RELATIONSHIP BETWEEN PTCR EFFECT AND OXYGEN GRAIN BOUNDARY DIFFUSION IN BARIUM TITANATE CERAMICS

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It is considered that the PTCR effect is a grain boundary phenomenon and relates to the grain boundary structure. (1, 2, 3 and 4). The grain boundary diffusion is an important parameter clarifying the grain boundary structure. However, experimental study for the grain boundary as a short-circuit path of oxygen ions in barium titanate is qualitative since there are no direct observations of oxygen grain boundary diffusion coefficients. Shirasaki et al. (5) have proposed that the grain boundary of lightly La-doped barium titanate enhances the oxygen diffusion but this method was indirect. The present paper is concerned with the direct observation of the enhanced oxygen diffusion along grain boundary. The PTCR effect is discussed in relation to characteristics of the oxygen grain boundary diffusion.

EXPERIMENTAL

A commercial barium titanyl oxalate, BaTiO(C2O4)2.4H2O, was used as the precursor material. This oxalate, anatase and lanthanum oxalate, 99.99% purity, as the doping elements to produced semiconducting barium titanate ceramics were wet milled using ethyl alcohol and dried, and the mixture was calcined at 1373K for 4h. The resultant powder was then molded into disks that were sintered at 1623K in Ar atmosphere (O2, a few ppm) for 24h, annealed in air for 2h, and cooled in the furnace at 100k/h to room temperature in air (oxidized sample, denoted O-BT). The reduced samples (R-BT) were sintered at the same condition as the oxidized samples and cooled in Ar atmosphere. X-ray diffraction pattern showed the sample’s structure is tetragonal perovskite one and the relative sintered density was 95%. Before measurement of resistivity temperature characteristics and oxygen diffusion annealing, the insulated skin of polycrystal was removed. Indium gallium electrodes were applied for measuring resistance values as a function of temperature in air by using a two probe method.

The oxygen self-diffusion was investigated by a gas-solid isotopic exchange technique using 18O as the tracer. The polished specimens were diffusion-annealed in O2 at 5.0x10^4Pa with 18O enrichment of 98% in a high-frequency induction furnace with Pt-Rh susceptor. The 18O concentration of the gaseous phase was measured using a double focusing massspectrometer. The change of 18O content in the gaseous phase could not be detected during diffusion annealing. The normal depth profile and the lateral distribution of oxygen isotopes were measured by a secondary massspectrometer(SIMS) with an electron multiplier as the detector. Cesium positive ions were used as the primary ions with the ion currents of 5 to 20nA. A normal induced electron gun was used for relieving the samples of the extra charge. To compare the results to other kind of samples, Y-doped ceramics were used, whose purity was lower than La-doped one(6).

RESULTS and DISCUSSION

The results of resistivities are shown in figure 1 and exhibited typical PTCR characteristics in oxidized sample(O-BT), whereas reduced sample(R-BT) has no PTCR effect. Figure 2 shows the normal depth profile of 18O in O-BT, and indicates the surface concentration of 18O was almost same as that of the gaseous phase(98%). The condition of the constant concentration at the surface for a semi-infinite medium can, therefore, be used. The solid line in Fig.2 indicates the fitted value using some date near surface(<100 to 200nm) with a simple error function (7). The profile has a long tail at large depth. It is obvious that the long tail is not due to the lattice diffusion but might be caused by the diffusion along grain boundaries and pores.

As seen in figure 3 of 18O ion image at 1um depth, the grain boundary network could be observed in O-BT samples. In contrast, the 18O concentration at deep position in the sample with no PTCR effect (R-sample) was almost same as natural abundance of 18O, so the grain boundary diffusion does not contribute to the depth profile.

The lattice diffusion coefficients of oxygen ions in two kinds of samples agreed with each other. These values are plotted in figure 4. For lower temperature region volume diffusion coefficient is almost same as the results of Saburi et al.(5). In this region, the activation energy of the oxygen lattice diffusion is considered to correspond to that of oxygen migration in oxygen sub lattice. The values increased at higher temperature because of an increasing number of oxygen defects due to the dissociation of oxygen from oxygen sub lattice that clamed by Shirasaki et al.
Fig. 1. Resistance vs temperature for the lightly La-doped Barium titanate. Solid line; oxidized sample (O-BT), dashed line; reduced sample (R-BT).

Le Claire (8) have proposed the relation between the grain boundary diffusion coefficient and concentration at large depth, which is useful in the present case. Using his equation, the value of $D'$ is estimated from the slope of Fig. 5. Estimated values are listed in Fig. 4. A TEM observation shows the typical lattice fringe image about grain boundary, which indicates that no second phase exists at grain boundary, so the result of $^{18}$O photo image in figure long tail at the large depth in the depth profile was caused by grain boundary diffusion, but not by a diffusion in second phase. Atkinson et al. (9) have reported the cation self diffusion along grain boundary in nickel oxide and claimed that the width of the boundary is about $1 \times 10^{-7}$ cm. The grain boundary diffusion coefficient is four orders of magnitude larger.
larger than the lattice diffusion coefficient. This degree is in agreement with the results reported by Atkinson et al. (9).

Fig. 3. The lateral distribution of oxygen-18 after diffusion-annealing. (a); reduced sample (R-BT), (b); oxidized (O-BT).

Fig. 4. Arrhenius plot of the tracer diffusion coefficient for 18O in the La- and Y-doped barium titanate. Solid line; volume diffusion (present results), dashed line; volume diffusion (Ref. (6)). Closed marks; obsd. volume diffusion coefficients, open marks; products of grain boundary diffusion coefficients and grain boundary width. Circles; La-doped samples, rectangulars; Y-doped samples.

The grain boundary diffusion of oxygen ions could not play the role of a short circuit diffusion in R-sample mentioned above. If the grain boundary diffusion mechanism for oxygen ions should be oxygen vacancy mechanism that occurred in the lattice diffusion, the grain boundary diffusivity of oxygen ions might be larger in R-sample than O-sample, since the possibility of oxygen vacancy
formation is larger in reducing atmosphere than in oxidizing atmosphere. In the present results, the characteristic of oxygen grain boundary diffusion tendency is opposite to the normal tendency as above mentioned. Kondo et al. have reported the compositional change near the grain boundary. As their results the behavior of compositional variation was same as each other both in oxidized and reduced samples. We, therefore, believe that the change of grain boundary diffusion mechanism occurred between O- and R-samples.

Fig.5. $^{18}$O concentration change at the large penetration depth as a function of the value, $x^{6/5}$. Circles; obsd. values, solid line; clcd. value, using Le Claire's analysis for grain boundary diffusion. One can calculate products of grain boundary width, $\delta$, and grain boundary diffusion coefficient, $D'$, using the slope of this treatment(Ref.(7)).

Saburi et al. have reported the relation between the characteristics of the grain boundary diffusion and the PTCR effect(6). As their results, the diffusivities of oxygen along the grain boundary in the PTCR-samples were greater than those in non-PTCR samples. The grain boundary diffusion characteristics drastically changed at the oxygen partial pressure of appearing the PTCR effect. Our results supported their results.

It is, therefore, concluded that the structural change at grain boundary in polycrystalline barium titanate occurred at the oxidizing process and enhanced oxygen grain boundary diffusion. The origin of the barrier layer of the PTCR effect is considered to be same.

REFERENCES