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Effect of amphoteric dopant on the dielectric and structural properties of yttrium doped potassium sodium niobate thin film

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ABSTRACT

The amphoteric dopant effects on dielectric and structural properties of KNN were studied. The trace amounts of dopant were incorporated into the KNN lattice and formed the orthorhombic perovskite structure. The distribution of yttrium dopant on the perovskite lattice is responsible for enhancement of dielectric behaviors of KNN films. The dielectric loss is reduced from 0.18% to 0.0125%, owing to the distribution of yttrium dopant at A-site lattice. Meanwhile, the tendency of Y^{3+} to occupy the B-site lattice at high dopant concentration causes an increase in dielectric loss. The particles size of the KNN at 0.5 mol% yttrium was found to be uniform while porous structures were formed with increasing dopant concentration.

1. Introduction

K$_{0.5}$Na$_{0.5}$NbO$_3$ or KNN-based piezoceramics is important in the fabrication of electric and electronic devices such as capacitors, sensors, energy harvesters, and actuators [1,2]. Much of the focus was on improvements of the electrical properties of KNN by accommodating the KNN lattice with a large number of dopants with different ionic radius. Currently, there is growing interest on the influence of trivalent rare-earth dopants (Nd^{3+}, Dy^{3+}, and La^{3+}) on the electrical properties of KNN [3,4]. The reason for this is that rare-earth dopants are known as a catalytically active material with low diffusivity characteristics, which lowers the dissipation factor thus, suit for many applications [5]. For example, Yb^{3+} was incorporated into fiber for optical switching whereas Tb^{3+} was doped on glass for high-power laser devices [6,7]. Apart from these rare-earths, yttrium (Y^{3+}) is desirable for KNN based materials principally due to ability to improve remanent polarization, leakage current and fatigue endurance [8,9]. These characteristics are important for ensuring the stability of material performances in various conditions and applications.

The ionic radius is an important parameter that mainly determines the distribution site in the KNN lattice. La^{3+}(1.15 Å) and Nd^{3+}(1.08 Å) are exclusively distributed at K$^+$, Na$^+$ (1.02 Å and 1.38 Å) site, because their size is incompatible with that Nb^{5+}. However, Y^{3+} was extensively investigated in other piezoceramics since the distribution site is not exclusive but depends on dopant concentrations [10,11]. Yttrium is known as amphoteric dopants, because it could distribute at A-site and B-site lattices with respect to the concentration up to three stages [12]. In the first two stages, dopant located at the A-site and B-site lattices, respectively. The third stage is over the limit of dopant and a secondary phase appears [13]. The effects of amphoteric dopant on KNN properties are difficult to find in the literature [14]. In this work, the yttrium-doped KNN films were synthesized at different concentrations using sol gel and spin coating techniques. The thin film was preferred in this study instead of the bulk ceramic for easy miniaturization in electronic devices.

2. Experimental procedure

KNN thin films were deposited on silicon substrates by sol-gel and a spin coating technique. Potassium acetate (CH$_3$COOK), sodium acetate (CH$_3$COONa), and niobium ethoxide (Nb$_2$OC$_2$H$_5$)$_{10}$ were used as starting precursors. 2-methoxyethanol (2-ME) was used as solvent. Yttrium nitrate hexahydrate (Y (NO$_3$)$_3$6H$_2$O) was used as a source dopant. All precursors and dopant source were dissolved in 2-ME with added acetylacetone as sol stabilizer. The concentration of dopant varies at mol%=0, 0.1, 0.3, 0.5, 0.7, and 0.9. The solution was stirred vigorously for 1.5 h to yield a clear and homogenous solution. Subsequently, the mixed solution was

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spun onto the Si substrate at 3000 rpm for 60 s to produce the thin films. After spinning, the wet films were pyrolysed at 200 °C for 5 min. The procedures from the coating to pyrolyse were repeated five times until a well-defined thickness was achieved. The thin films were then annealed in the rapid thermal annealing furnace (RTP-1000D4, MTI) for 5 min at 650 °C. The crystalline phase and orientation were determined by X-ray diffraction (XRD) using PANalytical X'Pert Pro with CuKα radiation. The morphology of grown thin films was examined by field emission scanning electron microscopy (FESEM, Hitachi-51400) operating at 10 kV. Further investigations on microstructure of thin films were performed by using high resolution transmission electron microscopy (HRTEM, FEI Technai). The thinned lamellae for HRTEM were prepared with focused ion beam (FIB) with operating voltage of 30 kV. The dielectric properties were then measured using LCR meter (Agilent, U1700) at frequency of 100 kHz.

3. Results and discussion

Fig. 1 shows XRD patterns of yttrium-doped KNN thin film at various concentrations. The diffraction peaks could be clearly indexed to a perovskite structure of KNN. After analyzing the peak located between 20° < 2θ < 80°, KNN films show the existence of rich orthorhombic phase with no secondary peak detected. Additionally, no formation of yttrium oxide phase depicted that Y^{3+} dopant successfully distribute at KNN lattice. However, the intensity of KNN peak depends on the Y^{3+} concentration. A weak perovskite peak was observed in the KNN films as the concentrations continue to increase. This indicates that increasing Y^{3+} concentration would deteriorate the crystallinity of films [15]. Fig. 2 shows the lattice parameter determined by XRD. It is believed that yttrium occupies the A-site lattice at lower dopant concentration and lattice parameter decrease sharply due to r (Y^{3+}) < r (K^+/Na^+). However, the increase of dopant concentration leads the increase in the lattice parameter. When the yttrium concentration increases, it tends to accommodate the B-site lattice rather that A-site. Since r(Y^{3+}) > r (Nb^+), the crystal lattice is expanded by occupation of Y^{3+} at B-site therefore rise up the lattice parameter [16,17].

Fig. 3 shows the plotted variation of dielectric properties with respect to yttrium concentration. The dielectric loss lowered greatly from 0.18% for pure film to 0.012% at 0.5 mol% doped KNN. However, the permittivity does not get greatly reduced. Subsequently, the loss tangent rises and relative permittivity continues to fall as the Y^{3+} concentration continues to increase. From the result, it can be seen that Y^{3+} ion can restrain the dielectric loss of KNN films significantly. This might be related to the consequence of yttrium distribute at A- site at the first stage. According to Eq. (1), when the Y^{3+} is distributed at A-site, the excess charge will be formed (·2e) and the charge in the B-site will be electronically compensated. Theoretically, the major charge carriers before doping are A-site vacancies and oxygen vacancies. Hence, after being added with dopant, the major carriers will be reduced and causes the dielectric loss to be lowered remarkably as more conduction electron formed.

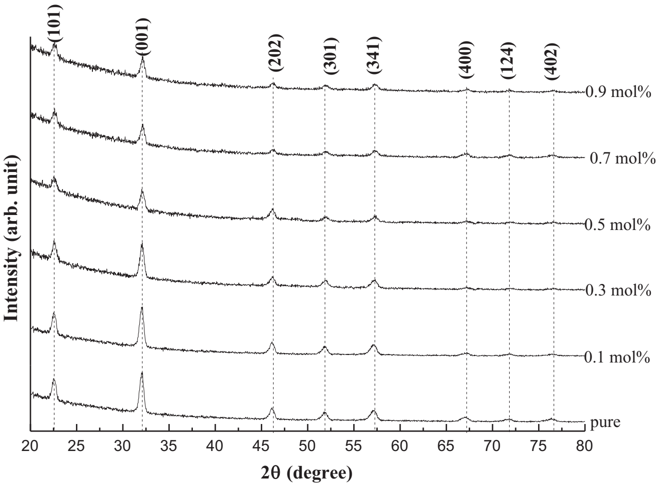

Fig. 1. X-ray diffraction patterns of yttrium-doped KNN films.

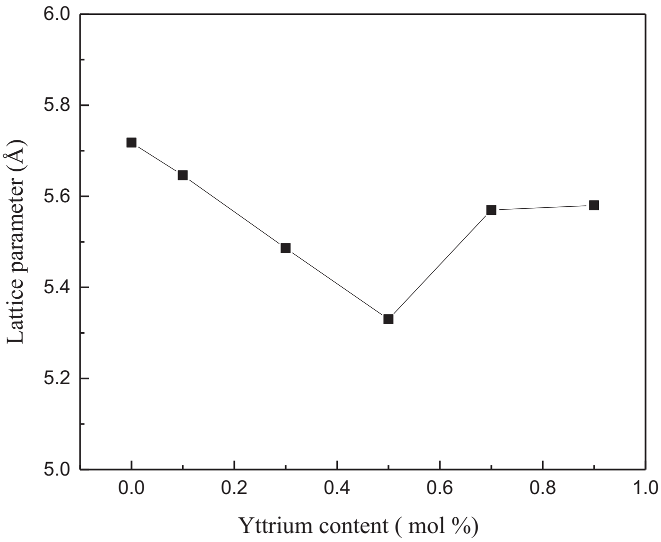

Fig. 2. Lattice parameter of yttrium doped KNN ad different dopant concentration.

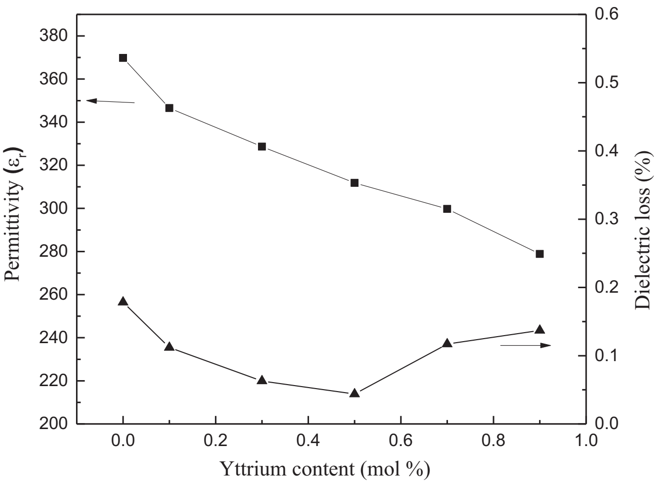

Fig. 3. Variation of dielectric properties as regard to yttrium content in KNN films.

$$xY^{3+} + (K^+, Na^+)NbO_3 \rightarrow (K^+, Na^+)1 - xY_x^{3+})[Nb_{1-x}^{5+}(Nb^{5+}\cdot 2e)x] O_3 + x(K^+, Na^+) \qquad (1)$$

In contrast, Y^{3+} tends to occupy the B-site lattice with increasing dopant concentration. At this stage, Y^{3+} is ionically compensated by Nb^{5+} to maintain electroneutrality and behaves as an acceptor, as shown in Eq. (2). Due to charge compensation at B-site, the interaction between Nb^{5+} and O^{2-} become weaker which makes the oxygen easily volatile, resulting in the formation of oxygen vacancies [18]. Afterwards, the oxygen vacancies promote localised point defects which in turn increase the dielectric loss [12]. The oxygen vacancies also contribute to the dielectric relaxation therefore cause the permittivity to decrease