Enhancement of Electrical Conductivity of Polycrystalline β-PbO by Exposure to Ozone Gas at Room Temperature

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Polycrystalline β-PbO pellets were exposed to ozone gas at room temperature. They were oxidized rapidly up to the composition of $PbO_{1.01}$ for 1 h. Then, a color change from bright yellow to greenish brown and an enhancement of electrical conductivity from 10^{-11} to 10^{-3} $S\ cm^{-1}$ were observed. The pellets appeared to have been oxidized up to inside uniformly for 10 min by visual observation. Formation of secondary crystalline phases was not detected by X-ray powder diffraction. Differential thermal analysis showed a broad distinct exothermic peak locating at ∼520 K, which was ascribed to a release of the strain energy accumulated by the room-temperature oxidation. The temperature region corresponded to that of a decrease in conductivity, indicating that the carrier annihilation was closely related to the lattice relaxation. A tentative mechanism that atomic oxygen is a diffusing species with a high rate was proposed.

Introduction

It is well-known that post-transition-metallic cations take two valence states, depending on the environment of the ions. The electronic configurations of these valence states are M^{m+} ($(n-1)d^{10}ns^2np^0$) and $M^{(m+2)+}$-($(n-1)d^{10}ns^0np^0$), respectively, where M stands for the post-transition-metallic cation and n is the principal quantum number. In the family, lead ion is one of the cations whose valence states are easily changeable between these two states (Pb^{2+} and Pb^{4+}) under moderate redox conditions. In lead oxides, a wide variety of crystalline phases have been identified including α-PbO, β-PbO, Pb_3O_4, Pb_2O_3, $Pb_{12}O_{19}$, α-PbO_2, and β-PbO_2.[1] The redox reactions accompanied by uptake or release of oxygen often take place at relatively low temperatures under moderate redox conditions. There is a possibility that the redox reaction can occur even at room temperature under application of an external field. The control of oxidation states of Pb in lead oxides has often been performed by means of electrochemical methods so far.[2−5] The sensitive redox reaction is required for gas-sensing applications. However, no such application of lead oxides has been developed so far, to our knowledge.

In the present study, we report the oxidation behavior of polycrystalline β-PbO with ozone gas at room temperature. Drastic changes in both electrical conductivity and color were found. These changes are discussed from the point of view of thermal stability of the introduced oxygens.

Brief Description of Structural Characteristics of PbO

Lead monoxide has two polymorphic forms whose structures are shown in Figure 1. The transition temperature between these two phases is ∼860 K. The low-temperature phase, α-PbO (litherge, tetragonal, *P4/nmm*) has a two-dimensional layer structure.[6] The layer composed by lead ions comes face to face with each other and is bound by van der Waals interaction. The $6s^2$ inert pair of Pb^{2+} located in the interlayer between two Pb layers contributes to the interaction. Also, the crystal structure of the high-temperature phase, β-PbO (massicot, orthorhombic, *Pbcm*) consists of stacking of zig-zag chains of [Pb−O].[7] In this phase, the lead ion coordinates two oxygens at distances of ∼0.22 nm by a covalent bonding force. As seen in the figure, the cations are very close to each other in the two phases, however, the anions are located at different positions. Accordingly, α- and β-PbO have some characteristics of molecular crystal, which originate from a cationic inert pair.

Experimental Section

The starting material for preparation of a pellet was β-PbO (Koujyundo Kagaku, 99.9% purity). The powder was ground and pressed into a pellet (10 mm diameter and 2 mm thickness). The pellets were heated in air for 10 h at 973 K. Crystalline phases were identified by X-ray powder diffraction

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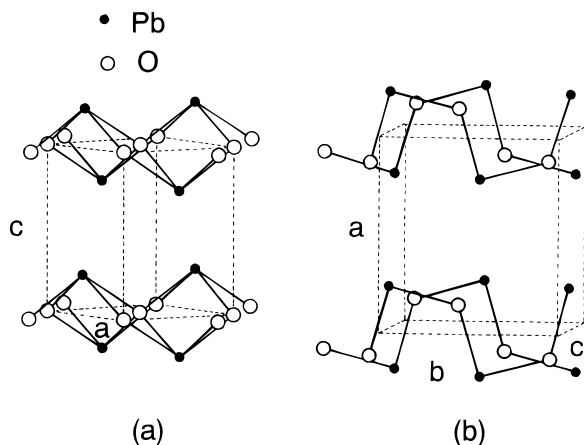(2) Houston, J. R.; Michels, W. C. *J. Chem. Phys.* **1972**, *56*, 1090.
(3) Shea, M. J.; Michels, W. C. *J. Chem. Phys.* **1973**, *59*, 2764.
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Figure 1. Schematic crystal structure of (a) α-PbO or (b) β-PbO.

with a Rigaku RINT2500 diffractometer using Cu Kα radiation (voltage 50 kV, current 200 mA).

Ozone treatment of β-PbO pellets was carried out in the following way: The pellet on an alumina boat was placed in a silica glass tube and exposed to the flow of O_3 at room temperature. O_3 was supplied from an ozonizer (Koyo Kensetsu KW-701K). The average concentration of the gas was 95% O_2−5% O_3 in volume. The flow rate of the gas was 250 mL/min.
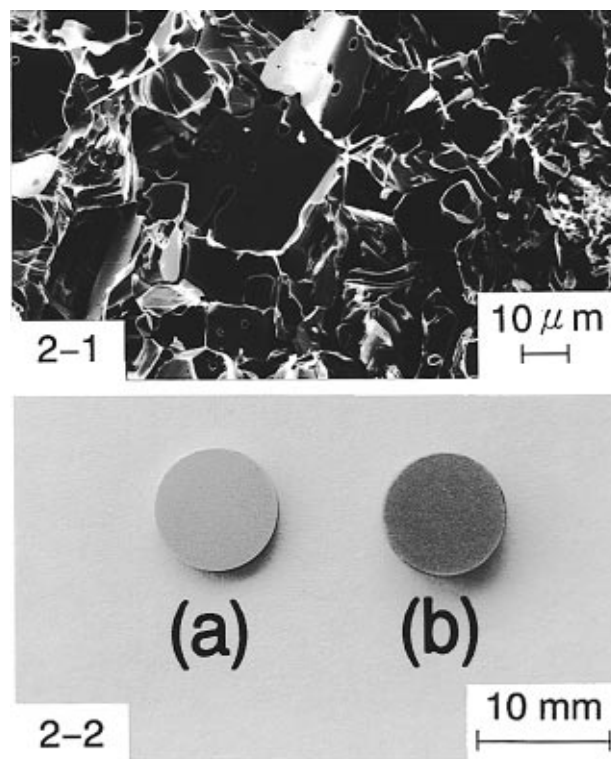
To determine the excess oxygen content and to study the thermal behavior of the samples, thermogravimetry and differential thermal analysis (TG-DTA) measurements were made with a Rigaku TAS-200 under an atmosphere of nitrogen. Mass spectrometry was carried out with a HP 5971A mass spectrometer under an atmosphere of He to analyze the species and content of the evolved gases. The heating rate employed was 10 K/min. Electrical conductivities were measured by dc two-probe method in the temperature region 77−790 K. Gold thin films were sputtered on both sides of the disk of PbO as electrodes. The measurement of Seebeck coefficient was carried out at room temperature under an atmosphere of O_3. The gold wires were pinned down on gold electrodes as leads for measurement of thermoelectric powers. Diffuse reflectance spectra were measured from violet region to near-infrared region with a Hitachi U-4000 double-beam spectrometer. Al_2O_3 powder was used as a reference. To examine valence states of lead ions, X-ray photoelectron spectra were obtained at 300 K with a Shimadzu ESCA-850, using Mg Kα radiation.

Results

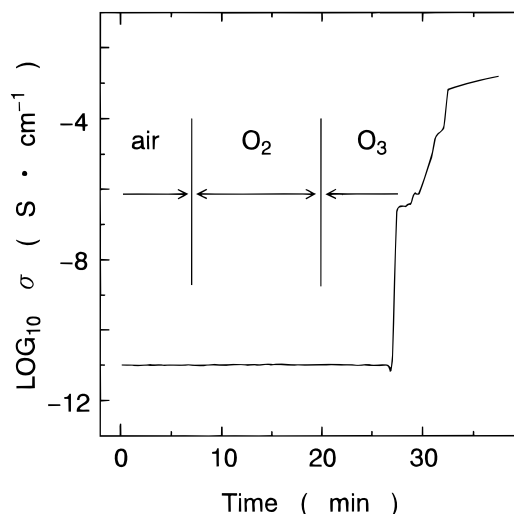The phase formed in the pellets was identified as β-PbO by X-ray powder diffraction. The apparent density of the ceramic pellets was ∼90% of the theoretical value. Figure 2-1 shows SEM photograph of the sintered pellet, indicating that the grain size was 2−30 μm.

After several seconds from the start of exposure to O_3, the color of the pellets changed from bright yellow to greenish brown (Figure 2-2). The pellets appeared to have been oxidized up to inside uniformly at 10 min by visual observation. No diffraction peaks of any phase other than β-PbO and no change in lattice constants of β-PbO were observed in the X-ray diffraction pattern of the O_3-treated sample. No significant change in Pb 4f spin−orbit pair in X-ray photoelectron spectra was observed before and after O_3 treatments.

Figure 3 shows the change in electrical conductivity of the pellet, when an atmosphere was changed from air through O_2 to O_3. Under an atmosphere of air to O_2, the conductivities of the sample were smaller than

Figure 2. (2-1) SEM photograph of fractured surface of β-PbO sintered pellet. (2-2) Photo of β-PbO sintered pellet (a) before and (b) after O_3 treatment.
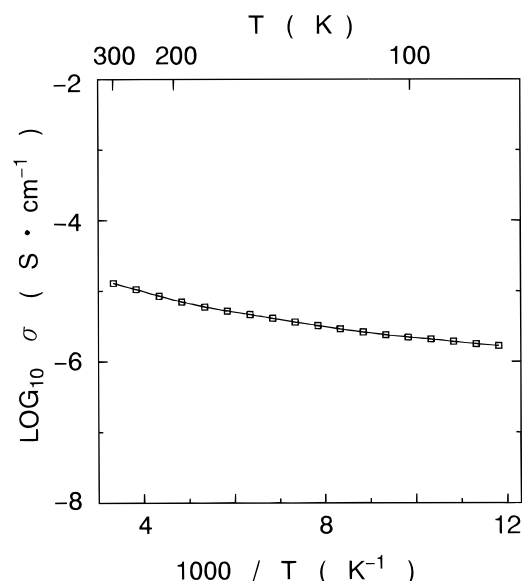

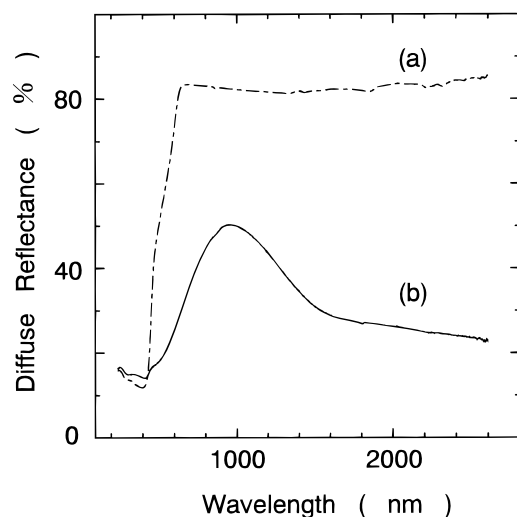**Figure 3.** Change in electrical conductivity of polycrystalline β-PbO at room temperature as a function of time.

10^{-11} S cm^{-1}. It was noted that exposure of the sample to an atmosphere of O_3 even at room temperature resulted in an increase of the conductivity over 8 orders of magnitude. Just after the induction time of ∼7 min in the beginning of the exposure to O_3, a pass for electrical conduction seemed to be formed between two gold electrodes with a distance of 2 mm.

Figure 4 shows temperature dependence of electrical conductivity of the O_3-treated β-PbO pellet. An electrical conduction of an almost thermally activated type was observed. Assuming that electrical conduction behavior is an Arrhenius type, then the activation energy was calculated to be 0.02 eV.

A large decrease in conductivity was observed in several days when the pellet was stored in air or in the chamber with a pressure of 0.1 Pa. The Seebeck

Figure 4. Electrical conductivity vs reciprocal temperature for the β-PbO pellet after 2 h from O_3 treatment for 1 h.
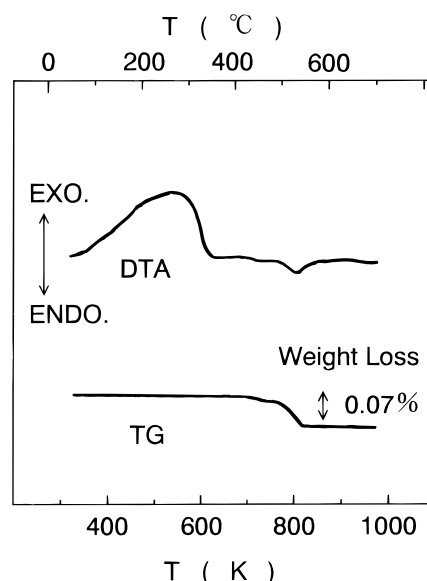

Figure 6. Thermogravimetry and differential thermal analysis of β-PbO treated with O_3 for 1 h. The measurements were carried out in a flow of N_2 gas.

Figure 5. Diffuse reflectance spectra of β-PbO (a) before and (b) after O_3 treatment.

Figure 7. Electrical conductivity vs reciprocal temperature for β-PbO pellet treated with O_3 for 1 h. The measurements were carried out under the atmosphere of N_2. Arrows indicate temperature scanning direction.
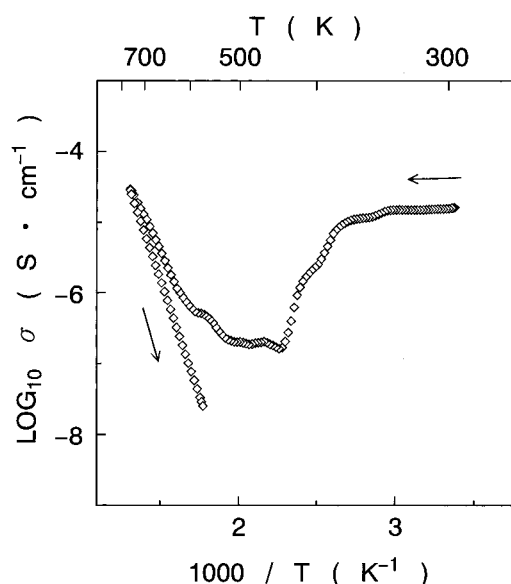
coefficient at 300 K was measured as $-3\ \mu$V/K, indicating that the major carriers were electrons.

Figure 5 shows the diffuse reflectance spectra of the β-PbO powders. The absorption edge of nontreated sample corresponds to the steep change at 450 nm. When the sample was treated with O_3 gas, the new two broad absorptions appeared at 430−900 nm and near-infrared region.

Figure 6 shows TG and DTA data traces under an atmosphere of N_2. No endothermic peak corresponding to the phase transition from β to α was observed. It should be noted that a distinct exothermic peak was observed which started at ∼330 K and ended at 620 K. In this temperature range, no change could be detected in the TG trace. Another feature noted in the DTA curve was a sharp endothermic peak at ∼780 K, which was accompanied by a distinct loss (0.07%) in weight due to the evolution of O_2 (which was confirmed by mass spectrometry). These changes were not observed in nontreated β-PbO. The exothermic peak which does not have an accompanying with a change in TG disappeared after the sample was once heated up to a

temperature above ∼573 K. At the same time, the color was restored.

Figure 7 shows an irreversible change in electrical conductivity of the O_3-treated β-PbO pellet in the temperature range 300−740 K under an atmosphere of N_2. The heating and cooling rates are 5 and −5 K/min, respectively. In the heating process, the observed electrical conductivity of the O_3-treated pellet under an atmosphere of N_2 remained almost constant up to ∼330 K and started to decrease above this temperature, which corresponds to that where the broad exothermic peak in DTA started to increase. The conductivity at 430 K was smaller by 2 orders of magnitude than that at 300 K. The conduction behavior showed thermally activated process at above 600 K. In the temperature range 570 $< T <$ 790 K (oxygen release starts at ∼780 K) in the cooling process, intrinsic semiconductive behavior became dominant.

Discussion

First, the origin of the fast oxidation in polycrystalline β-PbO is discussed. Although the diffusion coefficient of a chemical species dominating the oxidation in β-PbO was not determined in the present experiments, it must be extraordinarily large, judging from the observed room-temperature color change. In typical oxygen ionic conductors such as Y_2O_3-doped Bi_2O_3 and CaO-doped ZrO_2, O^{2-} cannot diffuse to a measurable extent at ~300K,[8,9] because of large charge state and large ionic radius of O^{2-}. Accordingly, in β-PbO, to show large mobility at room temperature, the diffusion species is required to have small charge state and size as well as oxidizing capability. A plausible species is an atomic oxygen, which is created by decomposition of O_3 ($O_3 \rightarrow O_2 + O^{\bullet}$).

On the other hand, intercalation which often takes place in a low-dimensional molecular crystal is well-known as a phenomenon which proceeds at a relatively high rate even at relatively low temperature. In fact, an iodine intercalation in $Bi_2Sr_2CaCu_2O_8$, having the [Bi$-$O] planes similar to the [Pb$-$O] planes in α-PbO was observed at 373$-$523 K.[10,11] Although a superlattice line was not observed experimentally in the X-ray diffraction pattern, there is a possibility that the molecular nature of β-PbO is one of the origins of the fast diffusion of the oxidized species as well as diffusion along grain boundaries.

Second, the formation of a semiconductive phase in O_3-treated sample is discussed. The average composition of the O_3-treated sample, calculated from the weight loss (0.07%), can be expressed as $PbO_{1.01}$. In oxides, the carriers of electrical conduction are classified into two types generally, electron (positive hole) and ion. However, the small activation energy (0.02 eV) of electrical conduction indicated that the major carrier in the polycrystalline sample was the former. Although it was expected that the oxidation of β-PbO gave rise to formation of positive holes, the sign of the thermoelectric power was negative. The following three factors indicated the formation of the conductive phase induced by O_3 treatment other than β-PbO: (1) Although β-PbO has been known as a semiconductor with a bandgap of 2.7 eV, successful doping of positive hole or electron at room temperature has not been reported on this material so far. (2) In typical semiconductive post-transition-metal oxides such as In_2O_3, SnO_2, or PbO_2, the activation energy dose not take small value such as 0.02 eV when conductivity, $\sigma = 10^{-5}-10^{-6}$ S cm^{-1}.[12-15] (3) The Seebeck coefficient of those oxides at room temperature is on the order of several tens to several thousands in unit of μV/K.[16,17] The relatively small value of -3 μV/K

in O_3-treated sample suggests that the fraction of semiconductive phase in the β-PbO pellet is very small or that both electrons and positive holes comparatively contribute to the conductivity. Therefore, it is reasonable to assume that the change in conductivity is originating from the formation of the conductive phase other than β-PbO, although a secondary one was not perceived by powder X-ray diffraction or X-ray photoelectron spectroscopy. The small content of excess oxygen disturbed the detections; moreover, the small chemical shift in Pb 4f core levels in X-ray photoelectron spectra[18] also seemed to do so.

There are a variety of suboxides in the system Pb$-$O, such as PbO, Pb_3O_4, and Pb_2O_3, and PbO_2. In this family, only PbO_2 shows high electronic conductivity at room temperature. This crystal has two polymorphic forms, α and β type, both of which have large conductivities, $\sigma = 10^2-10^4$ S cm^{-1} at room temperature by electron injection via formation of an oxygen vacancy.[19] It is well-known that an oxide of post-transition-metallic cation with $(n - 1)d^{10}ns^0$ electronic configuration, for instance Tl_2O_3, In_2O_3, SnO_2, or CdO, has a high electronic conductivity whose type is n.[20] Therefore, we tentatively ascribe the origin of enhancement of electrical conductivity to formation of a thin layer related to Pb^{4+} such as PbO_2, in grain surfaces and/or grain boundaries.

Finally, thermal stability of carrier is discussed. In the heating process in Figure 7 the conductivity started to decrease at ~330 K which is much lower than desorbing temperature of O_2, 780 K. Most of the excess oxygens did not release yet in the temperature range from 330 to 430 K. The temperature region in which conductivity decreases corresponds to that of broad exothermic peak. The fact that the peak disappeared after the O_3-treated sample was heated at above ~573 K led us to consider tentatively that the exothermic peak was originated from the relaxation of the strain energy of lattice distortion induced by the O_3 treatment. The excess oxygens were inserted at room temperature by O_3 treatment, and it is rational for the crystal lattice to be distorted. On the other hand, in the cooling process in Figure 7, the activated energy for electrical conduction was estimated to be 1.25 eV, which was ~$^1/_2$ of the bandgap (2.7 eV) of β-PbO, indicating that the sample shows intrinsic semiconductive behavior in this temperature region.

We consider briefly the relation between the decrease in conductivity and the lattice relaxation. The value of conductivity may be due to that of carrier mobility and/or carrier concentration. We may rule out the possibility of a decrease in mobility over the two orders, because no structural phase transformation was noted in DTA trace. Then, only possible factor seems to be a decrease in carrier concentration. One possible explanation of a decrease in carrier concentration is due to carrier trapping induced by the relaxation of lattice, for instance, formation of mixed valence state ($2Pb^{3+} \rightarrow Pb^{4+} + Pb^{2+}$).

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Conclusions

Polycrystalline β-PbO pellet was oxidized at 300 K by exposure to O_3 gas. The results obtained are summarized as follows:

The average composition of the oxidized phase determined by TG was estimated as $PbO_{1.01}$. Formation of secondary crystalline phase was not perceived by X-ray powder diffraction or X-ray photoelectron spectroscopy.

Color changed from yellow to brown and electrical conductivity at room temperature increased drastically from 10^{-11} to 10^{-3} S·cm^{-1} by exposure to O_3. Temperature dependence of electrical conductivity measured in the temperature range $77 < T < 300$ K showed thermal activation type with an energy of 0.02 eV. The Seebeck coefficient measured at 300 K under an atmosphere of O_3 was -3 μV/K, indicating that conduction is n-type.

A broad and distinct exothermic peak located at 520 K on DTA trace was assigned to relaxation of stress induced by accommodation of excess oxygens. When the oxidized specimen was heated at above $\sim$573 K, this peak disappeared and the conductivity was reduced over 2 orders of magnitude.

The small values of both Seebeck coefficient and activation energy for conduction suggested that observed high electrical conductivity originated from a certain electroconductive phase associated with Pb^{4+}.