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Electro-caloric properties of $KTa_{0.60}Nb_{0.40}O_3$ thin films prepared by sol-gel method

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In this study, $K(Ta_{0.60}Nb_{0.40})O_3$ (KTN) thin films were prepared by the spin-coating method on Pt(111)/Ti/SiO2/Si substrates and varying sintering temperature. KTN coating solutions were synthesized by sol-gel method using metal alkoxide materials. As a result of DTA analysis, an exothermic peak for the crystallization reaction was observed in the temperature range of from 700 °C to 750 °C. KTN thin films sintered at 700-750 °C showed the typical XRD patterns of a polycrystalline perovskite structure. The thickness of the KTN was approximately 203 nm. The dielectric constant and dielectric loss at 1 kHz of the KTN films sintered at 750 °C were 200, 0.08, respectively. Remnant polarization decreased with increasing the temperature, and the value of thin film sintered at 750 °C was 0.18 μC/cm^2 at room temperature. The maximum electrocaloric temperature change ΔT of the thin film sintered at 750 °C was about 1.04 °C under a field of 400 kV/cm at 25 °C.

Key words: Electrocaloric effect, KTN, Ferroelectricity, Hysteresis loop, Sol-gel method.

Introduction

Most cooling devices nowadays, such as air conditioners and refrigerators, use vapor compression to improve the quality and comfortability of daily human life. However, these cooling systems emit by-products like CFCs and carbon dioxide, causing environmental problems such as global warming, and have poor energy efficiency because they consume large amounts of power. To combat this, solid state cooling technology has studied a variety of calorie-efficient effects, such as electrical, piezoelectric and magnetic, in a way that is different from the current thermoelectric devices. The basis of this principle is that it creates a cooling effect by converting electrical, mechanical and magnetic forces into thermal energy that is economical, environmentally friendly and, theoretically, highly energy efficient [1, 2].

The electrocaloric (EC) effect reaching 60% to 70% is higher than the vapor compression technique or thermal electric devices in terms of energy efficiency, and larger electric fields can be found in thin films as opposed to in bulk materials. The EC effects are expected to be applicable in a wide range of locations, making it possible to miniaturize cooling systems when making thin films. EC effect is a phenomenon in which a material shows a reversible temperature change under an applied electric field [3]. In order to understand the EC effect, the most important thing is to comprehend the relationship between entropy and polarization. For such a large EC effect, a large entropy change is related with the polarization change, which is derived from the dielectric under an external electric field. Because this polarization change is best met with the transition from ferroelectric to paraelectric, the EC effect in the near curie temperature shows the maximum values, and gradually reduced characteristics based on the transition to paraelectric [4].

In this study, we would like to examine the applicability of potassium tantalate niobate as the EC effect material. Generally, KTN materials have been mainly applied to optical and microwave devices, however, there has been little research as EC materials at home and abroad. Fig. 1 presents the transition temperature can be adjusted to approximately room temperature by selecting the appropriate $KTaO_3$-$KNbO_3$ composition ratio. Therefore, we decided the $K(Ta_{0.6}Nb_{0.4})O_3$ composition and measured the structural and electrical properties to investigate its applicability in relation to electrocaloric materials.

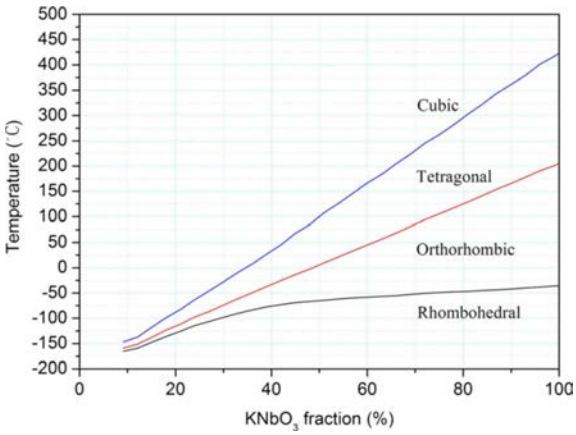

Fig. 1. Concentration dependence of the three transition temperature for KTN.

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Experimental

Potassium ethoxide, tantalum ethoxide and niobium ethoxide were used as starting materials with 2-methoxyethanol as the solvent. The solution synthesis procedure was conducted in a N_2 atmosphere because metal alkoxides are very sensitive to moisture. A suitable amount of potassium was first dissolved in 2-methoxyethanol, then mixed with the 2-methoxyethanol solution of tantalum ethoxide and niobium ethoxide which was prepared beforehand according to the molar ratio 60 : 40, and then stirred. The mixed solution was refluxed for 24 hrs. The homogeneous precursor solutions were well prepared. KTN coating solution was spin-coated at 3500 rpm for 30sec on Pt(111)/Ti/SiO_2/Si substrate, followed by a drying step at 200 °C for 20 min in air to form gel films and a conducting pyrolysis step at 400 °C for 20 min to remove the organic materials, and finally annealed in the range 700-850 °C by using the rapid thermal annealing process. 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. A Pt-upper electrode with a diameter of 500μm was deposited on the film by dc sputtering method in order to measure the electrical properties. 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. 2 demonstrates the DTA-TG results of the dried $K(Ta_{0.6}Nb_{0.4})O_3$ powder prepared from the coating solution. The KTN powder was first exposed to air at room temperature for 3 days, and dried at 100 °C. A relatively large decrease in weight and an endothermic peak observed at about 100 °C might result from H_2O, C_2H_5OH and $HOCOCH_3$ evaporation. There are 2 exothermic peaks associated with pyrolysis of organics or crystallization of the material. From 220 °C to 400 °C, a broad exothermic peak on the DTA curve was observed, which might be the oxidation of organic components. From 700 °C to 750 °C, an exothermic peak on the DTA curve and about a 5% decrease in weight occurred in the crystallization reaction.

Fig. 3 shows the X-ray diffraction patterns of $K(Ta_{0.6}Nb_{0.4})O_3$ thin films annealed in an oxygen atmosphere according to sintering temperature. The thin films sintered at 700-750 °C showed a polycrystalline X-ray diffraction pattern with a perovskite crystal structure. However, $K_6Nb_{10.8}O_{30}$ (ICDD-705051) secondary phase of K-deficiency due to K ion volatilization was observed in $K(Ta_{0.6}Nb_{0.4})O_3$ thin films sintered above 800 °C.

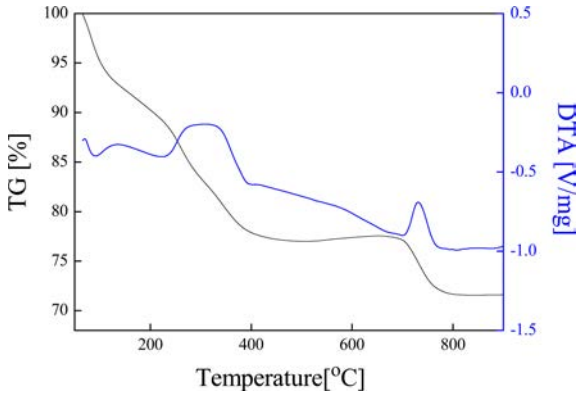

Fig. 2. TG-DTA analysis of $KTa_{0.6}Nb_{0.4}O_3$ powder by sol-gel method.

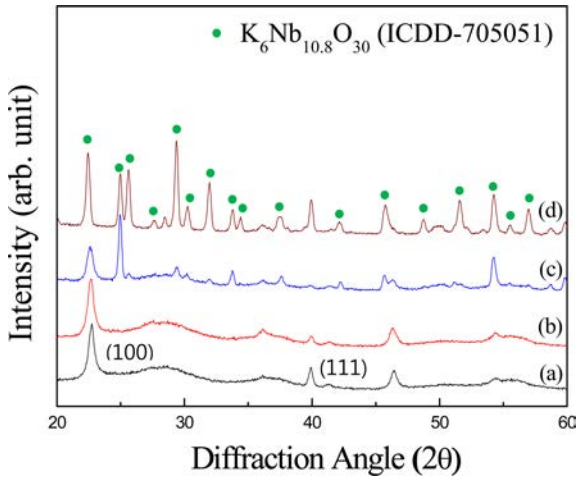

Fig. 3. XRD of $K(Ta_{0.6}Nb_{0.4})O_3$ thin films with the variations of sintering temperature; (a) 700 °C, (b) 750 °C, (c) 800 °C, (d) 850 °C.

Fig. 4 shows the cross-sectional microstructure of the $K(Ta_{0.6}Nb_{0.4})O_3$ thin film annealed at 750 °C. The average thickness of the thin films was about 203 nm and showed fine and flat microstructure in all specimens.

Fig. 5 shows the dielectric constant and dielectric loss of $K(Ta_{0.6}Nb_{0.4})O_3$ thin films with applied frequency and sintering temperature. In all specimens, the typical dielectric relaxation characteristics showed that the dielectric constant gradually decreased with increasing applied frequency [5]. The specimens sintered at 750 °C showed the good dielectric constant and dielectric loss characteristics. This is probably due to the excellent crystallinity as shown in Fig. 2.

Fig. 6 shows the hysteresis properties of $K(Ta_{0.6}Nb_{0.4})O_3$ thin films sintered at 750 °C. All specimens exhibited typical ferroelectric hysteresis characteristics and showed a tendency to decrease remnant polarizations and coercive fields with increasing temperature [6].

Fig. 6 shows the remnant polarization of $K(Ta_{0.6}Nb_{0.4})O_3$ thin film with increasing temperature. As the temperature increased, the remnant polarization decreased while increasing the disorder of the dipole

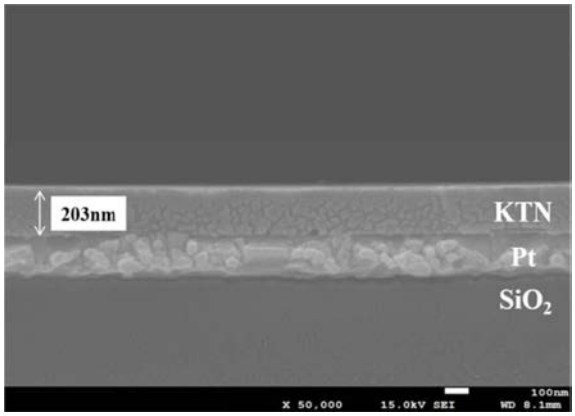

Fig. 4. Cross-sectional microstructure of $K(Ta_{0.6}Nb_{0.4})O_3$ thin film sintered at 750 °C.

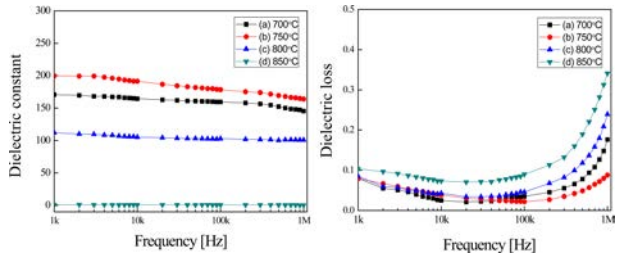

Fig. 5. Frequency dependence of dielectric constant(left) and dielectric loss(right) of $K(Ta_{0.6}Nb_{0.4})O_3$ thin films with variations of sintering temperature; (a) 700 °C, (b) 750 °C, (c) 800 °C, (d) 850 °C.

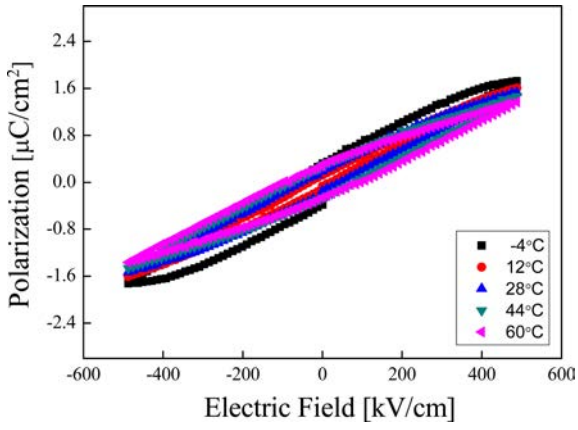

Fig. 6. P-E hysteresis loop of $K(Ta_{0.6}Nb_{0.4})O_3$ thin films sintered at 750 °C.

moment inside the specimen. As the applied electric field increases, the remnant polarization also tends to increase. In general, the phase transition temperature of the $K(Ta_{0.6}Nb_{0.4})O_3$ bulk specimen is approximately 25 °C [7]. However, in this thin films, no rapid polarization decrease, or phase transition characteristics were observed at the measurement temperature range. These properties are considered to be due to the diffused phase transition characteristics of $K(Ta_{0.6}Nb_{0.4})O_3$ thin film. Also the Curie temperature moved to the higher temperature side because of stress generated at the interface with the substrate, which is a typical

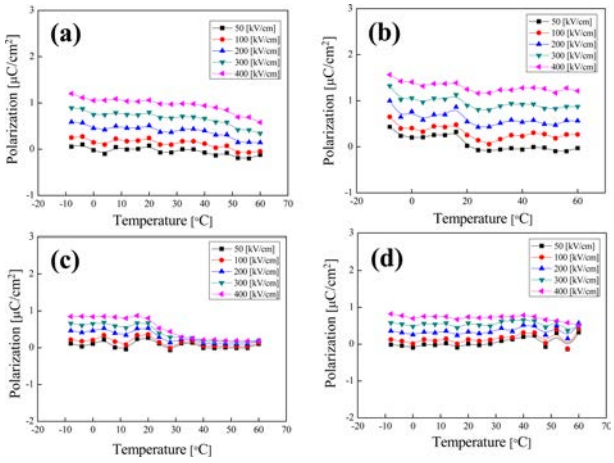

Fig. 7. Temperature dependence of polarization of $K(Ta_{0.6}Nb_{0.4})O_3$ thin films with variations of temperature and applied fields; (a) 700 °C, (b) 750 °C, (c) 800 °C, (d) 850 °C.

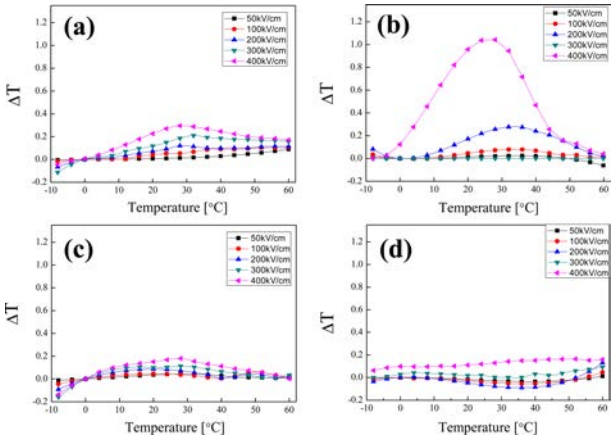

Fig. 8. Electrocaloric temperature change ΔT of $K(Ta_{0.6}Nb_{0.4})O_3$ thin film with variations in temperature; (a) 700 °C, (b) 750 °C, (c) 800 °C, (d) 850 °C.

characteristic of the thin film specimens [8].

Fig. 7 shows the electrocaloric temperature change ΔT of the $K(Ta_{0.6}Nb_{0.4})O_3$ thin film with variation of temperature. The temperature change ΔT of the thin films was calculated from the slope beginning with a maximum field and ending at a zero field as shown in Fig. 6, and the following equation [9].

$$\Delta T = -\int_{E_1}^{E_2} \frac{T}{C\rho}\left(\frac{\delta P}{\delta T}\right)_E dE \quad (1)$$

Here, specific heat(C) and theoretical density(ρ) of the specimen were 430 J/KgK and 6.231 g/cm^3, respectively [10].

The specimens sintered at 700-800 °C exhibited the good ΔT characteristics at around 30 °C, which is attributed to the increase in entropy as the specimen changes from ferroelectric phase to paraelectric phase as observed in the temperature-polarization properties. However, the specimens sintered at 850 °C did not show the electrocaloric properties because of the

formation of a secondary phase caused by to the volatilization of K ion. As the applied electric field increases, the ΔT increases, which is probably due to the increase of the induced polarization depending on the electric field application [11]. When the electric field of 400 kV/cm was applied to the $K(Ta_{0.6}Nb_{0.4})O_3$ thin film sintered at 750 ºC, the good ΔT of 1.04 ºC was obtained.

Conclusions

$K(Ta_{0.6}Nb_{0.4})O_3$ thin films were prepared by the spin-coating method on Pt(111)/Ti/SiO2/Si substrates and varying sintering temperature. We investigated the structural and electrical properties of KTN thin films for application to electrocaloric materials. In all specimens, the typical dielectric relaxation characteristics showed that the dielectric constant gradually decreased with increasing applied frequency. As the temperature increased, the remnant polarization decreased while increasing the disorder of the dipole moment inside the specimen. No rapid polarization decrease, or phase transition characteristics were observed at the measurement temperature range, which are attributed to the diffused phase transition characteristics of KTN thin film. The Curie temperature moved to the high temperature side because of the stress generated at the interface with the substrate, which is a typical characteristic of the thin film specimens. KTN thin films sintered at 700-800 ºC exhibited the good ΔT characteristics at around 30 ºC, which is thought to be due to the increase in entropy as the changes from the ferroelectric phase to the paraelectric phase.

Acknowledgments

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