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ENHANCED STRUCTURAL AND ELECTRICAL PROPERTIES OF LEAD-FREE Y-DOPED (K, Na) NbO_3 THIN FILMS

Maziati Akmal[a], Umar Al-Amani[b]*, Mohd Warikh[a], Nurul Azuwa[a]

[a]Fakulti Kejuruteraan Pembuatan, Universiti Teknikal Malaysia Melaka, 76100, Melaka, Malaysia
[b]Fakulti Teknologi Kejuruteraan, Universiti Teknikal Malaysia Melaka, 76100, Melaka, Malaysia

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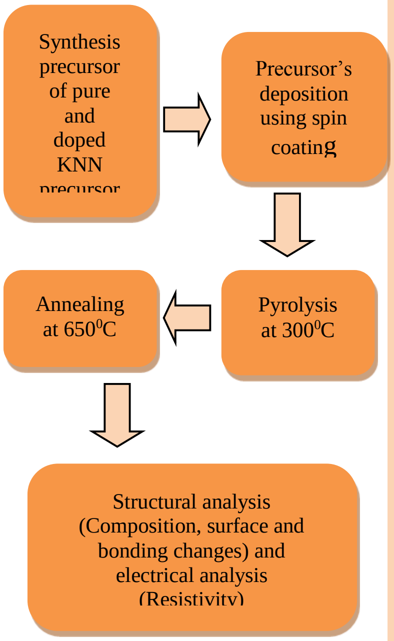
*Corresponding author
umar@utem.edu.my

Graphical abstract



Abstract

Yttrium- doped KNN thin films were grown on Si substrates using the sol-gel technique. The profound effects of Yttrium with different content element (mol % = 0, 0.1, 0.3, 0.5, 0.7 and 0.9) on the structural and electrical properties of KNN films were analyzed. The doped samples demonstrated a mainly uniform and homogenous microstructure with grain size less than 100 nm. The existence of Y Ka line shown in EDX spectrum confirmed the presence of Y-dopant in KNN based-compound. Small shift position of the Raman peaks indicated that Y incorporated on the interstitial A-site while broaden FWHM ascribed that Y preferably enters B-site lattice at high dopant concentration. The enhanced electrical resistivity at 0.5 mol % Y suggested that more conduction electrons were formed in KNN lattice structure.

Keywords: KNN; yttrium; thin film; doped; rare-earth

Abstrak

Filem nipis Y-dop KNN telah dihasilkan pada substrat Si menggunakan teknik sol-gel. Kesan Yttrium dengan unsur kandungan yang berbeza (mol % = 0, 0.1, 0.3, 0.5, 0.7 dan 0.9) terhadap ciri-ciri struktur dan elektrik filem KNN dianalisis. Sampel yang mangandungi unsur dop menunjukkan struktur permukaan yan seragam dengan saiz ira kurang dari 100 nm. Kehadiran spectra Y Ka yang ditunjukkan pada spectrum EDX mengesahkan kehadiran Yttrium sebagai unsur dop dalam komposisi asas, KNN. Perubahan kecil pada kedudukan puncak Raman menunjukkan bahawa Y telah ditempatkan pada kekisi A manakala pelebaran FWHM menunjukkan Y telah memasuki kekisi B pada kandungan dopan yang tinggi. Peningkatan kadar rintangan elektrik pada kandungan 0.5 mol% mencadangkan bahawa lebih banyak pengaliran elektron dibentuk dalam struktur kekisi KNN.

Keywords: KNN; yttrium; filem nipis; dop; nadir bumi

1.0 INTRODUCTION

Piezoelectric and ferroelectric materials belong to the group of smart materials as their properties can be significantly modified by external stimuli [1]. Lead zirconate titanate or PZT have dominated the market of ferroelectric materials for last five decades. However, the preparation and application of PZT caused severe lead pollution and environmental problems. Hence, this is a rationale to develop new lead-free piezoelectric materials substituting PZT. Potassium sodium niobate (KNN) is the one of the most promising candidates for this aim.

Alkaline niobate possess high electromechanical coupling coefficient (0.55), and high phase transition temperature (420°C) favor the use of high-temperature applications [2-3]. However, it was reported that the proportion of K, Na and Nb is likely to deviate from stoichiometry due to the volatilization of K and Na at elevated temperature. Theoretically, the intrinsic defects resulted from volatility issues led to poor ferroelectric and piezoelectric properties of KNN [4-5]. This makes the substitution of conventional PZT with KNN is very challenging.

To solve this problem, several options have been studied. This could be achieved by doping of A-site ions, $(K_{0.5}, Na_{0.5})^+$ and/or B-site ion Nb^{5+} [6]. Moreover, the doping technique is believed to be an effective way to improve ferroelectric and piezoelectric properties of KNN. Through this approach, KNN based materials have chemical stability by equilibrating the ions charge which would reduce local stress and reduces the concentration of oxygen vacancies [7].

Rare-earth elements (i.e., Y_2O_3, Nd_2O_3, CeO) were suitable dopants to be substituted in the perovskite structure of KNN. It was stated that rare-earth elements are known to demonstrate useful functions of stabilizing and lowering dissipation factor in dielectric ceramics [8]. In previous work on barium titanate ($BaTiO_3$ or BT) with ABO_3 structure, it is known that the appropriate amount of CeO_2 could enhance piezoelectric and dielectric constant of lead-free piezoelectric ceramics. A similar technique could be used to compensate the volatility of K and Na in KNN.

However, the research of Yttrium-doped KNN has not been reported so far. Notably, the ionic radii of Y^{3+} is 0.91 Å, in between the radius of K^+, Na^+ (1.02 Å and 1.38) Å and Nb^{5+} (0.69 Å). Thus, Y ion can be called as amphoteric ion as $r(Nb^{5+}) \leq r(Y^{3+}) \leq r(K^+, Na^+)$ [9]. Therefore, the intermediate ion would occupy both A-site and B-site of KNN lattice.

In this present study, Y-doped KNN thin film was synthesized using the sol-gel technique. The compositional dependence of structural evolution and electrical properties were studied to provide an alternative approach for lead-free materials development.

2.0 EXPERIMENTAL

The KNN solutions were prepared using sol-gel synthesis. Two alkaline precursors which are potassium acetate and sodium acetate were used as starting solutions. In order to compensate the loss of alkaline element, different content of rare-earth element (mol % = 0, 0.1, 0.3, 0.5, 0.7 and 0.9) was added to precursor solutions. These chemicals were dissolved in a polar organic solvent, 2-methyoxyethanol with constant stirring at room temperature. After stirring vigorously for 1 hour at room temperature, a mixed solution of niobium ethoxide and acetylacetone was added dropwise to the prepared KNN precursors.

The resultant solutions were kept standing at 80°C for 1 hour. The solutions were then deposited on the Si substrates to produce the thin films. The films were spun onto the wafer at 2000-3000 rpm for 60 seconds. After spinning, the wet films were heated at 650°C for 5 minutes. Then, the thin films were annealed for 30 minutes at 650°C in the furnace. The thickness of the film was set at approximately 200 nm by repeating the coating/heat treatment cycle.

The grain morphology and the chemical composition of grown thin film were examined by Field Emission Scanning Electron Microscopy (FE-SEM) with the electric potential of 10 kV. Phonon vibration properties of KNN thin films with different compositions were measured by using Raman scattering spectrometer with a wavelength of 588 nm. The resistivity of these films was measured at room temperature with the testing frequency of 1 kHz. Figure 1 shows a sequence of processes involved in this work.

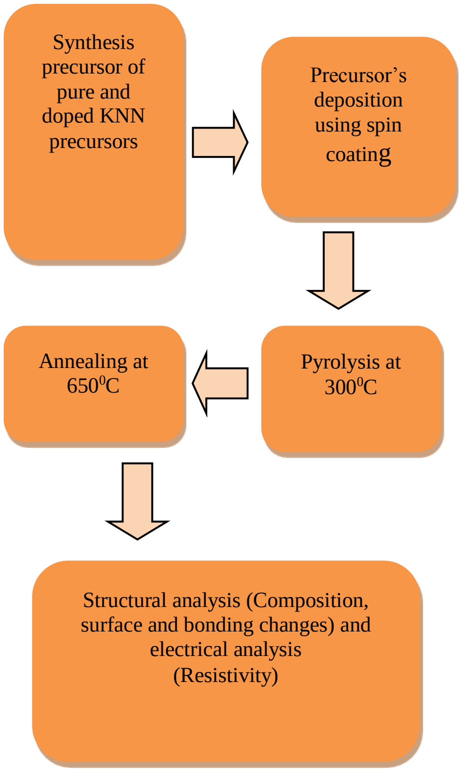


Figure 1 A sequence of experimental procedures

3.0 RESULTS AND DISCUSSION

3.1 Chemical composition and structure of KNN films

Figure 2 depicts the EDX spectrum of KNN films with nominal heterogeneities. The elemental composition composed of K, Na, Y, Nb, and O elements. It is confirmed that Y dopant is successfully doped on the KNN crystal lattice due to high level of Yttrium in the average KNN spectra.

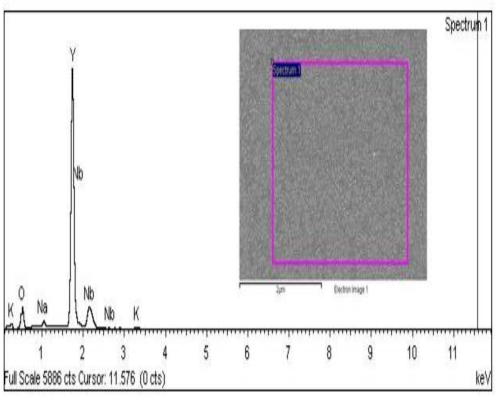


Figure 2 EDX spectrums for Y-doped KNN

Grain formation of pure and doped KNN films is presented in Figure 3. It can be seen that the grain size is less than 100 nm. The existence of inhomogeneous grains and open matrix implied that the evaporation of alkaline element occurs in pure KNN as presented in Figure 3a. The microstructure becomes denser at yttrium = 0.5 mol % (Figure 3b). Hence, it confirms that Y^{3+} readily enters the crystal lattice [10].It is believed that formation dense and fine grain is due to the restrained grain-growth. This result is in line with other findings which found that the rare-earth materials would inhibit the grain growth of host material as the lattice diffusion is decreased and the mass transportation is weakened. Consequently, this behavior promotes to the dense and fine structure [11-13].

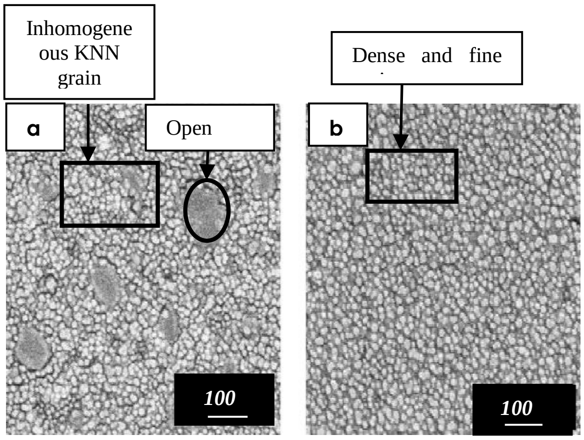


Figure 3 FESEM micrographs of a) undoped KNN (b) 0.5 mol % Y-doped KNN.

3.2 Vibration States Of KNN Molecules

As prepared KNN and Y-KNN thin films were analyzed by Raman spectroscopy. The typical vibration (Figure 4) confirmed the presence of KNN perovskite structure [14]. A high Raman intensity at 520 cm^{-1} can be observed due to the typical signal of Si substrate [15]. Additionally, the result depicted the present of three dominant peaks A_1 (LO) and A_1 (TO) modes evolved around 300 cm^{-1}, 619 cm^{-1}, and 860 cm^{-1}.These peaks were identified as internal vibration of the NbO_6 octahedron, namely the O–Nb–O bending vibration (300cm^{-1}) and Nb-O stretching vibration (619cm^{-1} and 860cm^{-1}) [16-17].

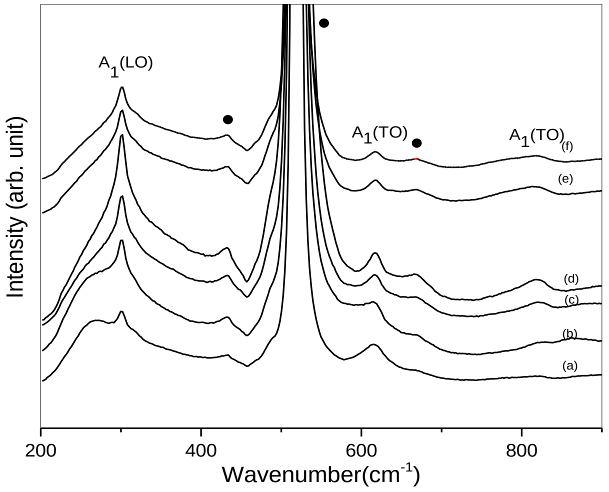


Figure 4 KNN thin films deposited on Si substrate with different Yttrium concentration, where (a) - (f), mol % = 0, 0.1, 0.3, 0.5, 0.7, 0.9 respectively. • Indicates the bands corresponding to Si substrate.

Raman peak frequencies as well as FWHMs of the two strong internal modes (300 cm^{-1} and 619 cm^{-1}) were extracted (Figure 5 (b) and (d)) through fitting the focused profile (Figure 5 (a) and (c)) with individual Lorentzian function. The decrease of full-width half maximum (FWHM) with Yttrium content < 0.5 mol%, reflecting a better crystallinity of doped KNN structure. Upon substitution of Yttrium dopant, the two vibration modes were shifted to the higher wave number. It was reported that the vibration shifts between KNN and doped KNN films prove that dopant was substituted into the KNN lattice structure [18-19].

Notably, no obvious frequency shifting of these two modes when Y- doped KNN in the range of Y = 0.1 - 0.5 mol %. This phenomenon implies that Y prefers to substitute into A- site of KNN due to less octahedron distortion [18]. However, the vibration peaks shifted gradually with increasing Y doping > 0.5 mol %, accompanied by substantial changes in Raman scattering intensity and FWHM. This might be attributed to the Nb-O angles distortion as a result of Y^{3+} substitution into Nb^{5+} sites [12]. Hence, the interaction between dopant with Nb ions is responsible for forward shifting of the frequency [12, 20].

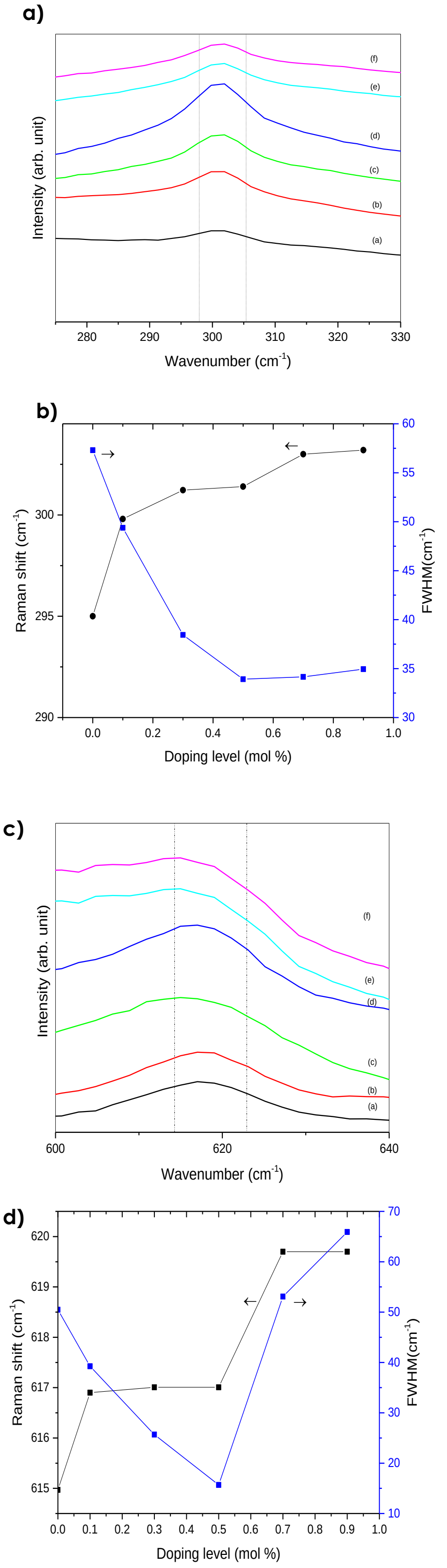


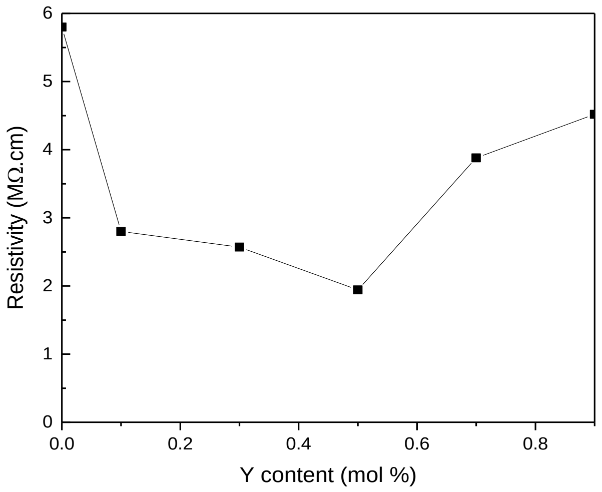
Figure 5 a) Magnified view of 300 cm $^{-1}$, b) The frequency shifts and FWHMs of 300 cm $^{-1}$ at various mol%, c) Magnified view of 619 cm $^{-1}$ d) The shifts and FWHMs of 300 cm $^{-1}$ various mol%

3.3 Electrical Resisitivity Behaviour

Figure 6 depicts the resistivity of thin films at room temperature. The introductions of Y dopant in the range of 0.1- 0.5 mol% reduce the resistivity of KNN films significantly. The enhanced resistance magnitude in doped KNN films is due to the introduction of Y dopant. Due to extra positive charge at A- site of doped KNN lattice, charge imbalance created and compensated by cation vacancies [21-22]. Thus, as Y concentration increases, the number of conduction electron increases, causing an abrupt decrease in resistivity. It is generally attributed to electronic compensation of the incorporated cation.

Yet, the effect of Y on KNN resistivity is negligible at Y> 0.5 mol % due to immobility of cation vacancies. Hence, the dominant ionic mechanism results in substantial increase in electrical resistivity of KNN films at Y> 0.5 mol %. Similar compensation mechanisms were found in A-site and B-site perovskite lattice of BaTiO3 which give the comparable result [22]

Figure 6 Resistivity of KNN films as a function of Yttrium content



4.0 CONCLUSION

The significant conclusion may be drawn from the present work:

a) Y dopant promotes densification and produces fine microstructure.
b) The broaden FWHM at higher dopant concentration is due to the octahedron distortion at B-site of KNN perovskite structure.
c) The electrical resistivity is mainly controlled by Y-doping on A-site or B site of KNN lattice. The doped KNN films with low content of Y exhibit excellent electrical properties.
d) The variation in structural and electrical properties indicates strong dependency of KNN on Y substitution.

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