectric constant and temperature stability for $x(Na_{0.5}K_{0.5})NbO_3$–$(1-x)BaTiO_3$ (NKN–BT) as a function of the NKN dopant concentration (x). In particular, we attribute the enhancement of dielectric properties to the polarization induced by conduction electron from donor substitution on the B-site.

2. Experimental procedure

$x(Na_{0.5}K_{0.5})NbO_3$–$(1-x)BaTiO_3$ (NKN–BT, $x=0$, 0.01, 0.05) powders were prepared by solid-state reaction. The oxide compounds of $BaCO_3$ (Aldrich, ≥99%), TiO_2 (Aldrich, 99.8%), Na_2CO_3 (Junsei, 99.0%), K_2CO_3 (Junsei, 99.5%), and Nb_2O_5 (Alfa, 99.9985%) were mixed and ball-milled with zirconia grinding media in ethanol for 24 h, and then dried in an oven. The dried powders were calcined at 1000 °C for 3 h. After remilling for 24 h, the powders were dried and pressed into disks at a pressure of 1000 psi. The samples were sintered at 1320 °C for 2 h in a reduced-oxygen atmosphere. Ag paste was applied on both sides of the sintered bodies to obtain contact electrodes. Table 1 summarizes the samples and their short-hand denotations according to their $(Na_{0.5}K_{0.5})NbO_3$ content.

The dielectric constant and the temperature coefficient of capacitance (TCC) were measured over a temperature range from −55 to +150 °C, using an LCR meter (Agilent, E4980A) at 1 kHz ± 10% and 1.0 ± 0.2 V. X-ray absorption spectroscopy (XAS) experiments were performed at the Ti and Nb *K*-edge using the extended x-ray absorption fine structure (EXAFS) facility installed at the 1D and 7D beam line in the Pohang Accelerator Laboratory (Korea), respectively. The storage ring operated at 2.5 GeV with an injection current of 200 mA. The samples were ground to a fine powder in a mortar and were then packed into a 0.5 mm thick cell. The XAS data were collected at room temperature in transmission mode, using Ar/He gas-ionization detectors. In order to accurately retrieve the x-ray absorption near edge structure (XANES) spectra, data were recorded at a step size of 0.2 eV in the edge region, where a Si (111) double crystal monochromator was employed.

Table 1
Denotation of $x(Na_{0.5}K_{0.5})NbO_3$–$(1-x)BaTiO_3$, according to $(Na_{0.5}K_{0.5})NbO_3$ content.

$(Na_{0.5}K_{0.5})NbO_3$ content	Composition	Denotation
$x=0.00$	$BaTiO_3$	BT
$x=0.01$	$0.01(Na_{0.5}K_{0.5})NbO_3$–$0.99BaTiO_3$	NKN01–BT
$x=0.05$	$0.05(Na_{0.5}K_{0.5})NbO_3$–$0.95BaTiO_3$	NKN05–BT

3. Results and discussion

The dielectric constant and temperature coefficient of capacitance (TCC) of the NKN–BT ceramics with different NKN concentrations were measured as a function of temperature as shown in Fig. 1. Considering the both effect upon the dielectric constant and TCC values, NKN05-BT was optimized condition with the maintenance of a high and stable dielectric properties over a broad temperature range. At the allowable operating temperature of the electric component (55 °C), NKN05–BT exhibited the highest dielectric constant ($\varepsilon \approx 3500$), an enhancement of 105% compared to pure $BaTiO_3$. The TCC characteristics also satisfied the X7R specification (−55 to +125 °C, ±15%).

The enhancement of the dielectric properties can be explained by local structural changes caused by the substitution behavior of NKN in $BaTiO_3$. Local structure changes are primarily attributed to the B-site substitution of Nb^{5+} ions [10]. Nb-doping of the B-site can be represented by the following defect equation.

$$Nb_2O_5 + 2Ti_{Ti} \rightarrow 2Nb_{Ti}^{o} + 1/2O_2 + 2e' + 2TiO_2 \quad (1)$$

The substitution of Nb^{5+} ions on the Ti^{4+} site generates conduction electrons to maintain charge neutrality (donor–dopant electron compensation). The addition of Nb^{5+} ions as donor impurities contributes electron energy levels high in the $BaTiO_3$ band-gap so that electrons can be easily excited into the conduction band. The donor–dopant shifts the effective Fermi level to a point about halfway between the donor levels and the conduction band [11,12]. That is, the Fermi level of NKN-BT is higher than that of pure BT, and approaches the conduction band with increasing content of the donor dopant.

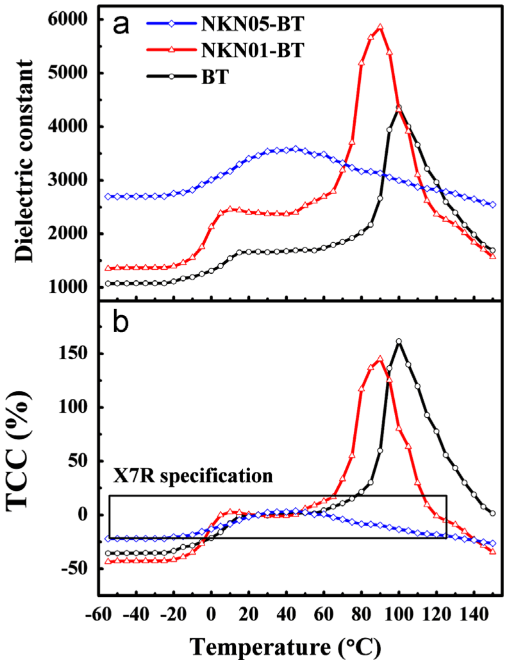

Fig. 1. Temperature dependence of: (a) the dielectric constant and (b) the temperature coefficient of capacitance (%) for $x(Na_{0.5}K_{0.5})NbO_3$–$(1-x)BaTiO_3$ with $x=0.00$, 0.01, and 0.05.