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Activation Analysis of Oxygen in SnO_2 and Zn_2SnO_4 Crystals

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Synopsis. Oxygen content of SnO_2 and Zn_2SnO_4 crystals grown by the vapor phase method was determined by 14 MeV neutron activation analysis. The oxygen contents in the crystals were a little smaller than the theoretical values. The oxygen deficiency in the crystals was found to be related to their inherent semiconductive properties and density.

Many oxides show a semiconductive property originating in the deviation of oxygen from stoichiometry. The authors have already reported on the growth of SnO_2,[1-3] ZnO,[4] and Zn_2SnO_4[5] crystals by the vapor phase method. There is a possible of oxygen deficiency in these crystals because they grew with high growth rate. Therefore, informations on the deviation of oxygen from stoichiometry is important to understand their properties.

Activation analysis has been applied to the determination of the oxygen contents in many organic or inorganic compounds.[6-10] However, its application of oxygen analysis to oxide single crystals is quite a few.

In the present paper, the determination of oxygen contents in SnO_2 and Zn_2SnO_4 crystals was carried out by activation analysis.

Experimental

Samples used in this study were SnO_2 (with/without additives), and Zn_2SnO_4 crystals grown at 1300 °C for 2 hours in porcelain crucible by the vapor phase method. The SnO_2 crystals were obtained from the mixture of SnO_2 and Sn powders, and the Zn_2SnO_4 were also from ZnO and Sn powders. SnO_2 powder (chemical reagent) and ZnO_2 powder (special reagent) were used as reference sample. Sample (ca. 0.1 g) and graphite powder (reagent for spectroscopy, ca. 2.7 g) were mixed sufficiently. The pellets (1.25 cm×1 cm) of the mixed sample were sealed in cylindrical polyethylene containers of 1.5 cm×2 cm. The containers containing samples were transferred from the position of the sample charger to the target area with a pneumatic tube. Samples in the containers were bombarded with 14 MeV neutron with 5×10^9 n s^{-1} of neutron intensity for 30 second at target area. After being bombarded, the containers were transferred to a 4.44 cm×5 cm sodium iodide well-type detector with a pneumatic tube to measure the 6.13 MeV γ-ray from 7.35 sec-halflife ^{16}N produced by the reaction of $^{16}O(n,p)^{16}N$. A neutron generator (by Toshiba Co. Ltd) accelerates deuterium ion to generate 14 MeV neutron by the $^{3}T(d,n)^{4}He$ reaction: $^{3}_{1}T+^{2}_{1}d\rightarrow^{4}_{2}He+^{1}_{0}n+17.59$ (MeV). As a standard sample for calibration, sucrose (guaranteed reagent) was used. The calibration curve on the basis of sucrose-graphite standard sample shows a good linearity in the range of 0 mg to 26.0 mg of oxygen.

Results and Discussion

Table 1 shows the average values on measurements of 3 to 4 times. The values of SnO_2 powder and ZrO_2 powder as reference samples show close agreement with their theoretical values. The values of undoped, antimony-doped and chromium-doped SnO_2 crystals were of the same value, 20.9%. There are no significant differences between the theoretical and the measured values within experimental errors. The oxygen contents is nearly theoretical value. On the other hand, that of vanadium-doped SnO_2 crystals showed clearly a smaller value, 19.9%, than the three others. The density of V-doped crystals was between 5.4 and 5.8. The values were smaller than 6.15 for undoped SnO_2 crystals and 6.12—6.29 for Sb-doped crystals grown at the same vapor phase method. The electrical resistivitiy of the crystals along the growth direction of an a-axis showed semiconductivity at temperatures from 150° to 400 °C. Accordingly, the semiconductive property of V-doped SnO_2 crystals will be due to oxygen defect.[2]

In regards to Zn_2SnO_4 crystals grown under the same conditions, dendrite crystals grown in the initial stage of reaction contain somewhat lower oxygen (19.3%) than that (19.6%) of needle crystals grown in the latter stage of reaction. Both Zn_2SnO_4 crystals showed a lower oxygen content than the theoretical value (20.4%). The electrical resistivity of the needle crystals along growth direction was about 10^3—10^4 ohm cm at room temperature.

On a survey of analytical results, the values of oxygen contents in the vanadium-doped SnO_2 and Zn_2SnO_4 crystals were somewhat smaller than the theoretical values, though antimony-doped and

Table 1. Oxygen Content in SnO_2 and Zn_2SnO_4 Crystals by 14 MeV Newtron Activation Analysis

Crystals	Radiated sample Irradiated /mg	Oxygen content %	Theoretical value/%
SnO_2 powder	80.7	21.0	21.2
ZrO_2 powder	82.6	26.1	26.0
SnO_2	83.7	20.9	21.2
Sb-doped SnO_2	93.9	20.9	21.2
V-doped SnO_2	95.7	19.9	21.2
Cr-doped SnO_2	87.4	20.9	21.2
Zn_2SnO_4(needle)	87.1	19.6	20.4
Zn_2SnO_4(dendrite)	89.8	19.3	20.4

chromium-doped ones had nearly theoretical value. Accordingly, the crystals with low oxygen contents used in the present experiments will have an oxygen deficiency leading to semiconductivity.

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