Self Diffusion of Oxygen in PLZT Ceramics

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PLZT セラミックス中の酸素自己拡散

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[Received July 27, 1992; Accepted October 15, 1992]

Self diffusion coefficients of oxygen in PLZT ceramics were evaluated to estimate the vacancy structure by the oxygen-18 isotope exchange reaction and the isotope analysis by the secondary ion mass spectroscopy (SIMS). In the piezoelectric composition of PLZT (10/50/50), the oxygen vacancy concentration was estimated as about one ppm/mol by means of oxygen diffusion measurements and it did not change by doping impurities except for manganese. It was considered that point defects existed at all sites of the perovskite structure of PLZT. On the other hand, the oxygen vacancy concentration increased to 100 ppm/mol for manganese doped samples, and the reason was considered that manganese ions were reduced during sintering and that the oxygen vacancies were created to compensate the charge imbalance. In the transparent PLZT (9/65/35), the oxygen vacancy was ten times as much as that in PLZT (10/50/50). The increase in oxygen vacancy was ascribed to volatilization of lead or variation of solubility of lanthanum in B site. All samples showed extraordinary oxygen diffusion at high temperatures near the surface, which was ascribed to the volatilization of PbO.

Key-words : PLZT, Oxygen diffusion, Manganese, Oxygen vacancy, Vacancy structure, Piezoelectric ceramics

been many reports concerning to this field. However, only cation defects have been focused in almost all of those reports, and the general defect structure including the oxygen sublattice defect has been rarely discussed.^{4),5)}

The authors have been studied the fabrications, especially sintering process of transparent PLZT,⁶⁾ and impurity effects on the properties of PLZT for piezoelectric application.⁷⁾ It is well known that the sintering process of ceramics has been connected directly with diffusion. On the other hand, as concerning to the impurity effect, there is an interesting fact that manganese doping decreases the mechanical vibration loss of PLZT. The authors estimated that such improvement in vibration loss is affected by the variation of the defect structure and the valence state of manganese ions.⁸⁾ In this paper, oxygen sublattice structure was focused to make basic comprehension of those phenomena.

The self diffusion coefficient of oxygen is almost proportional to the amount of the lattice oxygen defects,⁹⁾ so it is very useful to measure oxygen diffusion to evaluate the oxygen vacancy. The effects of composition, impurity and processing on the oxygen defect structure are discussed here.

2. Experimental

2.1 Sample preparations

The composition of PLZT for piezoelectric use was estimated as PLZT (10/50/50) and aluminum, iron, magnesium and manganese were doped to study impurity effects. The detailed compositions are listed in Table 1.

The composition of PLZT for electro-optic use was estimated as (9/65/35) and the samples were prepared by two processes: one was synthesized by dry method (powder calcination) and hot pressed (abbreviated H.P. hereafter), and the other was synthesized by wet method (co-precipitation) and sintered in air (abbreviated N.S. hereafter).

1. Introduction

Pb(Zr,Ti)O₃ (PZT) ceramic is widely used as piezoelectric material and various dopants are applied to control its properties.¹⁾ Especially lanthanum doped (Pb, La) (Zr, Ti)O₃ (PLZT) has been applied not only for piezoelectric use, but also for electro-optic devices since Haertling and Land developed transparent ceramic by hot pressing and reported the effects of applied electric field on its light scattering and double refraction.²⁾ These electro-optic and piezoelectric properties are affected by its composition, impurity and processing.³⁾ It has been considered that these factors are related to the lattice defect structure of PLZT, and there have

Table 1. Nominal compositions and the grain sizes of PLZT(10/50/50) ceramics with M and x in $[\text{Pb}_{0.9}\text{La}_{0.1}][(\text{Zr}_{0.5}\text{Ti}_{0.5})_{1-x}\text{M}_x]\text{O}_3$.

M	x	Grain Size [μm]
Pure	0	4.7
Al	0.02	3.8
Al	0.06	3.7
Fe	0.02	3.5
Fe	0.06	2.4
Mn	0.001	3.2
Mn	0.02	3.4
Mn	0.06	0.8

2.2 Oxygen diffusion annealing and oxygen isotope analysis

The sintered rods were sliced and polished to mirror surface. They were placed in a platinum crucible and annealed in the high frequency induction furnace to induce the oxygen exchange reaction between gas phase and solid phase. The apparatus and diffusion annealing process were reported by Oishi and Kingery.⁸⁾ Condensed oxygen-18 with the concentration of 20–95% was used as the gas phase.

The depth profile of the concentration of the oxygen isotope was analyzed by means of secondary ion mass spectroscopy (CAMECA IMS 4f, noted SIMS further). Cs^+ of 10–100 nA was used as the primary ion, and the secondary O^- ion was detected with the secondary electron amplifier tube. Planar distribution image of ions was detected with digital planar detector (Charles Evans Co.: RAE). To keep constant surface potential, thin gold layer was sputtered on the sample surface and horizontal electron beam gun was applied during the analysis.

3. Results

3.1 Characterization of samples

All samples were single perovskite phase except for manganese doped ones, and solubility limit of manganese into B site of PLZT was estimated as 1–2% from the variation of lattice constants.⁷⁾

The sintered density showed more than 95% of the theoretical for the all samples and concerning to iron and aluminum doped compositions, transparent and pore free samples were obtained as shown in Fig. 1.

The grain size of sintered samples was evaluated by SEM. For PLZT(10/50/50) based samples, they are listed in Table 1, and for PLZT(9/65/35) composition, the grain sizes were 11.5 μm for H.P. sample and 7.0 μm for N.S. sample.

To estimate the diffusion mechanism, planar distribution of oxygen isotope was investigated and the case for not well sintered sample is shown in Fig. 2. The oxygen isotope is condensed at the colored points in the figure and they coincided the pores, but

Fig. 1. Pictures of sintered PLZT(10/50/50): pure, Fe 2% doped, Al 2% doped and Mn 2% doped samples (from the top to the bottom).

Fig. 2. Planar distribution SIMS image of oxygen-18.

such phenomenon is not observed in well sintered samples.

3.2 The depth profile of the oxygen isotope and the evaluation of diffusion coefficients

Figure 3 shows the typical cases of the depth profiles of oxygen-18 isotope. Figure 3(a) shows the case of no doped PLZT(10/50/50) sample, and the oxygen diffusion coefficient is obtained by the following equation because the oxygen-18 concentration at the surface was equal to that of gas phase:¹¹⁾

$$\frac{c - c_1}{c_0 - c_1} = \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (1)$$

where x is depth from the surface, c is concentration

Fig. 3 Depth profile of concentration of oxygen-18 in (a) pure PLZT (10/50/50) annealed at 973 K, (b) Mn-doped PLZT (10/50/50) annealed at 973 K and (c) Al-doped PLZT (10/50/50) annealed at 1273 K.

at x , c_0 is initial concentration in the solid phase, c_1 is concentration in the gas phase, D is diffusion coefficient and t is time. The calculated result is shown as solid line in Fig. 3.

As far as the samples doped with manganese more than 0.1%, the oxygen-18 concentration at the surface was rather smaller than those of the other samples (Fig. 3(b)). Several mechanisms are possible to explain this, but following equation which includes the effect of the exchange reaction at the surface is applied here:¹¹⁾

$$\frac{c-c_1}{c_0-c_1} = \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) - e^{hx+h^2Dt} \times \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}} + h\sqrt{Dt}\right) \quad (2)$$

where $h = \alpha/D$ and α is exchange reaction coefficient. The calculated result is also shown in Fig. 3.

On the other hand, for all samples studied here, when they are annealed at higher temperature, a layer with high oxygen-18 concentration was detected near the surface. In such a case, the following Eq. (3) is applied. It includes the effects of the movement of gas-solid phase boundary during annealing:¹²⁾

$$\frac{c-c_1}{c_0-c_1} = \frac{1}{2} \left[\operatorname{erfc}\left(\frac{x+vt}{\sqrt{Dt}}\right) + e^{-vx/D} \times \operatorname{erfc}\left(\frac{x-vt}{2\sqrt{Dt}}\right) \right] \quad (3)$$

where v is velocity of boundary migration. As shown in Fig. 3(c), the measured values agreed with the calculation at near surface.

3.3 Oxygen diffusion coefficients

The oxygen diffusion coefficients of PLZT (10/50/50) based samples showed almost the same level, as shown in Fig. 4, except for samples doped with man-

Fig. 4 Temperature dependence of oxygen diffusion coefficients of PLZT (10/50/50) doped with various impurities except for Mn.

Fig. 5 Temperature dependence of oxygen diffusion coefficients of PLZT (10/50/50) doped with manganese.

ganese more than 0.1%. The temperature dependence of the diffusion coefficients for these samples is expressed by the Arrhenius relationship noted as follows.

$$D = 3.44 \times 10^{-5} \times \exp[-167(\text{kJ/mol})/RT] (\text{cm}^2/\text{s}) \quad (4)$$

As shown in Fig. 5, the diffusion coefficients of manganese doped samples were 10^2 times as large as Eq. (4). The diffusion coefficients increased with manganese doping concentration (Fig. 6), but showed almost the same value between samples doped with manganese at 2 % and 6 %. Temperature dependence of diffusion coefficients of samples doped with manganese at high concentration are expressed as follows.

$$D = 1.34 \times 10^{-3} \times \exp[-143(\text{kJ/mol})/RT] (\text{cm}^2/\text{s}) \quad (5)$$

On the other hand, as shown in Fig. 7, the diffusion coefficient of PLZT (9/65/35) showed about $10^{1.5}$ times as large as PLZT (10/50/50). However,

Fig. 6. The relationship between oxygen diffusion coefficient at 973 K and manganese concentration in PLZT(10/50/50).

Fig. 7. Temperature dependence of oxygen diffusion coefficients of PLZT(9/65/35) prepared by various process.

the diffusion coefficients showed almost the same values between PLZT(9/65/35) samples which were fabricated by two different processes. The solid line indicates the least square of the results of hot pressed samples. Temperature dependence of diffusion coefficient for transparent PLZT is expressed as follows.

$$D = 4.29 \times 10^{-5} \times \exp[-141(\text{kJ/mol})/RT] (\text{cm}^2/\text{s}) \quad (6)$$

4. Discussion

4.1 Diffusion mechanisms

Generally, the effects of grain boundaries on diffusion have to be considered for polycrystalline ceramics, and they are revealed as the tail shape in the depth profile of oxygen-18 concentration at deep part.¹³⁾ However, the tail shapes were not observed in well sintered samples, while they were observed in not well sintered samples. The origin of fast diffusion is able to be evaluated from the ion distribution image, as shown in Fig. 2. Because the grain bounda-

ry effects were not observed, the obtained oxygen diffusion coefficient approximately equals to volume diffusion in well sintered samples.

Shirasaki et al. pointed out that since oxygen diffusion coefficient significantly decreased in donor doped barium titanate, oxygen diffusion takes a vacancy mechanism.¹⁴⁾ It is considered that oxygen also diffuse through oxygen vacancy in PLZT because the crystal structure of PLZT is as same as that of barium titanate.

Concerning to the Arrhenius equation as expressed in Eqs. (4), (5) and (6), the activation energy for all of the samples showed almost the same value, but the levels of coefficients were different. Accordingly, it is estimated that the activation energy corresponds to the migration energy of the oxygen vacancy, and the level of the diffusion coefficient corresponds to the oxygen vacancy concentration.

4.2 Point defect structure of PLZT

The characterization of point defects in PLZT is rather difficult because the composition is complex, and it is subject to alter by the lead volatilization during sintering.

The defect structure have been reported by Holman¹⁵⁾ and Okazaki.¹⁶⁾ They proposed the following seven possible cases, and the defect structures are listed for some important cases.

(i) La substitutes A site and charge compensation by A site vacancy.

(ii) La substitutes A site and charge compensation by B site vacancy.

(iii) La substitutes A site and charge compensation both by A and B site vacancies:

where $z=x+y$.

(iv) La substitutes both A and B site, and charge compensation both by A site and oxygen vacancies.

(v) La substitutes both A and B site, and charge compensation by A site vacancy.

(vi) La substitutes both A and B site, and charge compensation both by B site and oxygen vacancies.

(vii) La substitutes both A and B site, and charge compensation both by A and B site vacancies.

Holman reported that three phases were observed in PLZT as volatilizing PbO by Knudsen cell measurement: PLZT with excess PbO (abbreviated as PbO-rich composition), single phase of PLZT and PLZT with deficient PbO. He estimated that lanthanum substitutes only A site and that the defect structure takes Eq. (7) form, i.e. the charge is compensated both by A and B site vacancies by the X-ray analysis. He also reported that single phase of PLZT is kept even if some part of PbO is volatilized, then the charge is compensated both by A site and oxygen

vacancies, as expressed in Eq. (11).

In pure PLZT (10/50/50), the defect structure is thought to be PbO-rich composition because the oxygen diffusion coefficient is independent of various dopants except for manganese. According to Eq. (7), the oxygen vacancy should not be generated, then the oxygen diffusion should be related only to the intrinsic oxygen vacancies, and then the activation energy should include the enthalpy change corresponding to both the formation and migration of oxygen vacancy. Then oxygen vacancies should be generated by Schottky equilibrium. However, our result of the activation energy is about 150 kJ, and it is too small to consider as including the energy to make oxygen vacancies since activation change is about 450 kJ in the perovskite structure, according to Shirasaki et al.¹⁴⁾

On the other hand, Okazaki pointed out the possibility that a little part of lanthanum substitute the B site when lanthanum is doped more than $z=0.008$. And such explanation is reasonable because extrinsic oxygen vacancy will not exist when all of lanthanum ions substitute the A site.

The models which include oxygen vacancy are Eqs. (8) and (9), but the possibility for both equations are denied in Holman's paper: Eq. (8) can be applied to Knudsen cell measurements but contradict X-ray analysis, and Eq. (9) contradict weight change analysis. Hence, the defect structure should not be expressed by single equation listed above.

The above discussions suggest a complex defect structure between Eqs. (7) and (9), that means Schottky type vacancies in A, B and oxygen sites, and it does not contradict X-ray analysis because lanthanum concentration in B site is thought in a ppm order, as discussed later.

The generation mechanism of oxygen vacancy is expressed as follows.

If the amount of oxygen vacancy is a equilibrium value, the equilibrium constant, K_{12} can be expressed as follows because La_A , V_A and V_B is almost constant.

$$K_{12} = [\text{La}_\text{B}^{\prime}] \times [\text{V}_\text{O}^{\prime\prime}]^{1/2} \quad (13)$$

Within the temperature range discussed here, the level of oxygen diffusion coefficients of the samples which shows the lowest diffusion are independent of temperature, and the reason is considered that the temperature dependence of K_{12} is rather small, or the amount of oxygen vacancy is stabilized by some other reasons.

4.3 Manganese doping effects

It is considered that all of manganese ions substitute the B site of PLZT from the variation of lattice constant.⁷⁾

As shown in Fig. 6, the diffusion coefficients of

manganese doped samples varied into following three phases by manganese concentration. Below 100 ppm, the diffusion coefficient showed the same value as pure PLZT (10/50/50). Between 100 ppm and 2 %, the diffusion coefficient increased proportionally with manganese content, i.e. the amount of oxygen vacancy was proportional to manganese. The samples doped with manganese at 2 % and 6 % showed about the same diffusion coefficients, and the reason is considered to be due to the solubility limit of manganese into PLZT.

The authors previously reported that some part of manganese ion is reduced to divalent state during sintering, and the Mn^{2+} concentration increases as raising sintering temperature from the results of ESR and magnetic susceptibility measurements.⁸⁾ However, the existence of divalent ions does not always generate oxygen vacancy as like as magnesium (Fig. 4). When the stabilized ion like magnesium and aluminum is substituted, the charge is thought to be compensated by cation site vacancies since the oxygen diffusion coefficient showed the same value as pure PLZT (10/50/50). Hence, the generation of oxygen vacancy is ascribed to the reduction of manganese, expressed as follows:

where the initial valence state of manganese ion is assumed as trivalent.

The reason for generation of oxygen vacancy in manganese doped samples is explained as follows. Initially, when the crystal is formed, Mn^{3+} dissolves into the lattice and the charge is compensated by cation sites vacancies. But when it is sintered at higher temperature, Mn^{3+} is reduced and another charge compensation is necessary: it is considered that the generation of oxygen vacancy is easier than cation vacancies because in a stable perovskite, oxygen vacancy is easier to move. For iron, the valence state is thought to be not varied at high temperature because oxygen diffusion coefficient was the same level as pure PLZT.

Because the valence state of manganese ion is variable, the defect structure should be a metastable state, and it is revealed as the isotope concentration at the surface, which is smaller than gas phase. The same depth profile is obtained when low oxygen diffusion layer is appeared near the surface and then the depth profile can be calculated using double layer model.¹¹⁾ The relationship is shown in Fig. 8, where the surface concentration is normalized as 100%. Solid line indicates the calculated depth profile of double layer model, which agrees with the values calculated by Eq. (3) (closed circles) at deep position. The layer with low oxygen diffusion is considered to be generated during annealing at low temperature, where the Mn^{2+} ions are oxidized to Mn^{3+} , resulting in a decrease of oxygen vacancy near the surface.

From the ESR result, it is considered that about

Fig. 8. Fitting of simulation results for the concentration of oxygen-18 depth profile by various models.

seven percents of total manganese is reduced to divalent state.⁷⁾ Assuming that the solubility limit of manganese into PLZT is about two percents, the concentration of Mn^{2+} becomes 1400 ppm. Also assuming that all of the oxygen vacancies given in Eq. (14) are generated, the oxygen vacancy concentration in the sample becomes 700 ppm. Therefore, the oxygen vacancy concentration of low diffusion samples are about 1 ppm, but it should be noticed that such value is the upper limit.

4.4 Effects of PbO volatilization and the diffusion coefficient of transparent PLZT

Holman reported that perovskite structure of PLZT is stable even if three percents of total PbO is volatilized. As introduced earlier, he reported that when PbO is volatilized, the charge is compensated both by A site and oxygen vacancies, as expressed by Eq. (11). Then, the oxygen diffusion coefficient is expected to increase. Actually, as shown in Fig. 3(c), oxygen-18 is detected in a deeper part in the sample annealed at 1273 K than 973 K. The discrepancy between observed and calculated values are ascribed to the fast diffusion through pores.

The diffusion coefficient of the transparent PLZT (9/65/35) is evaluated as about $10^{1.5}$ times as large as that of PLZT (10/50/50). The reason can be considered in two ways. One is the volatilization of PbO in PLZT (9/65/35) is easier to occur, then the diffusion coefficient is expected to be proportional to the amount of deficient PbO. The other is that the solubility of lanthanum in the B site is subject to change with Zr/Ti ratio, and it is possible because the unit volume of PZT changes with Zr/Ti ratio.¹⁷⁾ So the unit volume of PLZT (9/65/35) is considered to be larger than that of PLZT (10/50/50) and the more La substitute the B site in PLZT (9/65/35) comparing to PLZT (10/50/50). Anyway, it is necessary that about 20 ppm of La substitute the B site to

realize those hypotheses.

It is difficult to judge which consideration is proper for PLZT (9/65/35) because it needs quantitative analysis of whole lead volume with the accuracy of five digits, or detection of 20 ppm of lanthanum in B site. Therefore we should only conclude that 10 ppm order of oxygen vacancy exists in transparent PLZT.

5. Conclusion

The oxygen vacancy concentration of PLZT is evaluated by the measurement of oxygen diffusion coefficients. In the PbO-rich composition of PLZT (10/50/50), the oxygen vacancy concentration is considered to be about 1 ppm. The reasonable vacancy structure for that sample is; Schottky type point defects exist in all of the site of perovskite structure.

For PLZT (10/50/50) doped with manganese more than 100 ppm/mol, the amount of the oxygen vacancies increased with manganese concentration, and it was ascribed to the charge compensation effect due to the reduction of Mn ions during sintering.

On the other hand, for transparent PLZT (9/65/35), about ten ppm of oxygen vacancy is thought to exist. It is considered to be derived from the volatilization of lead or variation of solubility of lanthanum in B site. For all samples annealed at high temperature, abnormal fast oxygen diffusion near the surface due to PbO volatilization was observed.

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