

Structural and electrical properties of Ba(Sr,Ti)O₃/K(Ta,Nb)O₃ multilayer thin film for the application of electro-caloric devices

Min-Su Kwon^a, Sung-Gap Lee^{a,*}, Kyeong-Min Kim^a and Seungkeun Choi^b

^aDept. of Materials Engineering and Convergence Technology, ERI, Gyeongsang National University, Jinju 52828, Korea

^bSchool of STEM, Univ. of Washington, Bothell, WA, 98011, USA

In this study, the multilayered thin films of Ba(Sr,Ti)O₃/K(Ta,Nb)O₃ were fabricated by the sol-gel and spin coating methods, and their structural and electrical properties were investigated. The specimen showed polycrystalline X-ray diffraction (XRD) characteristics with a tetragonal structure. The average grain size and film thickness for one coating were about 30–40nm and 60nm, respectively. The phase transition temperature of specimen was lower than 10 °C. The dielectric constant and loss at 20 °C of the specimen coated six times were 1,231 and 0.69, respectively. The rate of change in dielectric constant at an applied direct current (DC) voltage of the six times coated thin films was 17.3%/V. The electrocaloric effect was the highest around the temperature at which the remanent polarization rapidly changed. When an electric field of 660kV/cm was applied to the triply coated thin films, the highest electrocaloric property of 4.41 °C was observed.

Key words: Ba(Sr,Ti)O₃, K(Ta,Nb)O₃, Multilayer thin film, Ferroelectric effect, Electro-caloric effect, Remanent polarization, Interface properties.

Introduction

BaTiO₃ ceramics with ABO₃ perovskite crystal structure is a typical ferroelectric material and has been studied for application to various devices such as capacitors, piezoelectric transducers, and infrared sensors using excellent structural and electrical properties [1, 2]. Also, K(Ta,Nb)O₃ ceramics with the same perovskite structure have been studied for application to electro-optic devices, memory devices, and sensors by using various structural characteristics and electrical properties depending on the composition ratio of Ta and Nb [3, 4]. Recently, BaTiO₃ and K(Ta,Nb)O₃ ceramics have attracted attention as lead-free materials as environmental issues become important social issues.

Studies on thin films have mainly been focused on the changes in the manufacturing process and improvement of properties of materials [5, 6]. Also, research on the interfacial phenomenon of thin film devices has mainly focused on the interface between substrate and thin film [7]. Multilayer thin films, which have been stacked alternately with different composition or materials, exhibit excellent electrical properties due to the formation of super-lattice structures or mixture compositions in the interfacial layer through epitaxial growth. However, studies on the various electronic properties occurring at the interface by laminating different materials have

been carried out only in part, despite a theoretical possibility.

Electronic devices have become more sophisticated and complex, and devices are becoming more and more micronized. As a result, heat generation problems in circuits and devices are recognized as important factors affecting the performance of devices. The problems of heat generation of devices are generally solved by using a heat dissipation properties of substrates, but it is limited in performance and price. Recently, as the need for cooling solutions for micro- or nanoelectronic devices with high power or high density heat generation has increased, research has been actively conducted on the electrocaloric effect in ferroelectric materials using small and highly energy efficient properties. In 2005, A. S. Mischenko et al. [9] reported a study on the application on ferroelectric Pb(Zr_{0.95}Ti_{0.05})O₃ thin films as cooling devices using electrocaloric characteristics. However, since Pb(Zr,Ti)O₃-based materials have a phase transition temperature higher than 240 °C, applications of cooling devices at room temperature are limited, and researches have been limited by environmental problems caused by Pb element.

In this study, Ba(Sr,Ti)O₃/K(Ta,Nb)₃ (BST/KTN) multilayer thin films were prepared by alternately laminating of lead-free Ba(Sr,Ti)O₃ and K(Ta,Nb)O₃ thin films. And their structural and electrical properties were investigated according to the number of coatings of the specimens in order to investigate the application as cooling devices.

*Corresponding author:
Tel : +82-55-772-1687
E-mail: lsgap@gnu.ac.kr

Experimental

$(\text{Ba}_{0.7}\text{Sr}_{0.3})\text{TiO}_3$ (BST) and $\text{K}(\text{Ta}_{0.6}\text{Nb}_{0.4})\text{O}_3$ (KTN) with low phase transition temperature were selected to investigate the feasibility of the application as a cooling element capable of operating at room temperature [10, 11].

BST precursor solutions were prepared by the sol-gel method from barium acetate (Junsei Chemical Co., Japan, 99.0%), strontium acetate 0.5-water (KANTO Chemical Co., Japan, 99.0%), titanium (IV) iso-propoxide (Junsei Chemical Co., Japan, 99.0%), as starting materials, with acetic acid and 2-methoxyethanol as solvents. And KTN precursor solutions were synthesized from potassium acetate (CH_3COOK , Sigma Aldrich, 99%), niobium ethoxide ($\text{Nb}(\text{COH}_2\text{CH}_3)_5$, Alfa aesar, 99.999%), tantalum ethoxide ($\text{Ta}(\text{COH}_2\text{CH}_3)_5$, Alfa aesar, 99.999%) with 2-methoxyethanol used as a solvent. The molar concentration of solution was adjusted to 0.3 M, and 10 mol% of excess potassium acetate was added to compensate for the expected K_2O losses during annealing.

BST/KTN multilayer thin films were prepared by alternately coating BST and KTN. Especially, to suppress ion diffusion at interface between thin films and Pt/Ti/ SiO_2 /Si substrates, BST thin films having excellent chemical stability were coated on the substrate as the first layer. Structural and electrical properties of BST/KTN multilayer thin films were investigated according to the number of coatings.

Results and Discussion

Fig. 1 shows X-ray diffraction (XRD) patterns of

BST/KTN multilayer thin films according to the number of coatings. BST and KTN thin films were repeatedly coated from 3 times to 6 times on Pt/Ti/ SiO_2 /Si substrates. Generally, single KTN thin films were observed with a secondary phase such as $\text{K}_2\text{Ta}_2\text{O}_6$ pyrochlore phase. However, in this study, all specimens showed homogeneous polycrystalline XRD patterns with tetragonal structure. This is because the BST thin film coated with the first layer acts as a seed layer for KTN upper layer crystallization and the crystal structure of ABO_3 perovskite having the same BST thin film and KTN thin film [12]. As the number of coatings increased, crystallinity of multilayer thin films improved as increasing XRD

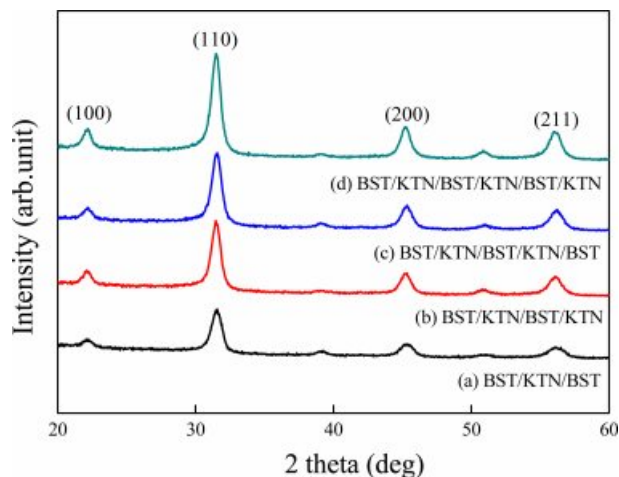


Fig. 1. X-ray diffraction patterns of BST/KTN multilayer thin films with the variation of the number of coatings.

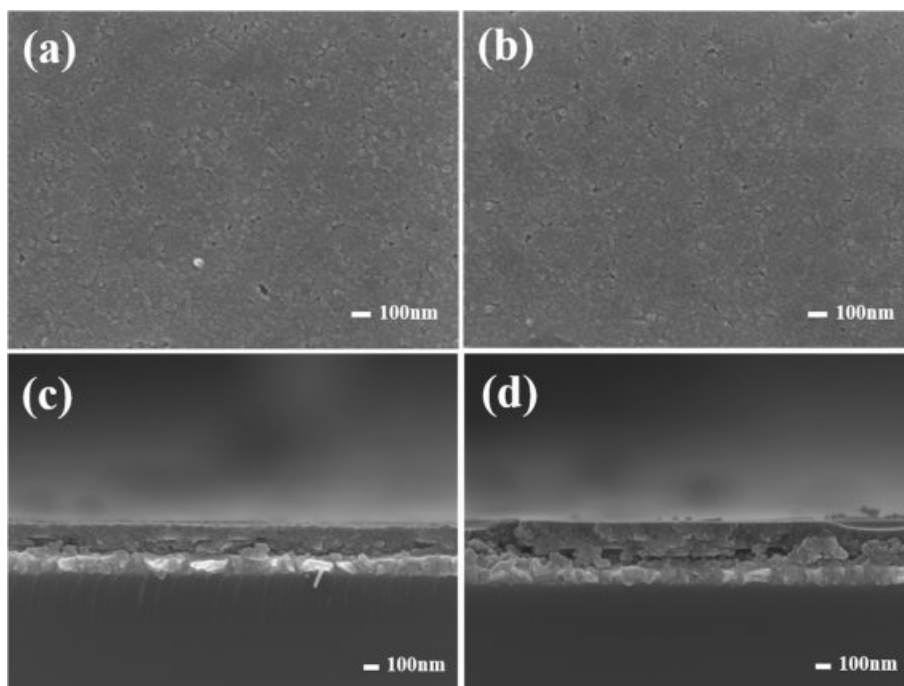


Fig. 2. Surface and cross-sectional microstructures of BST/KTN multilayer thin films with the variation of the number of coatings; (a) surface-3 times, (b) surface-4 times, (c) cross-sectional-3 times, and (d) cross-sectional-4 times.

peaks intensities and decreasing FWHM (full width at half maximum) values.

Fig. 2 shows surface and cross-sectional microstructures of BST/KTN multilayer thin films according to the number of coatings. All specimens showed dense crystal structure composed of small and homogeneous grains, and average grain size was about 30~40 nm. In general, KTN thin films are difficult to fabricate specimens with homogeneous structure due to high vapor pressure characteristics of K ions, and many pores are distributed [13]. However, BST/KTN multilayer thin films showed homogeneous and dense microstructure, probably due to the microstructure of the lower BST thin film acting as the nucleation site of the upper KTN thin film. Average thickness for one-time coated thin films was about 60 nm.

Fig. 3 shows dielectric constant and dielectric loss of BST/KTN multilayer thin films with frequency application. All specimens showed the typical dielectric relaxation characteristics [14]. Dielectric constant and dielectric loss increased with increasing the number of coatings. This is probably due to the decrease in the stress on interfaces due to the difference in lattice constant between Pt substrate and BST thin film. Also, as the number of coatings increased, the slope of decrease in dielectric constant with increasing frequency was increased due to the distribution of space charge

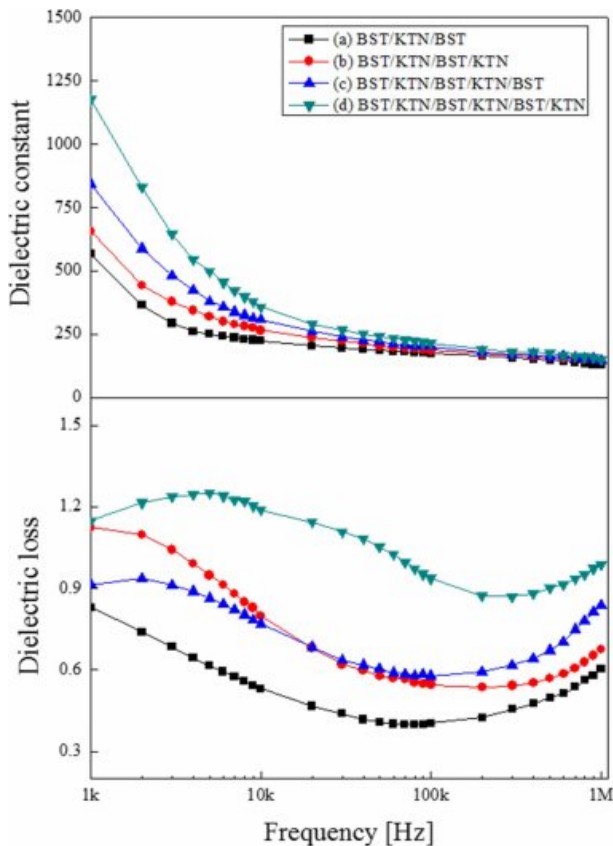


Fig. 3. Dielectric constant and dielectric loss of BST/KTN multilayer thin films with the variation of frequency.

formed at interfaces between BST and KTN thin films [15, 16].

Fig. 4 shows dielectric constant and dielectric loss of BST/KTN multilayer thin films with temperature variation. Dielectric constant and dielectric loss increased as the number of coatings increased. This is attributed to the formation of interfacial polarization due to space charge between BST and KTN thin films [17]. Also, it is considered that dielectric constant decreased with increasing temperature in the measurement temperature range of 10~80 °C because the phase transition temperatures were located below 10 °C. Dielectric constant and dielectric loss of the 6 coated BST/KTN multilayer thin films at 20 °C were 1,231 and 0.69, respectively.

Fig. 5 shows dielectric constant of BST/KTN multilayer thin films with DC voltage applied. Dielectric constant decreased with increasing DC applied voltage, which is considered to be due to the suppression of the displacement of ions [18]. As the number of coating increased, the distribution of space charge formed between BST thin film and KTN thin film and the dependence on DC electric field increased, so the rate of decrease of dielectric constant according to the applied voltage increased. The 6 coated BST/KTN multilayer thin films showed the highest change rate of 17.3%/V.

Fig. 6 shows hysteresis loops of BST/KTN multilayer thin films with the number of coatings and temperature.

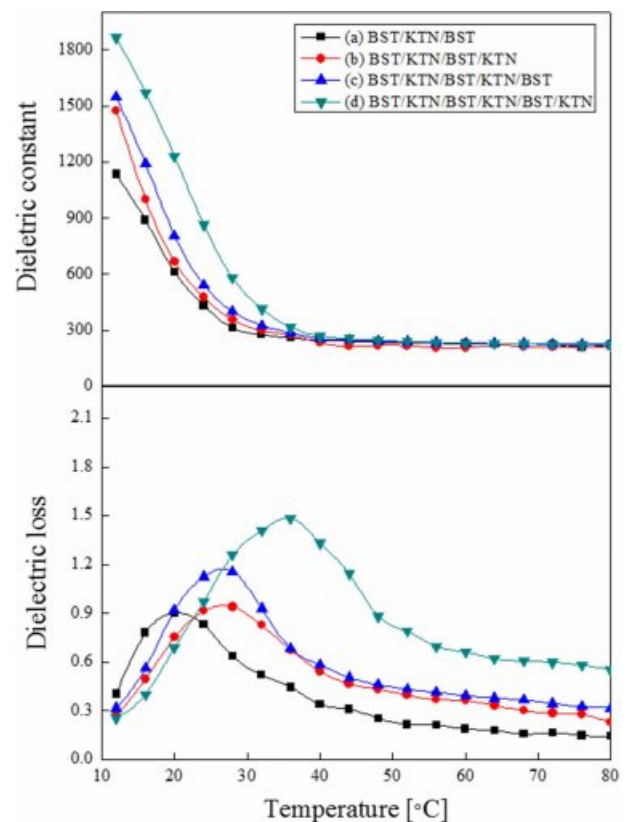


Fig. 4. Dielectric constant and dielectric loss of BST/KTN multilayer thin films with the variation of temperature.

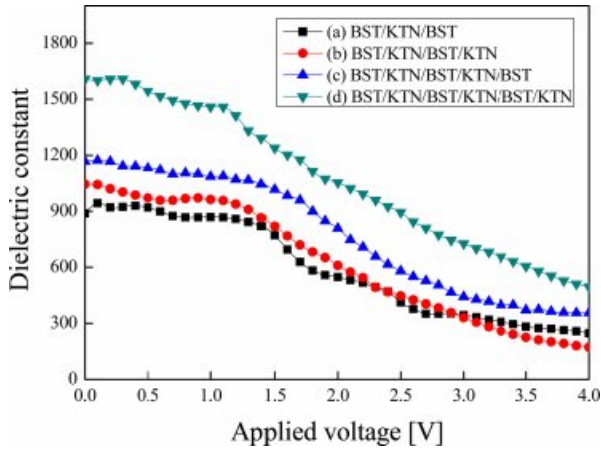


Fig. 5. Dielectric constant of BST/KTN multilayer thin films with the variation of DC voltage applied.

As the temperature and the number of coatings increased, remanent polarization and the coercive field decreased. As shown in Fig. 4, because the phase transition temperature of specimens were distributed below 10 °C, the phase structure of BST/KTN multilayer thin films gradually changed to the paraelectric phase as the temperature increased. Also, it is considered that the influence of the stress formed at the interface between thin films and Pt substrate decreased with

increasing the thickness of thin films.

Fig. 7 shows remanent polarization of BST/KTN multilayer thin films with temperature change. Remanent polarization measured at 10 °C were fixed at a maximum value and then the temperature dependent properties were shown. As the number of coatings increased, temperatures at which remanent polarization rapidly decreased were shifted to the lower temperature side, and the rate of change of remanent polarization was decreased with temperature. This is because the volume ratio of BST and KTN having a phase transition temperature lower than room temperature increased as the number of coatings increased, as shown in Fig. 4 and 6.

Fig. 8 shows electrocaloric properties (ΔT) of BST/KTN multilayer thin films according to temperature and applied voltage. Electrocaloric properties showed the highest values at the temperature where the remanent polarization rapidly changes. Electrocaloric properties increased with increasing the applied electric field. This is probably due to the decrease in entropy and the temperature dependence of dipoles arrangement as the displacement of dipoles increased when an electric field was applied near the phase transition [19]. When the electric field of 660 kV/cm was applied to the 3 times coated BST/KTN multilayer thin films, the highest electrocaloric property of 4.41 °C was shown.

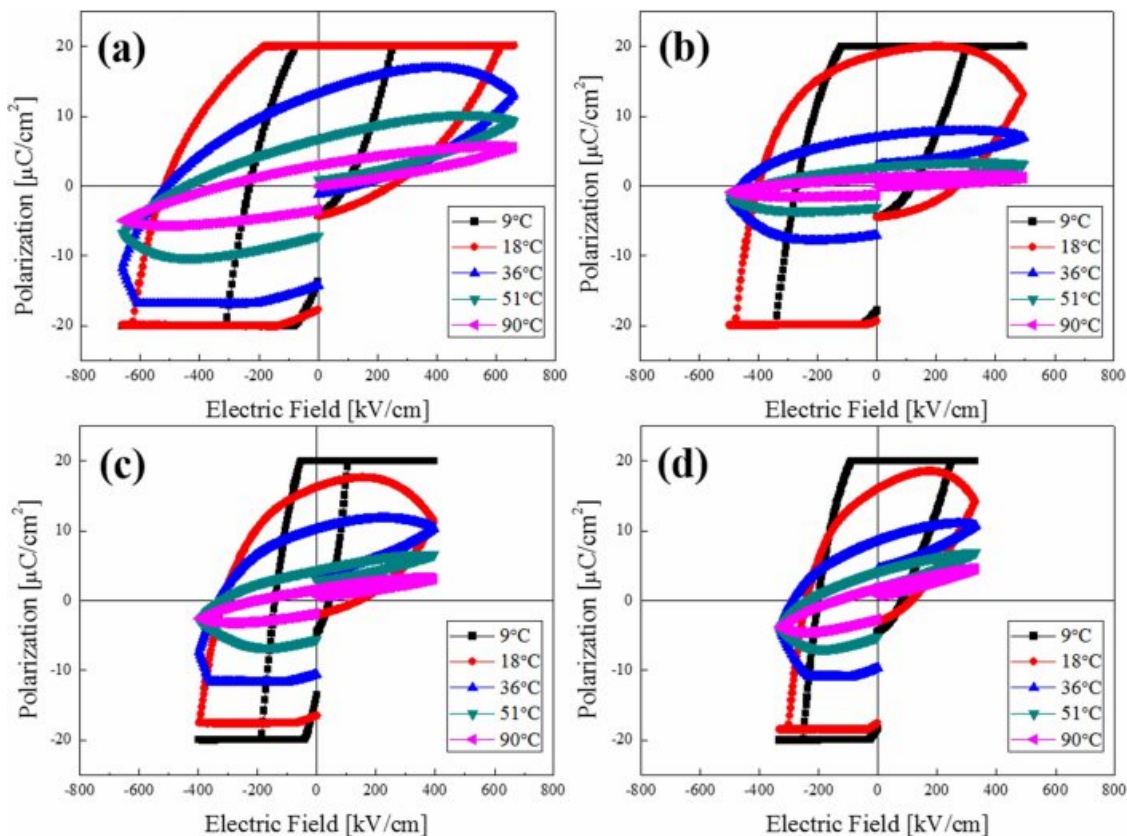


Fig. 6. Hysteresis loops of BST/KTN multilayer thin films with the variation of the number of coatings and temperature.

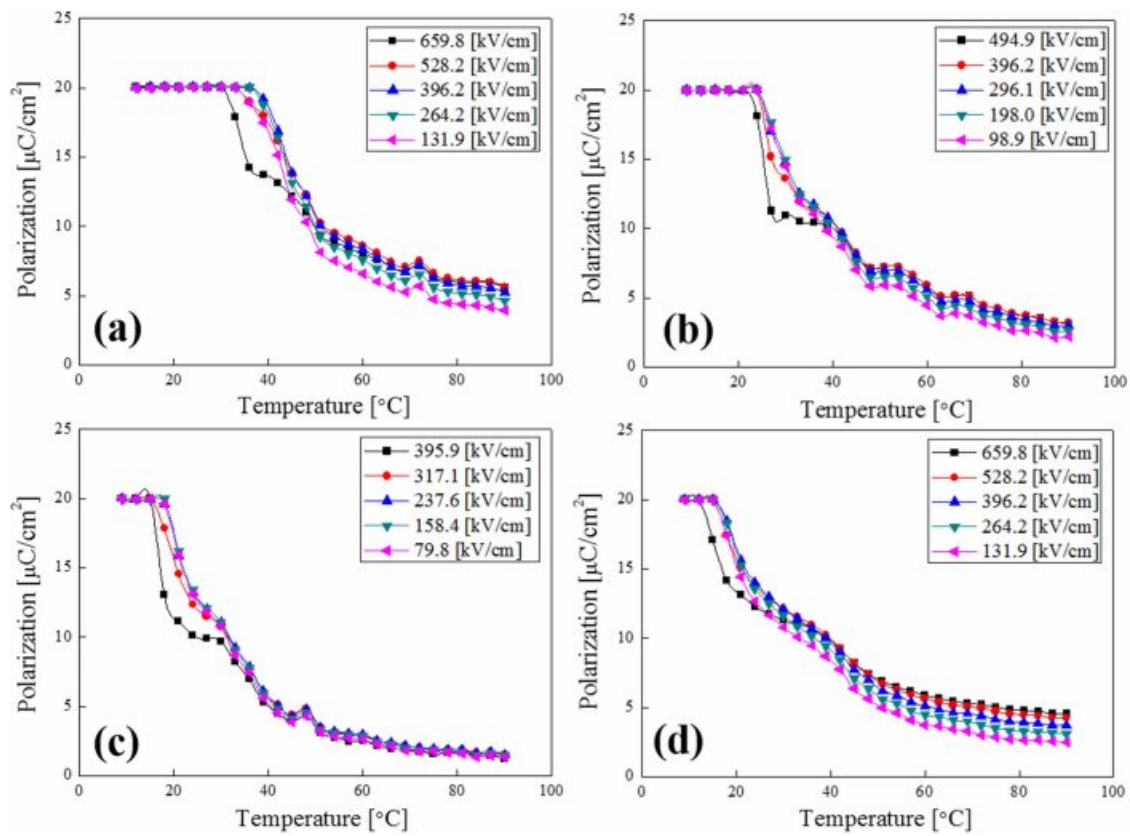


Fig. 7. Remanent polarization of BST/KTN multilayer thin films with the variation of temperature.

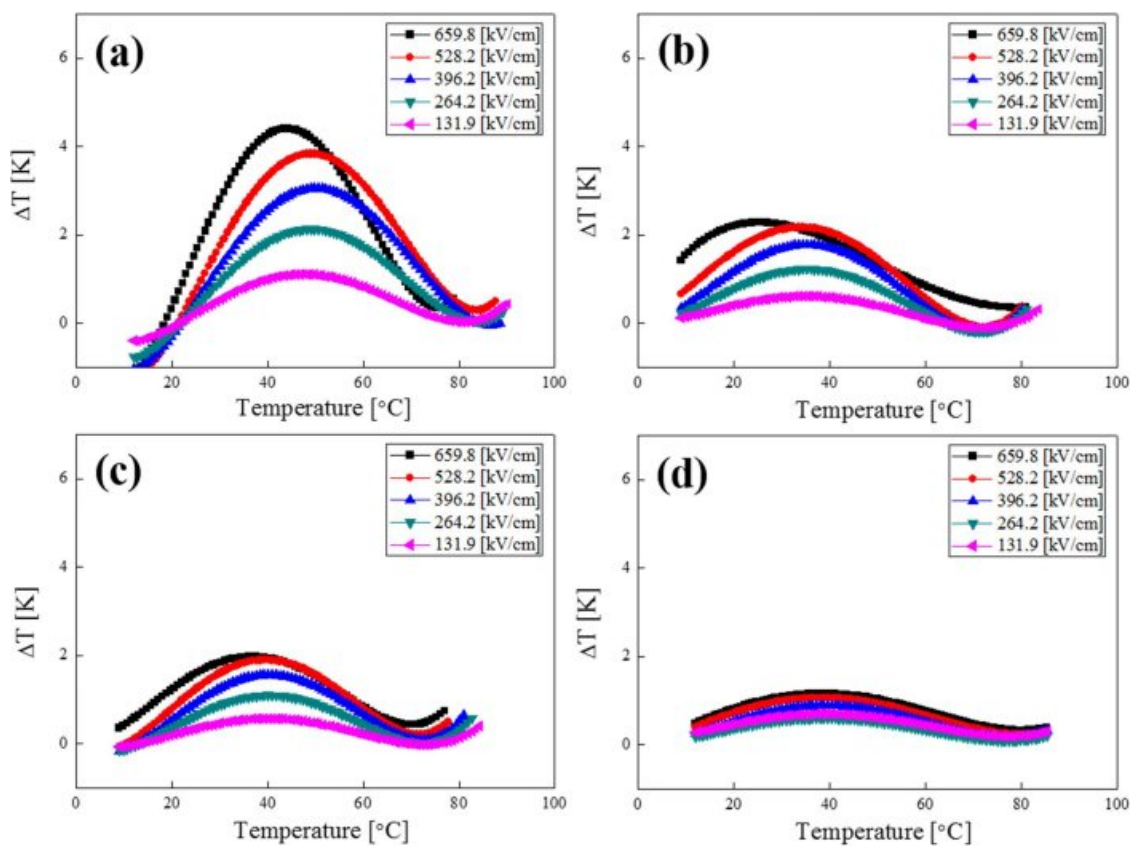


Fig. 8. Electrocaloric properties (ΔT) of BST/KTN multilayer thin films with the variation of temperature and applied voltage.

Conclusions

BST/KTN multilayer thin films were prepared by alternately coating (Ba,Sr)TiO₃ thin films and K(Ta,Nb)O₃ thin films. Structural and electrical properties were measured according to the number of coatings. All specimens showed homogeneous dense polycrystalline microstructure without secondary phase such as K₂Ta₂O₆ pyrochlore phase. This indicates that BST thin film coated on the Pt/Ti/SiO₂/Si substrate as the seed layer for the upper layer crystallization. Dielectric constant and dielectric loss increased with increasing the number of coatings. It is considered that the influence on the stress formed at the interface due to the difference in lattice constant between Pt substrate and BST thin film was reduced. As an applied DC voltage increased, dielectric constant decreased as the displacement of the space charge was suppressed. Electrocaloric properties showed the highest value near the temperature at which the remanent polarization suddenly changed, and it increased as the applied electric field increased.

Acknowledgement

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (No. 2017R1D1A3 B03032164) and by the Gyeongsang National University Fund for Professors on Sabbatical Leave, 2018 and by Korea Institute of Planning and Evaluation for Technology in Food, Agriculture, Forestry and Fisheries (IPET) through Agriculture, Food and Rural Affairs Research Center Support Program, funded by Ministry of Agriculture, Food and Rural Affairs (MAFRA)(717001-7).

References

1. H. Kishi, Y. Mizuno, and H. Chazono, *Jpn. J. Appl. Phys.* 42 (2003) 1-15.
2. A.S. Bhalla, R. Guo, and R. Roy, *Mater. Res. Innov.* 4[1] (2000) 3-26.
3. B. Liu, X. Wang, Y. Zhang, X. Lv, and Y. Yang, *Ionics* 20[12] (2014) 1795-1799.
4. S. Glinšek, I. Arčon, B. Malič, A. Kodre, and M. Kosec, *J. Solgel. Sci. Technol.* 62[1] (2012) 1-6.
5. S. Sharma, A. Kumar, V. Gupta, and M. Tomar, *Vacuum* 160 (2019) 233-237.
6. C.M. Raghavan, J.Y. Choi, and S.S. Kim, *Ceram. Int.* 42[8] (2016) 9577-9582.
7. W. Hu, C. Yang, W. Zhang, G. Liu, and D. Dong, *J. Solgel. Sci. Technol.* 39[3] (2006) 293-298.
8. H. Sui, H. Sun, X. Liu, D. Zhou, and R. Xu, *J. Eur. Ceram. Soc.* 38[16] (2018) 5382-5387.
9. A.S. Mischenko, Q. Zhang, J.F. Scott, R.W. Whatmore, and N.D. Mathur, *Science* 311 (2006) 1270-1271.
10. M.W. Cole, C. Hubbard, E. Ngo, M. Ervin, M. Wood, and R.G. Geyer, *J. Appl. Phys.* 92[1] (2002) 475-483.
11. A. Nazeri, M. Kahn, B. Bender, and C. Allen, *J. Am. Ceram. Soc.* 194445 (1993) 2450-2454.
12. T. Ohno, M., Fujimoto, T. Ota, M. Fuji, M. Takahashi, and H. Suzuki, *J. Eur. Ceram. Soc.* 26[10-11] (2006) 2143-2146.
13. B. Tunaboylu, S.R. Sashital, P. Harvey, S.C. Esener, and A. Bhalla, *Ferroelectrics Lett.* 28[3-4] (2001) 75-84.
14. Ch. Rayssi, S. El. Kossi, J. Dhahri, and K. Khirouni, *RSC Adv.* 8 (2018) 17139.
15. S. Dash, R.N.P. Choudhary, P.R. Das, and A. Kumar, *Canadian Journal of Physics* 93 (2015) 738.
16. G. Abadias, E. Chason, J. Keckes, M. Sebastiani, G.B. Thompson, E. Barthel, G.L. Doll, C.E. Murray, C.H. Stoessel, and L. Martinu, *J. Vac. Sci. Technol. A* 36 (2018) 020801.
17. C.C. Wang, M. He, F. Yang, J. Wen, G.Z. Liu, and H.B. Lu, *Appl. Phys. Lett.* 90[19] (2007) 0-3.
18. A.E.R. Mahmoud, A.S. Afify, and S.K.S. Parashar, *J. Mater. Sci.: Mater. Electron.* 30[3] (2019) 2659-2668.
19. Z. Luo, D. Zhang, Y. Liu, D. Zhou, Y. Yao, C. Liu, B. Dkhil, X. Ren, and X. Lou, *Appl. Phys. Lett.* 105[10] (2014) 102904.