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Electrocaloric Properties of (Pb,La)(Zr,Ti)O₃ and BaTiO₃ Ceramics

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Abstract

The electrocaloric properties of (Pb,La)(Zr,Ti)O₃ (PLZT) and BaTiO₃ ceramics were investigated by the indirect estimation and direct measurement of temperature–electric field (T–E) hysteresis loops. The measured T–E loops showed a similar shape to strain–electric field (s–E) loops. The adiabatic temperature change ΔT due to electrocaloric effects was estimated from the polarization change of these samples. ΔT s of 0.58 and 0.36 K were estimated for the (Pb,La)(Zr,Ti)O₃ (PLZT)(9.1/65/35) ceramics and BaTiO₃ ceramics sintered at 1400°C, respectively. The measured temperature changes ΔT s in these samples upon the release of the electric field from 30 kV/cm to zero were 0.26 and 0.29 K, respectively.

Keywords: Electrocaloric effect, PLZT, BaTiO₃, refrigerator

1. Introduction

The electrocaloric effect (ECE) is a phenomenon in which a material shows a reversible temperature change under an applied electric field [1, 2]. There has been some problem in the conventional refrigerator. Since the conventional refrigerator operates by using a compressor, vibration generation is inevitable. The conventional refrigerator uses Freon as refrigerants; however, Freon acts implicated in ozone depletion. The other disadvantage includes the difficulty in down-scaling. Thermoelectric cooling using the Peltier device has been considered as a solid state cooling device; however, low efficiency has been a hindrance to the wide applications. In addition, common thermoelectric materials used as semi-conductors include bismuth telluride, lead telluride, silicon germanium, and bismuth-antimony alloys. Some of them are toxic. Although new high-performance materials for thermoelectric cooling are being actively researched, the good results have not been obtained. From the viewpoint of the refrigerator innovation, new refrigerators based on the new mechanism are expected. ECE is

considered to be one of the new cooling mechanisms [1, 3, 4]. By using ECE, the application to compact a high energy-effective, inexpensive, and safe refrigerator would be considered, as shown in Fig. 1. ECE was discovered in 1930 by Kobeko and Kurchakov [5]. The research activities on ECE have been not active until the year 2006. In that year, “giant” temperature change in $\text{Pb}(\text{Zr},\text{TiO}_3$ (PZT) thin films were activated at one sweep [6]. Figure 2 shows the relation between the numbers of the published papers and the published year. After 2006, the number of papers on ECE increased rapidly [7-17]. The operation principle of the refrigerator using ECE is shown in Fig. 3. By applying the electric field, the ferroelectrics are heated by ECE. This process corresponds to the compression process in the compressor type refrigerator. By removing the electric field, the directions of the polarization become random. This process is endothermic, corresponds to the expansion process in the compressor type refrigerator, and the object is cooled. The electrocaloric effect (ECE) is a phenomenon in which a material shows a reversible temperature change under an applied electric field. In order to create ECE cooling devices, materials with large ECEs are required. The electrocaloric temperature change ΔT due to applied ΔE is calculated from the following equation [6]:

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

Here, C and ρ are the specific heat and density, respectively. Based on equation (1), a large $(\partial P / \partial T)_E$ (i.e., a large polarization change with temperature under high electric field) is desirable. With respect to achieving large $(\partial P / \partial T)_E$, relaxor materials have recently attracted attention [1, 3, 4]. For direct measurement of the ΔT , there are some difficulties. Most temperature changes are less than 1K. And heat dissipation from ferroelectric materials through electrode, wire, and/or the supporting jig for field application occurs. Most probably due to these difficulties, the reports on the direct measurement of ΔT are limited thus far [13, 17, 18]. In this study, the electrocaloric temperature change, ΔT , due to applied ΔE , of the PLZT ceramics and BaTiO_3 ceramics is estimated and directly measured. Concerning direct measurement of temperature–electric field (T–E) hysteresis loops, the reports have been limited. Detailed measurements of various measurements are required to clarify the insights of the ECE [4, 18, 19, 20].

2. Experimental procedure

PLZT(7/65/35) and PLZT(9.1/65/35) ceramics and BaTiO_3 ceramics were used for ECE measurement. PLZT(7/65/35) and PLZT(9.1/65/35) ceramics were sintered from the commercial powders (Hayashi Chemical) as starting materials. BaTiO_3 ceramics were sintered from the commercial powders (Toda Kogyo). The powders were fired at 1225–1275°C for PLZT ceramics at 1300–1400°C for BaTiO_3 ceramics, respectively [20-22].

The ceramics were polished and then produced electrodes using a silver paste. And the ceramics were polarized for 20 min in a silicone bath under a DC field of 20 kV/cm at room temperature. The dielectric constant and $\tan \delta$ were measured at 1 kHz with an oscillating

Figure 1. The merits of ECE cooler.

Figure 2. Year to year comparison of the numbers of papers on ECE, 1958-2014.

voltage of 1 V. An alternating electric field of 0.1 Hz was used in these measurements. The dielectric constant was measured using an Agilent Technology impedance analyzer, 4192A. Piezoelectric d_{33} meter (IACAS ZJ-3B) was used for piezoelectric measurements. Polarization–

Figure 3. The operation mechanism of the ECE cooler.

electric field (P–E) hysteresis loops of the samples at various temperatures were measured using a combination of a programmable signal generator and a charge amplifier (POEL 101). The samples were cut into 3–4 mm squares, and their temperatures were changed by immersing them in a heated or a cooled oil bath [21,22]. Strain–electric field (s–E) hysteresis loops of the samples at room temperature were measured using a combination of a programmable signal generator and a strain gauge. Triangular waves of 0.1 Hz with 30 kV/cm were applied to the samples in P–E and s–E measurements. The sample temperatures during the application of triangular waves of 0.1 Hz with 30 kV/cm field were measured using a platinum thermometer. The sample temperatures changed periodically in accordance with the external field. The polarization reversals of the samples were monitored on the basis of signals from the charge amplifier (POEL 101). By synchronization of electric field to sample temperature, temperature–electric field (T–E) hysteresis loops were obtained.

3. Results and discussion

3.1. Microstructure

Figure 4 shows SEM micrographs of the surface of the PLZT(7/65/35) and PLZT(9.1/65/35) ceramics sintered at 1225°C. Densely packed microstructures of both ceramics are observed. In the sintering temperature range between 1225°C and 1275°C, the grain growth was not remarkable for these samples; however, the surface roughening were observed in the ceramics sintered at 1275°C, suggesting the lead evaporation loss from the samples. Figure 5 shows SEM micrographs of the surface of the BaTiO₃ ceramics sintered at 1300°C, 1350°C, and 1400°C. The surface of the BaTiO₃ ceramics sintered at 1300°C consists of the small grains of 1–2 μm. The melted grains are observed in the BaTiO₃ ceramics sintered at 1350°C, and large grains at 50–200 μm grains were observed in the BaTiO₃ ceramics sintered at 1400°C. This suggests the abrupt grain growth happened in the sintering temperature above 1350°C.

PLZT (7/65/35)

PLZT(9.1/65/35)

50μm

Figure 4. SEM micrographs of the surface of the PLZT(7/65/35) and PLZT(9.1/65/35) ceramics sintered at 1225°C.

3.2. Electrical properties

Figure 6 shows the P-E hysteresis loops at 10°C, 27°C, and 100°C, s-E hysteresis loops at room temperature, and the T-E hysteresis loops of the PLZT(7/65/35) and PLZT(9.1/65/35) ceramics

BT 1300°C

BT 1350°C

BT 1400°C

50µm

Figure 5. SEM micrographs of the surface of the BaTiO_3 ceramics sintered at 1300°C, 1350°C, and 1400°C.

sintered at 1225°C. Those of the BaTiO_3 ceramics sintered at 1300°C, 1350°C, and 1400°C are shown in Fig. 7. The electrical properties of these ceramics are summarized in Table 1. The change to “soft” ferroelectrics with La content increase yields the increase in dielectric constant, the decrease in remanent polarization (P_r) and coercive force (E_c), the slanted and slim P-E hysteresis loops, and the parabolic s-E loops in the PLZT(9.1/65/35) ceramics, compared with the PLZT(7/65/35) ceramics. In the case of BaTiO_3 ceramics, ferroelectricity increases with the grain growth accompanying the higher sintering temperature. The increase in P_r and d_{33} , the more distinct shrink around E_c in s-E loops with sintering temperature would be due to the increase of ferroelectricity. The low E_c in the BaTiO_3 sintered at 1300°C is probably due to the

slim P-E loop in weaker ferroelectricity and the low E_c in the BaTiO₃ sintered at 1400°C is due to the high domain mobility in large grain ceramics. The higher dielectric constant in the BaTiO₃ sintered at 1300°C compared with those in the BaTiO₃ sintered at 1350°C and 1400°C is characteristic of BaTiO₃ ceramics, and the similar results that BaTiO₃ with grains with at around 1 μm size have been reported thus far [23-25].

	Dielectric constant	Pr (μC/cm ²)	Ec (kV/cm)	d ₃₃ (pC/N)
PLZT(7/65/35)	2464	15.5	6.9	490
PLZT(9.1/65/35)	5564	2.4	2.3	37
BT sintered at 1300°C	3927	4.7	3.3	97
BT sintered at 1350°C	1966	7.1	4.5	126
BT sintered at 1400°C	1591	7.2	3.2	137

Table 1. Electrical properties of PLZT and BaTiO₃ ceramics

3.3. Indirect estimation

The dP/dT between 10°C and 100°C for the PLZT and BaTiO₃ ceramics were calculated using P-E hysteresis loops. Estimated ΔT for from Equation (1) for these ceramics are shown in Table 2. Among the ceramics, PLZT(9.1/65/35), which contains relaxor behavior by introducing Lanthanum substitution, estimated the largest temperature change. Among the BaTiO₃ ceramics, the BaTiO₃ sintered at 1400°C with large grains and accompanying strong ferroelectricity estimated the largest temperature change.

Samples	dP/dT (μCcm ⁻² K ⁻¹)	Estimated ΔT (K)	Measured ΔT (K)
PLZT (7/65/35)	-0.031	0.35	0.07
PLZT (9.1/65/35)	-0.051	0.58	0.26
BT sintered at 1300°C	-0.030	0.29	0.12
BT sintered at 1350°C	-0.026	0.25	0.08
BT sintered at 1400°C	-0.037	0.36	0.29

Table 2. Electrocaloric properties of PLZT and BaTiO₃ ceramics

3.4. Direct measurement

Figures 6 and 7 contain s-E loops and T-E loops of the PLZT and BaTiO₃ ceramics. The similar shapes between s-E loops and T-E loops are observed in these samples. The similar results were reported by J. Wang et al. and our previous report. Field-induced displacement derives from the change in the polarization, and the appearance of similar loops is reasonable. The

(a) PLZT(7/65/35) ceramics   (b) PLZT(9.1/65/35) ceramics

Figure 6. Polarization–electric field (P–E) loops (above), strain–electric field (s–E) loop (middle), and temperature–electric field (T–E) loop (below) of the PLZT(7/65/35) and PLZT(9.1/65/35) ceramics sintered at 1225°C.

Figure 7. Polarization–electric field (P–E) loops (above), strain–electric field (s–E) loop (middle), and temperature–electric field (T–E) loop (below) of the BaTiO₃ ceramics sintered at 1300°C, 1350°C, and 1400°C.

temperature change ΔT of the samples was calculated from the slope beginning with maximum field and ending at the zero field. The temperature change, ΔT , in PLZT(9.1/65/35) ceramics induced by bipolar switching field of 30 kV/cm was 0.26K, and that in the BaTiO₃ sintered at 1400 °C by bipolar switching field of 30 kV/cm was 0.29K. The round T–E and s–E shapes around polarization switching observed in the loop from PLZT(9.1/65/35) attributes characteristic of relaxor ferroelectric materials. The decreasing transition temperature and increasing the polarization movements in relaxor ferroelectrics provide larger temperature change.

The direct measurement shows smaller values, compared with the estimation, generally. The reasons are unknown at present; heat dissipation may play a role in real systems. Although quantitative consistency is not obtained, it is safe to say that the materials with large dP/dT provided large temperature change generally.

4. Conclusion

The electrocaloric properties of (Pb,La)(Zr,Ti)O₃ (PLZT) and BaTiO₃ ceramics were investigated by the indirect estimation and direct measurement of temperature–electric field (T–E) hysteresis loops. The measured T–E loops showed a similar shape to strain–electric field (s–E) loops. This suggests the ECE of these materials are mainly governed by the change of their polarization. The extrinsic contribution from the multi-domain behavior to ECE is limited. The adiabatic temperature change ΔT due to electrocaloric effects was estimated from the polarization change of these samples. ΔT s of 0.58 and 0.36 K were estimated for the (Pb,La)(Zr,Ti)O₃ (PLZT)(9.1/65/35) ceramics and BaTiO₃ ceramics sintered at 1400°C, respectively. The measured temperature changes, ΔT s, in these samples upon the release of the electric field from 30 kV/cm to zero were 0.26 and 0.29 K, respectively.

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