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Structural and electrical properties of $K(Ta,Nb)O_3$ thin film prepared by sol-gel method for electrocaloric devices

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This study investigated the structural and electrical properties of thin $K(Ta_{0.6}Nb_{0.4})O_3$ films for their applicability to electrocaloric devices. Both of the sol-gel and spin coating methods were used to fabricate thin films. Those sintered at 650 °C showed a KTN phase with pyrochlore of $K_2Ta_2O_6$, but those sintered at 750 °C showed pure polycrystalline phase without a pyrochlore phase. The lattice constants observed were a= 3.990nm. The dielectric constant rapidly decreased due to decrease in polarization of space charge approximately at an applied frequency of 10 kHz. The dielectric constant and loss at 30 °C of the thin films sintered at 750 °C were 3,617 and 0.264. The dielectric constant of the specimen sintered at 750 °C decreased to about -8.27 %/V according to the applied DC field. The remanent polarization and coercive field at 36 °C of the specimen sintered at 750 °C were 20.0 μC/cm^2 and 122.6 kV/cm. When the electric field of 247 kV/cm was applied to the specimen sintered at 750 °C, the highest electrocaloric property of 3.02 °C was obtained.

Keywords: $K(Ta,Nb)O_3$ thin films, Ferroelectric, Electro-caloric effect, Sol-gel method.

Introduction

The $K(Ta,Nb)O_3$ materials with a crystal structure of ABO_3 perovskite is one of the example materials with ferroelectric properties. These exhibit changes in crystal structure and various electrical properties according to a composition ratio of Ta and Nb ions [1, 2]. In general, the $K(Ta,Nb)O_3$ materials have been studied for their structural and electrical properties according to fabrication conditions and composition ratios [3, 4]. By using their excellent crystallographic and ferroelectric properties, many studies have been conducted on their applicability to piezoelectric transducers, capacitors, infrared sensors, and electro-optical devices [5-8].

Recently, the integration and miniaturization of electronic components has been accelerated by the increasing demand for more miniaturized multifunctional electronic devices. Consequently, the heat generated from individual elements or substrates are recognized as an important issue that needs addressing. Not only does this heat have an impact on the components, but it also effects the performance of the electronic devices. Until now, studies on the heat generation problem in such electronic devices have mainly focused on the improvement of the heat dissipation characteristics of the substrates. Still, a small number of studies on the cooling of devices have been carried out [9-11]. Recently, feasibility of using the ferroelectric materials of $Pb(Zr,Ti)O_3$ as a cooling device has been reported [12]. However, the $Pb(Zr,Ti)O_3$-based materials are limited in practical use due to the environmental problems surrounding the Pb element and the characteristics of a high phase transition temperature.

This study investigated the applicability of thin lead-free ferroelectric films of $K(Ta_{0.6}Nb_{0.4})O_3$ (KTN) as a cooling device. After the films were fabricated by the sol-gel and screen printing methods, structural and electrical characteristics were measured by sintering temperature conditions.

Experimental

In this study, thin ferroelectric films of $K(Ta,Nb)O_3$ were maded by the sol-gel and spin coating methods that are simple to manufacture without requiring any expensive equipment. A phase transition temperature with a composition of Ta:Nb = 60:40 near room temperature was selected to investigate the availability of these films as a cooling device. In an advanced study [13], potassium ethoxide was used to make the $K(Ta_{0.60}Nb_{0.40})O_3$ coating solution, but the results were not good. So, in this study, the experiments were performed using potassium acetate. And, the sol-gel method used in this study is a simple fabrication process, and it is easy to control stoichiometric composition. Potassium acetate (Sigma Aldrich, USA), tantalum ethoxide (Alfa aesar, USA) and niobium ethoxide (Alfa aesar, USA) were used as starting materials with 2-

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methoxyethanol (Alfa aesar, USA) as the solvent. The metal alkoxides used in the experiment were susceptible to moisture, so the solution was manufactured in a nitrogen atmosphere. 10mol% potassium was added to compensate for the volatilization of potassium. Dissolved potassium acetate in 2-methoxyethanol first, then added tantalum ethoxide and niobium ethoxide mixed in 2-methoxyethanol in advance according to the molar ratio 60:40. The three mixed solutions were stirred for 24 h near 100 ºC. After 24 h, acetylacetone was added to stabilize the solution, completing a homogeneous precursor solution. The KTN coating solution was deposited on Pt/Ti/SiO_2/Si substrate, and conducted dried process at 200 ºC for 15 min, pyrolysis process at 400 ºC for 15 min. The previous coating and drying process were repeatd three to six times and finally sintered at 750 ºC for 2 h. The microstructure of the resultant thin film was observed by the field-emission scanning electron microscope (FE-SEM, Philips XL30S FEG) and the crystal structure was determined by X-ray diffraction (XRD) analysis. The electrical properties of films were measured using Pt on the KTN films as the top electrode by using dc sputtering method. Dielectric properties and polarization hysteresis loops were analyzed using a LCR meter (PM-6036, Fluke) and ferroelectric test system (RT66B, NM, USA), respectively.

Results and Discussion

Fig. 1 shows the X-ray diffraction patterns of KTN thin films according to sintering temperatures. The KTN thin films sintered at 650 degrees exhibited a coexistence of KTN crystal and $K_2Ta_2O_6$ pyrocholre phases at an initial stage of crystallization. At a sintering temperature of 700 ºC, the peak of pyrochlore phase was greatly reduced. In the thin films sintered at 750, 800, 850 ºC, only pure KTN phase were observed. The XRD peak's intensity increased and FWHM values decreased to 1.369, 0.364, 0.334, and 0.329 when the sintering temperatures were raised. The thin films sintered at 750 ºC showed a cubic crystal structure with the lattice constants of a = 3.990 nm [14, 15].

Fig. 2 shows the surface and cross-sectional micro-structures of thin KTN films by sintered temperature. The thin films sintered at 650 ºC showed many pores and the secondary phase of $K_2Ta_2O_6$ due to a low sintering temperature. In the specimen sintered at 700 degrees (Fig. 2(a)), no secondary phase was observed. As the sintering temperature increased, the pores decreased while the microstructure was relatively dense. However, pores were distributed in all thin films. In particular, the specimens sintered at 800 ºC (Fig. 2(c)) exhibited an increase in porosity due to volatilization of K ion. The thin films sintered at 750 ºC showed a dense and flat cross-sectional microstructure (Fig. 2(d)). The average thickness of thin KTN films was about 410 nm.

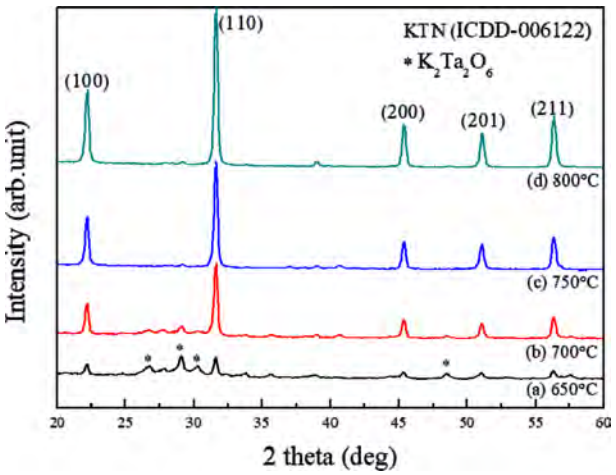

Fig. 1. X-ray diffraction patterns of $K(Ta_{0.6}Nb_{0.4})O_3$ thin films according to the sintering temperature.

Fig. 3 shows the relative dielectric constant and loss of thin KTN films by applied frequency. It shows the typical characteristic of dielectric relaxation [16] in which the dielectric constant decreased when the frequency was raised. The dielectric constant could have abruptly decreased at an applied frequency of around 10 kHz due to the reduced polarization of an internal space charge. The thin films sintered at 750 ºC showed good dielectric constant and loss properties. This is attributed to the reduction of the pyrochlore phase and pores, as shown in Fig. 2 [17].

Fig. 4 shows the relative dielectric constant and loss of KTN films at different temperatures. The relative dielectric constant decreased when the temperature was raised within the range of 10 ºC~90 ºC, while the maximum dielectric loss was around 20~40 ºC. From these properties, the phase transition temperature was considered to be slightly lower than 10 ºC. The phase transition temperature of thin KTN films slightly increased when compared to that of bulk specimens of the same composition (T_c=30 ºC [18]). This seems to have been caused by the stress generated at the interface between thin films and substrates. The thin films sintered at 650 ºC showed a high dielectric loss due to the distribution of secondary phase and pores. The relative dielectric constant and loss at 30 ºC of the specimens sintered at 750 ºC showed excellent properties of 3617 and 0.264, respectively.

Fig. 5 shows the relative dielectric constant of thin KTN films by applied DC voltage. The dielectric constant decreased when the applied DC voltages was raised. This is because the rotation and displacement of dipoles in the unit lattice were suppressed by the applied DC voltage. The slope of dielectric constant according to the DC voltage of the thin films sintered at 750 ºC was about -8.27 %/V.

Fig. 6 shows the hysteresis loops of thin KTN films sintered at 750 ºC as a functional temperature. In the thin films sintered at 650 ºC, crystallization was not

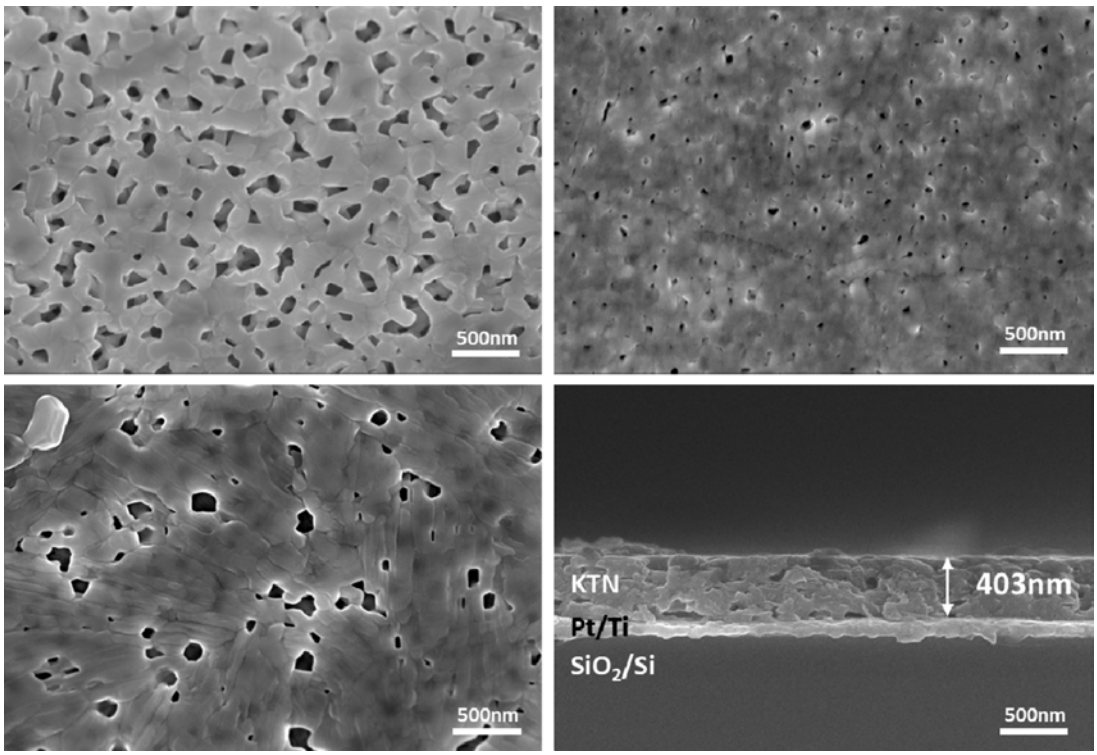

Fig. 2. Surface and cross-sectional microstructures of $K(Ta_{0.6}Nb_{0.4})O_3$ thin films with the sintering temperatures; (a) surface, 700 °C, (b) surface, 750 °C, (c) surface, 800 °C and (d) cross-section, 750 °C.

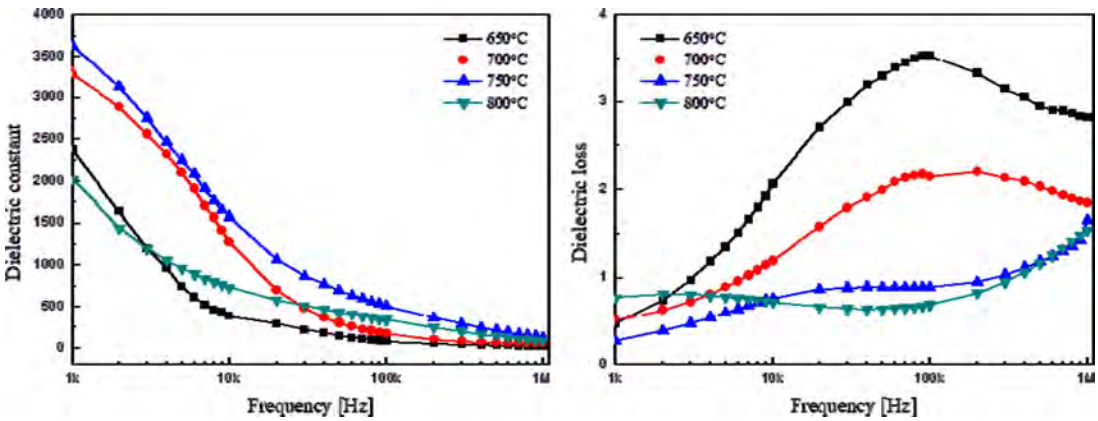

Fig. 3. Relative dielectric constant and dielectric loss of $K(Ta_{0.6}Nb_{0.4})O_3$ thin films with the applied frequency.

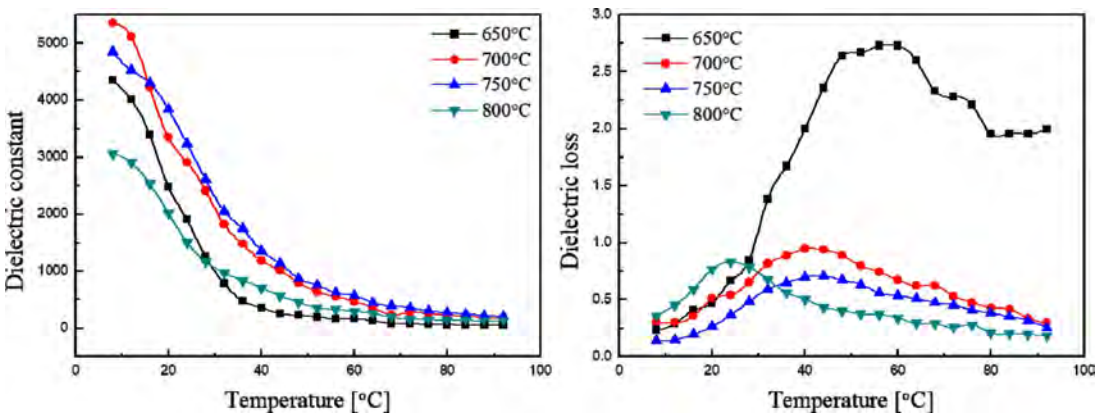

Fig. 4. Relative dielectric constant and dielectric loss of $K(Ta_{0.6}Nb_{0.4})O_3$ thin films.

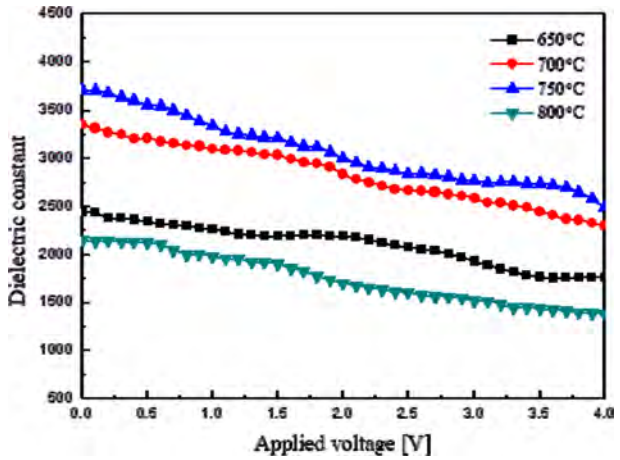

Fig. 5. Relative dielectric constant of $K(Ta_{0.6}Nb_{0.4})O_3$ thin films with DC voltage applied.

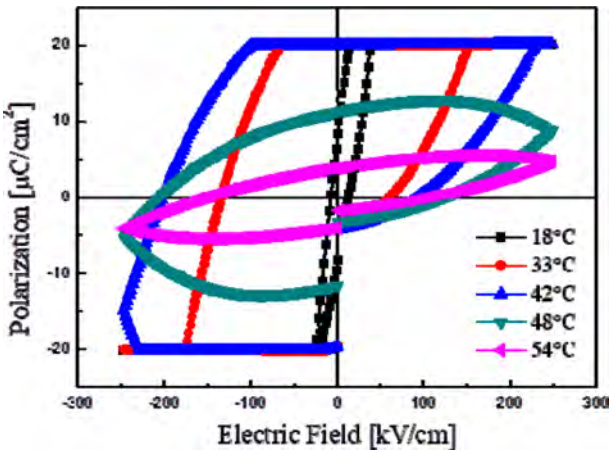

Fig. 6. Hysteresis loops of $K(Ta_{0.6}Nb_{0.4})O_3$ thin films sintered at 750 °C.

performed due to a low sintering temperature, as shown in the XRD properties of Fig. 1. The thin films sintered at 750 °C showed the highest remanent polarization as well as coercive field properties of 20.0 μC/cm^2, and 122.6 kV/cm at 36 °C, respectively. When the measured temperature became higher, the remanent polarization and coercive fields decreased, while disorder in the dipole arrangement increased. The ferroelectric properties of thin KTN films were greatly influenced by pores and crystallinity in the secondary phase.

Fig. 7 shows the remanent polarization of thin KTN films by temperature and applied voltage. While the remanent polarization at 10 °C were fixed at the maximum value, this figure shows the relative change in properties at different temperatures. In the thin films sintered at 750 °C (Fig. 7(b)), an abrupt decrease in remanent

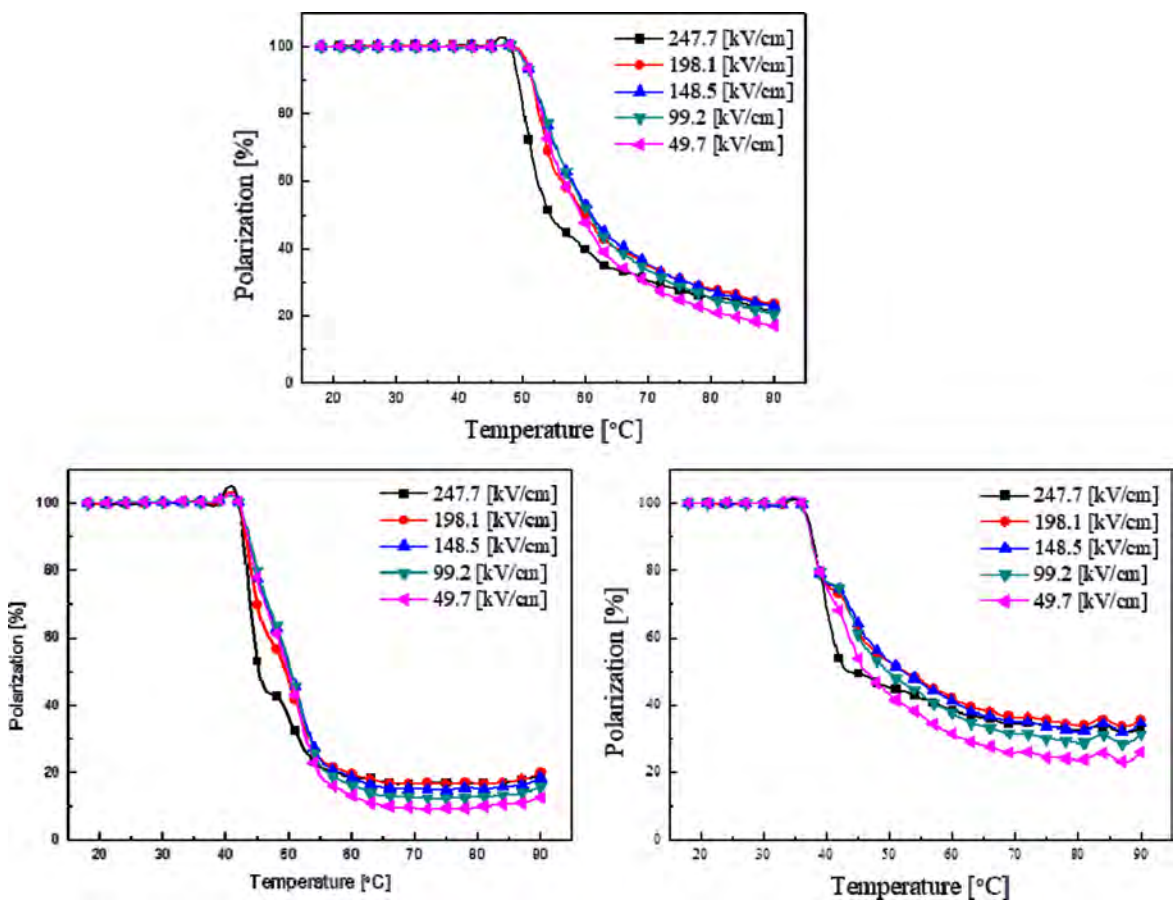

Fig. 7. Polarization of $K(Ta_{0.6}Nb_{0.4})O_3$ thin film with temperature and voltage application.

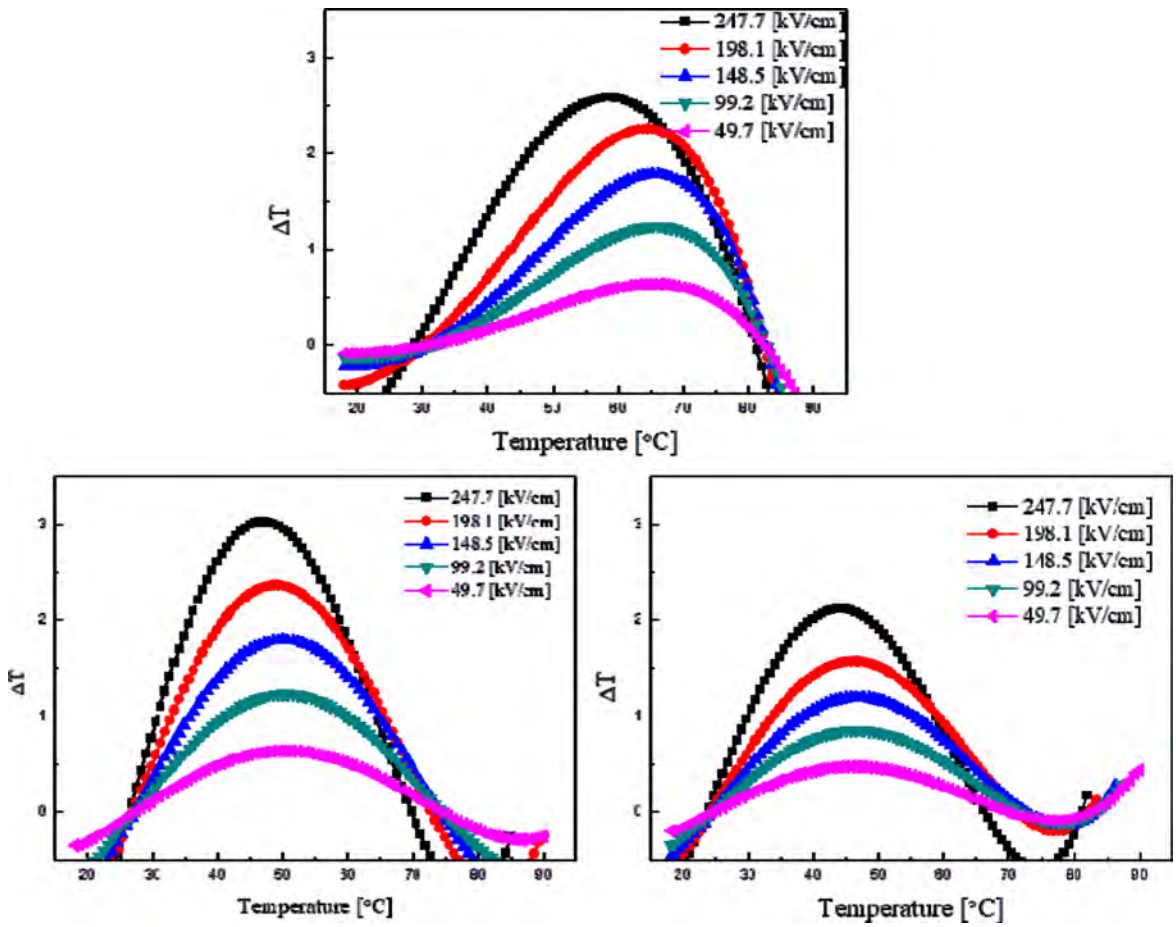

Fig. 8. Electrocaloric properties (ΔT) of $K(Ta_{0.6}Nb_{0.4})O_3$ thin films with temperature changes.

polarization was observed when the temperature was changed. According to temperatures, materials with higher crystallinity seem to have more sensitive electrical characteristics. This could also be observed when single ferroelectric substances displayed transition characteristics of the first phase.

Fig. 8 shows the electrocaloric properties (ΔT) of thin KTN films at different temperatures. When an electric field of 247 kV/cm was applied to the specimens sintered at 750 °C, the highest electrocaloric properties of 3.02 °C was observed. In all specimens, the maximum electrocaloric properties were obtained at the phase transition temperature of around 50 °C, which is higher than the Curie temperature. This could be attributed to dipoles' characteristics of field-induced polarization. This could also be attributed to the application of an electric field close to the phase transition temperature at which the ferroelectric and dielectric phases coexisted [19]. The thin films sintered at 650 °C were not crystallized due to a low sintering temperature and thus not applicable to a measurement of their electrocaloric properties. The specimens sintered at 800 °C showed low electrocaloric properties due to formation of pores caused by excessive sintering.

Conclusions

This study investigated the structural and electrical properties of thin $K(Ta_{0.6}Nb_{0.4})O_3$ films for their applicability to electrocaloric devices. In the specimen sintered at 650 °C, numerous pores and a pyrochlore phase of $K_2Ta_2O_6$ were observed. Also, a peak of pure KTN crystalline was observed in the sintering at 750 °C. The porosity of specimens sintered at 800 °C increased due to the volatilization of K ion caused by an excessive sintering temperature. The optimum sintering temperature of the specimens was 750 °C. A rapid reduction of the dielectric constant at an applied frequency of around 10 kHz could have been caused by the decrease in polarization of space charge. According to the temperatures, the higher crystallinity seems correlated to higher ferroelectric properties. In all specimens, the maximum electric energy was obtained at a temperature slightly higher than the phase transition temperature. This could be attributed to the dipoles characteristics of field-induced polarization. This could also be attributed to the application of an electric field close to the phase transition temperature at which the ferroelectric and dielectric phases coexisted. Also, when an electric field of 247 kV/cm was applied to the

specimens sintered at 750 °C, the highest electrocaloric properties of 3.02 °C was observed.

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