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Dependence of Poling Field on Pyroelectric Property of $Pb_{0.9}La_{0.1}TiO_3$ Ceramics

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The pyroelectric property of $Pb_{0.9}La_{0.1}TiO_3$ ceramics in a range of 1.3-4.1 μm, fabricated by conventional solid sintering, was investigated as a function of poling field. The pyroelectric coefficient of the 4.1 μm of $Pb_{0.9}La_{0.1}TiO_3$ ceramics is higher than that of the 1.3 μm and 1.7 μm of $Pb_{0.9}La_{0.1}TiO_3$ ceramics at a low poling field and the pyroelectric coefficient is 25 nC/cm^2K at a 4 kV/mm poling field in every grain size. In order to explain this phenomenon, the intrinsic and extrinsic effects in view of the definition of the pyroelectric coefficient are introduced. The intrinsic and extrinsic effects on the pyroelectric property were investigated by measuring the tetragonal ratio and the I_{002} with temperature with high temperature X-ray diffractometer. The change of spontaneous polarization and the 90° domain wall motion with temperature in the 1.3 μm and 4.2 μm of $Pb_{0.9}La_{0.1}TiO_3$ ceramics have no effects on the pyroelectric coefficient. In our study, it can be seen that the pyroelectric coefficient is related to the quantity of 180° domain switching after poling treatment.

Key words: Pyroelectric coefficient, Poling field, Ferroelectrics, Ceramics, Domain switching

I. Introduction

$PbTiO_3$ is a perovskite ferroelectric ceramic which has high pyroelectric property at room temperature. Especially, La-modified $PbTiO_3$ ceramics has the good sinterability while pure $PbTiO_3$ does not. It also shows high pyroelectric property at room temperature and has a application of infrared detectors.[1-3]

In polycrystalline ferroelectric ceramics, poling process is necessary to induce pyroelectric property. Poling property is affected by many variables such as poling time, field and grain size. Recently, numerous study on the relationship between among the poling property and the electrical property(piezoelectric and dielectric constant) has been reported.[4] For example, the piezoelectric constant and the coupling factor have been explained by the concept of N^{90}(%) which means the quantity of 90° domain reorientation during poling.[5-7] However, the relationship between poling field and pyroelectric property has not been investigated. Also it has not been known what has an major effect on pyroelectric property.

In the literature,[8] the ferroelectric property can be divided into the intrinsic and extrinsic effect. The material properties from a single domain material are denoted as the intrinsic properties, while the contributions from the other parts of the material, mainly from domain walls(90°- and 180°- domain wall), are denoted as extrinsic properties.

In this study, the pyroelectric property of $Pb_{0.9}La_{0.1}TiO_3$ ceramics with different grain size, fabricated by conventional solid sintering, was investigated as a function of poling field. In order to explain the pyroelectric property, the intrinsic and extrinsic effects in view of the definition of the pyroelectric coefficient were introduced. The intrinsic and extrinsic effects on the pyroelectric property were investigated by measuring the tetragonal ratio and the I_{002} with temperature using high temperature X-ray diffractometer.

II. Experimental Procedure

$Pb_{0.9}La_{0.1}TiO_3$ ceramics were prepared by a conventional solid sintering technique. PbO, La_2O_3 and TiO_2 (Aldrich chemiacal Co.) raw powders, of which the purity was greater than 99.9%, were mixed in acetone with Zirconia balls for a day. After drying, the mixtures were calcined at 900°C for 3 h. The calcined powders were ground with 1 wt% polyvinyl alcohol used as a binder in a ball mill for a day and dried on a hot plate. Samples were pressed into a 11mm disk and were then sintered at 1240°C on a Pt plate covered with an alumina crucible containing a powdered atmosphere consisting of $PbZrO_3$. The density of sintered specimens was above 95% of the theoretical value. Samples were then polished to 500 μm and annealed at 900°C for 3 hr to remove surface damage. Silver was electroded on both surfaces of disk samples, and baked at 630°C for 30 min. Specimens were subsequently poled in a silicone oil bath at 80°C for 5 min under a dc field of 1-6 kV/mm. The poled specimens had a aging time for a day before measuring pyroelectric current or high temperature XRD.

The microstructure of samples was characterized by scanning electron microscopy (SEM). The 0.5 h, 3 h, and 20 hr

sintered samples have 1.3 μm, 1.7 μm and 4.1 μm of average grain size, respectively. The average grain size was measured by linear intercept method.[9]

The pyroelectric current was measured with a pA meter (Keithly Model 486) to determine the pyroelectric coefficient. A high temperature X-ray diffractometer was used for observing I_{002} and tetrogonal ratio(c/a). I_{002} is expressed as $I_{002}/(I_{002}+I_{200})$ here. (I_{002}: Integrated intensity of (002) peak, I_{200}: Integrated intensity of (200) peak). The diffraction peaks of the (002) and (200) planes were measured at 0.5°/min in the range 44.5° 47.5°. Also amounts of 90o domain switching during poling treatment were calculated with Mendiolas equation by XRD measurement before and after poling treatment.[10]

III. Results and Discussion

1. Poling field dependence of the pyroelectric coefficient with different grain size

Fig. 1 shows the effect of the poling field on the pyroelectric coefficient at room temperature with different grain size, when the poling field was varied in a range of 1 to 6 kV/mm. Fig. 1 is considered to exhibit the bulk properties of PLT ceramics. The 1.3 and 1.7 μm samples have a similar tendency. The pyroelectric coefficients of 1.3 and 1.7 μm samples increase in a range of 1 to 4 kV/mm and are saturated above 4 kV/mm. This tendency has been reported numerously in the piezoelectric constant as a function of poling field. In the 4.1 μm sample, the pyroelectric coefficient is higher than that of the 1.3 μm and 1.7 μm samples at a low poling field and the saturation begins over 4 kV/mm. At 4 kV/mm of poling treatment, the pyroelectric coefficient is 25 nC/cm^{2}K in every grain size.

After 1 kV/mm of poling treatment, the pyroelectric coefficients of the 1.3 μm and 4.1 μm samples are 0.7 nC/cm^{2}K and 11.3 nC/cm^{2}K, respectively. This means that there is a different mechanism in the 1.3 μm and 4.1 μm samples at a low poling field. The pyroelectric coefficient is defined as the polarization change with temperature. The pyroelectric property in ferroelectrics is divided into the intrinsic and extrinsic effect.[8] Further polarization change with temperature is divided alike. The intrinsic effect on the pyroelectric property is considered as the spontaneous polarization change with temperature. The spontaneous polarization change with temperature is related to the tetragonal ratio change with temperature directly.[11] And the extrinsic effect on pyroelectric property is considered as the domain wall motion(90°- and 180°-domain wall motion), which causes the decrease of polarization with temperature. Next we have information of the tetragonal ratio and the 90° domain wall motion with temperature. These were measured for the 1.3 μm and 4.1 μm samples which have different tendency in Fig. 1.

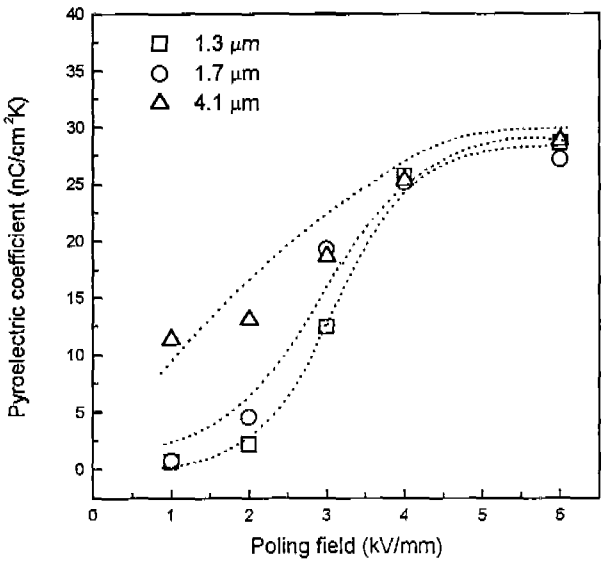

Fig. 1. Variation of pyroelectric coefficient at the room temperature of $Pb_{0.9}La_{0.1}TiO_3$ ceramics as a function of poling field.

2. Tetragonal ratio(c/a) and $I_{002}(I_{002}/(I_{002}+I_{200}))$ with temperature in PLT ceramics after 1 kV/mm of poling treatment

Fig. 2 shows the diffraction patterns with the temperature for 1 kV/mm poled PLT ceramics. It is observed through (002) and (200) of peak position that the length of c-

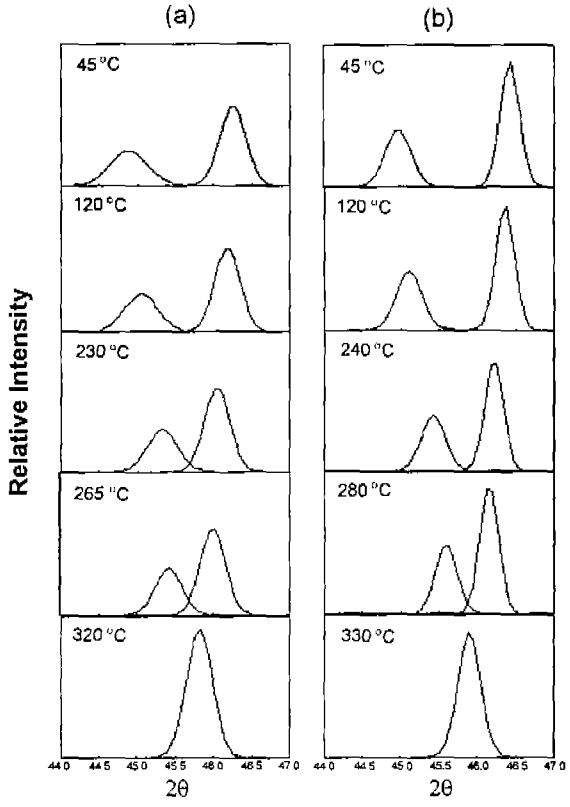

Fig. 2. The change of X-ray diffraction patterns with temperature for 1 kV/mm poled specimens. (a) 1.31 μm and (b) 4.12 μm of $Pb_{0.9}La_{0.1}TiO_3$ ceramics.

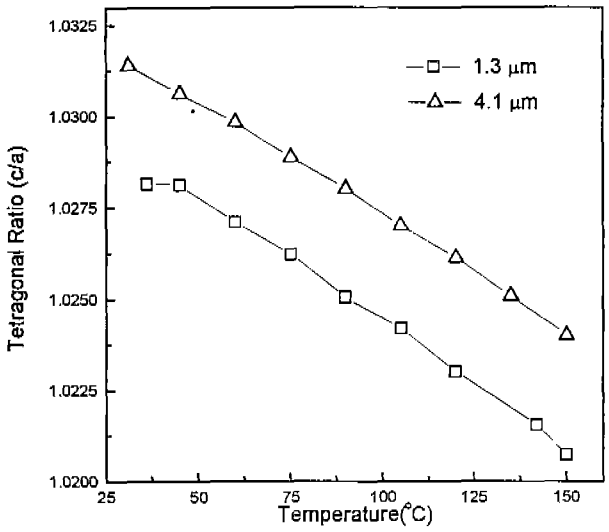

Fig. 3. Tetrogonal ratio as a function of temperature of 1 kV/mm poled $Pb_{0.9}La_{0.1}TiO_3$.

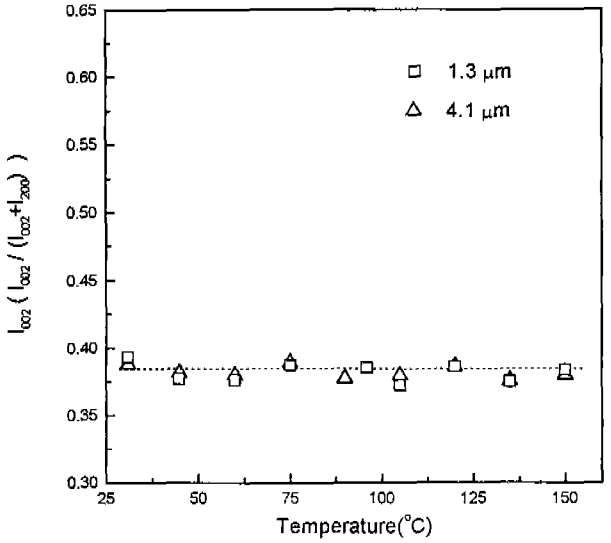

Fig. 4. $I_{002}(I_{002}/(I_{002}+I_{200}))$ as a function of temperature of 1 kV/mm poled $Pb_{0.9}La_{0.1}TiO_3$.

axis decreases rapidly compared to the increase of the length of a-axis. The tetragonal ratio and the relative integrated intensity(I_{002}) are acquired by this diagram with temperature.

Fig. 3 shows the temperature dependence of the tetragonal ratio of the 1.3 μm and 4.1 μm samples after 1 kV/mm of poling treatment. At a given temperature, 4.1 μm sample has higher value of the tetragonal ratio than that of 1.3 μm sample. This reason for the difference of tetragonal ratio is unclear. But the difference of tetragonal ratio between the 1.3 μm and 4.1 μm samples is very small. This result has been reported in the literature.[12] The gradient on the tetragonal ratio with temperature of the 1.3 μm and 4.1 μm samples is almost same. It is predicted that the spontaneous polarization(P_s) change with temperature of the 1.3 μm and 4.1 μm samples is same. (dP_s/dT(1.3 μm)=dP_s/dT(4.1 μm))

It can not be explained that, through the spontaneous polarization change with temperature, the pyroelectric coefficient is higher in the 4.1 μm specimen than in the 1.3 μm specimen after 1 kV/mm of poling treatment. Thus the spontaneous polarization change with temperature has no effect on the pyroelectric property. It has been reported that the piezoelectric effect of a ferroelectric ceramic comes mainly from extrinsic contributions at a relatively low to driving level.[13]

Fig. 4 shows the temperature dependence of I_{002} of the 1.3 μm and 4.1 μm specimens after 1 kV/mm of poling treatment. Before poling, I_{002} at room temperature is 33%-35%. The quantity of 90° domain reorientation is very small after poling treatment. Quantitatively of N^{90}(%) calculated by Mendiolas equation is 4-6% of 90° domain reorientation after poling treatment.[10] Gradients of I_{002} with temperature in the 1.3 μm and 4.1 μm of samples are zero in a range of 25°C to 160°C. This point is easily observed through unchanging each peaks area in Fig. 2.

The effects of 90° and 180° domain walls motion on the pyroelectric property during the temperature change are named as (dP_{90}/dT) and (dP_{180}/dT) for convenience. If 90° domain wall motion causes the polarization decrease when the temperature increases, I_{002} has to decrease. However,

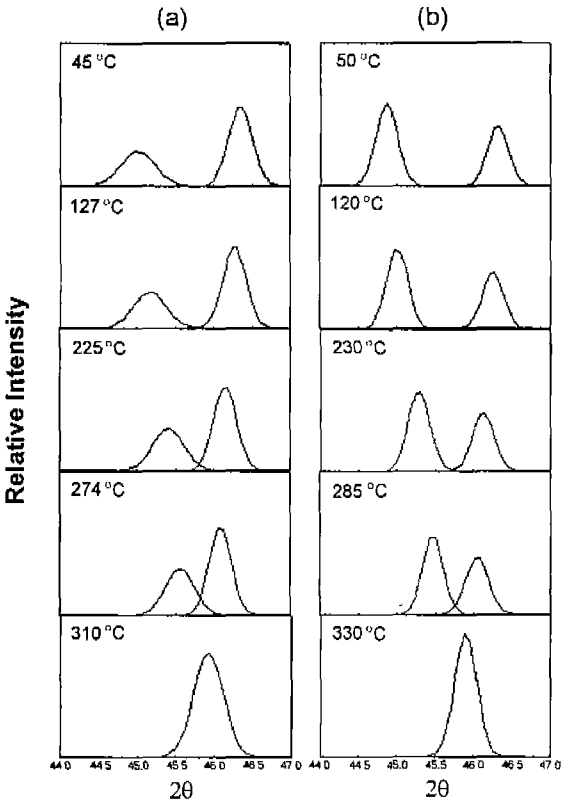

Fig. 5. The change of X-ray diffraction patterns with temperature for 4 kV/mm poled specimens. (a) 1.31 μm and (b) 4.12 μm of $Pb_{0.9}La_{0.1}TiO_3$ ceramics.

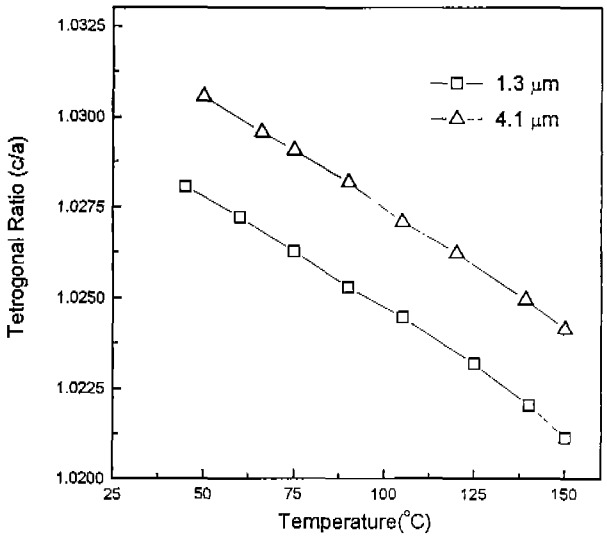

Fig. 6. The change of X-ray diffraction patterns with temperature for 4 kV/mm poled specimens. (a) 1.31 μm and (b) 4.12 μm of $Pb_{0.9}La_{0.1}TiO_3$ ceramics.

Fig. 4 shows that (dP_{90}/dT) is zero because (dI_{002}/dT)=0. This means that the pyroelectric property after 1 kV/mm of poling field is not affected by the 90° domain wall motion with the temperature.

3. Tetragonal ratio(c/a) and $I_{002}(I_{002}/(I_{002}+I_{200}))$ with temperature in PLT ceramics after 4 kV/mm of poling treatment

Fig. 5 shows the diffraction patterns with the temperature for 4 kV/mm poled PLT ceramics. It can be also seen like Fig. 2 that the length of c-axis decreases rapidly compared to the increase of the length of a-axis. Only the quantity of 90° domain reorientation in the 4.1 μm specimen seems to increase a little. Fig. 6 shows the temperature dependence

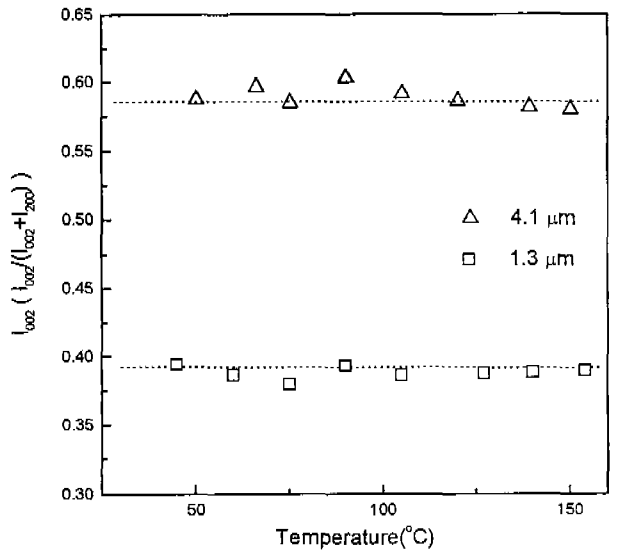

Fig. 7. $I_{002}(I_{002}/(I_{002}+I_{200}))$ as a function of temperature of 4 kV/mm poled $Pb_{0.9}La_{0.1}TiO_3$.

of tetragonal ratio of the 1.3 μm and 4.1 μm samples after 4 kV/mm of poling treatment. Tetragonal ratio and the change of tetragonal ratio with temperature is shown similarly as Fig. 3. As mentioned above, this means that the spontaneous polarization change with the temperature has no effects on the pyroelectric property after 4 kV/mm of poling treatment.

Fig. 7 shows the temperature dependence of I_{002} of the 1.3 μm and 4.1 μm samples after 4 kV/mm of poling treatment. Similarly as Fig. 4, Gradients of I_{002} with temperature of the 1.3 μm and 4.1 μm of samples are zero in a range of 25°C to 160°C. After 4 kV/mm poling treatment, 90° domain wall motion with temperature (dP_{90}/dT) has no effects on the pyroelectric property similarly as 1 kV/mm of poling treatment, because (dI_{002}/dT)=0. N^{90}(%) of the 1.3 μm and 4.1 μm samples are 9% and 17.2% respectively. The values of N^{90}(%) of 4 kV/mm poled samples are higher in compared to those of 1 kV/mm poled samples. However, the pyroelectric coefficients of 4 kV/mm poled samples are 25 nC/cm^2K regardless of grain size. Thus the pyroelectric coefficient is not affected by the quantity of 90° domain reorientation(N^{90}(%)) after poling treatment.

IV. Discussion

The pyroelectric coefficient in the polycrystalline ferroelectric ceramics is defined as the change in remanent polarization(P_r) with temperature by one degree.[14] It means that (dP_r/dT) is related to (dP_s/dT), (dP_{90}/dT), and (dP_{180}/dT). However, polarization means the quantity of electric charge per unit surface area.[14] Thus, when the value of polarization is larger, more electrons move into the pyroelectric current during the temperature change. This means that the value of polarization has an effect on the pyroelectric coefficient. The value of the remanent polarization with poling field increases before saturation. If the value of remanent polarization is related to the pyroelectric coefficient, the pyroelectric coefficient with poling field has to increase before saturation. This is verified easily through Fig. 1. So the value of the remanent polarization has an effect on the pyroelectric coefficient.

It is considered that the remanent polarization means the quantity of 90° domain reorientation and 180° domain switching during poling treatment. We are able to integrate P_{90}, P_{180}, (dP_s/dT), (dP_{90}/dT), and (dP_{180}/dT) contributing on pyroelectric property. (P_{90}, P_{180}: the quantity of 90°- and 180° domain switching during poling treatment, respectively) We have to summarize the above results in Table 1, Table 2 for understanding easily.

In Table 1, it is observed easily that the pyroelectric coefficient is not contributed mainly by (dP_s/dT), P_{90}, and (dP_{90}/dT). Major effect on the pyroelectric property is considered to be related with 180° domain. Effects of 180° domain were to divide into P_{180} and (dP_{180}/dT). If (dP_{180}/dT) is related as a major factor on the pyroelectric property, the pyroelectric coefficient of the 4.1 μm sample should have higher value

Table 1. Characteristics of the $Pb_{0.9}La_{0.1}TiO_3$ Ceramics after 1 kV/mm of Poling Treatment

Grain size	p (pyroelectric coefficient)	Tetragonal ratio (c/a)	(dPs/dT) Gradient of (c/a) with temp.	(P_{90}) N^{90}(%)	(dP_{90}/dT) Gradient of I_{002} with temp.
1.3 μm	0.7 nC/cm^{2}K	1.028	7.6 °C^{-1}	4.24(%)	0
4.1 μm	11.3 nC/cm^{2}K	1.031	7.3 °C^{-1}	5.81(%)	0

Table 2. Characteristics of the $Pb_{0.9}La_{0.1}TiO_3$ Ceramics after 4 kV/mm of Poling Treatment

Grain size	p (pyroelectric coefficient)	Tetragonal ratio (c/a)	(dPs/dT) Gradient of (c/a) with temp.	(P_{90}) N^{90}(%)	(dP_{90}/dT) Gradient of I_{002} with temp.
1.3 μm	25 nC/cm^{2}K	1.028	7.2 °C^{-1}	9.08(%)	0
4.1 μm	25 nC/cm^{2}K	1.031	7.4 °C^{-1}	17.27(%)	0

than that of 1.3 μm sample after 4 kV/mm of poling treatment in a similar as samples after 1 kV/mm of poling treatment. However, the pyroelectric coefficient in the 1.3 μm and 4.1 μm samples is 25 nC/cm^{2}K in Table 2. Thus P_{180} has an important role on the pyroelectric property. It is thought that 180° domain switching occurs more easily in the 4.1 μm specimen than in the 1.3 μm specimen after 1 kV/mm of poling treatment and occurs completely in both samples after 4 kV/mm of poling treatment.

V. Conclusion

The pyroelectric coefficient at room temperature of the 4.1 μm of $Pb_{0.9}La_{0.1}TiO_3$ ceramics is higher than that of the 1.3 μm and 1.7 μm of $Pb_{0.9}La_{0.1}TiO_3$ ceramics at a low poling field and the pyroelectric coefficient is 25 nC/cm^{2}K at a 4 kV/mm poling field in every grain size. In order to explain this phenomenon, the intrinsic and extrinsic effects in view of the definition of the pyroelectric coefficient are introduced. The change of spontaneous polarization and the 90° domain wall motion with temperature in the 1.3 μm and 4.2 μm of $Pb_{0.9}La_{0.1}TiO_3$ ceramics have no effects on the pyroelectric coefficient. In our study, it can be seen that the pyroelectric coefficient is related to the quantity of 180° domain switching after poling treatment.

Reference

1. K. Iijima, R. Takayama, Y. Tomita and I. Ueda, "Epitaxial Growth and the Crystallographic, Dielectric, and Pyroelectric Properties of Lanthanum-Modified Lead Titanate Thin Film," *J. Appl. Phys.*, **60**, 2914-2919 (1986).
2. Takayama and Y. Tomita, "Pyroelectric Properties and Application to Infrared Sensors of $PbTiO_3$, $PbLaTiO_3$ and $PbZrO_3$ Ferroelectric Thin Films," *Ferroelectrics*, **118**, 325-342 (1991).
3. R. Takayama, Y. Tomita, K. Iijima and I. Ueda, "Pyroelectric Linear Array Infrared Sensors Made of C-axis Oriented La-modified $PbTiO_3$ Thin Films," *J. Appl. Phys.*, **63**, 5868-5872 (1988).
4. S. Ikegami, I. Ueda and T. Nagata, "Electromechanical Properties of $PbTiO_3$ Ceramics Containing La and Mn," *J. Acou. Soc. Am.*, **50**, 1060 (1971).
5. Y. Lee, L. W. and J. C., "Domain Structure in Modified Lead Titanate Ferroelectrics," *Ceramics International*, **20**, 117-124 (1994).
6. A. Yamada, Y. Chung, M. Takahasl and T. Ogawa, "Poling Field Dependence of Ferroelecric Domain in Tetragonal Lead Zirconate Titanate Ceramics," *Jpn. J. Appl. Phys.*, **35**, 5232-5235 (1996).
7. S. Wi and H. Kim, "Domain Reorientation Effect on the Temperature Dependence of Piezoelectric Properties in $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$-$PbZrO_3$ Ceramics," *Jpn. J. Appl. Phys.*, **31**, 2825-2828 (1992).
8. Q. M. Zhang, H. Wang, N. Kim and L. E. Cross, "Direct Evaluation of Domain-wall and Intrinsic Contributions to the Dielectric and Piezoelectric Response and Their Temperature Dependence on Lead Zirconate-titanate Ceramics," *J. Appl. Phys.*, **75**, 454-459 (1994).
9. M. I. Meldelson, "Average Grain Size in Polycrystalline Ceramics," *J. Am. Ceram. Soc.*, **52**, 443-446 (1969).
10. Mendiola and L. Pardo, "A XRD Study of 90° Domains in Tetragonal PLZT under Poling," *Ferroelectrics*, **54**, 199-202(1984).
11. E. G. Fesemko, U. S. Filipv and M. F. Kupriyanov, "Homogeneous Parameters Characterizing the Deformation of a Perovskite Lattice," *Sov. Phys-solid state*, **11**, 366-369 (1969).
12. T. Yamamoto, H. Igarashi and K. Okazaki, "Dielectric, Electromechanical, Optical and Mechanical Properties of Lanthanum-Modified Lead Tiianate Ceramics," *J. Am. Ceram. Soc.*, **66**, 363-366 (1983).
13. S. Li, W. Cao and L. E. Cross, "The Extrinsic Nature of Nonlinear Behavior Observed in Lead Zirconate Titanate Ferroelectric Ceramics," *J. Appl. Phys.*, **69**, 7219-7224 (1991).
14. Y. Xu, "Ferroelectric Materials and Their Application," Elsevier Science Publisher, Holland, (1991).