熱処理時間はガラス組成によって約 10 倍ほどちがうが、 $\log t$ と $1/T$ の勾配はいずれも同じである。これらの関係から見掛けの分相の活性化エネルギーを求めると、62 kcal/mol となる。このように分相速度はガラス組成によって約 10 倍も異なるが活性化エネルギーは全く同じで、分相機構が同じであることを意味している。一方 R. Haul, E. Sucov らによってガラス中の酸素の拡散の活性化エネルギーが求められているが、これらの値は 30~70 kcal/mol のものが多い。これらのことから分相過程の活性化エネルギーはガラス中の酸素の拡散のエネルギーに相当すると考えられる。

(2) 充分分相したガラスの 1 N-H₂SO₄ 100°C での B₂O₃・Na₂O 相の溶出速度は、ガラスの SiO₂ 含有量と Na₂O/B₂O₃ 比によって約 10 倍変わり、SiO₂ 含有量、Na₂O/B₂O₃ 比が大きいほど小さい。60°C, 80°C, の 1 N-H₂SO₄ について同様の実験を行なったが傾向は同じで、いずれも $\log \delta_M^*$ と $\sqrt{t}$ とは直線関係が成立した。また $\delta_M^*/\sqrt{t}$ と $1/T$ にも直線関係が成立し、その勾配はいずれのガラスについても同じである。これらの関係から溶出の活性化エネルギーを求めると約 6.5~6.8 kcal/mol となる。これらのことから、ガラス組成によって B₂O₃・Na₂O 相の溶出速度が約 10 倍異なるが溶出機構はほとんど同じで、また律速段階として酸に満たされた SiO₂ 多孔質層中での B₂O₃・Na₂O の拡散を考えることができる。また溶出速度 $\log \delta_M^*/\sqrt{t}$ とのガラスの SiO₂ 含有量、Na₂O/B₂O₃ 比の間には大略直線

関係がある。

終りに、終始御指導を頂いた当所第四部長桜井泰博士に深く感謝します。

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(3/5/1969 受付)

Optical Properties of Impurities-doped Hydrothermally Grown Zinc Oxide

By

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1. Introduction

Zinc oxide single crystal is typical material in oxide semiconductors of *n*-type, and plays a subordinate role as a photoconductor and piezoelectrics. Recently there is an anticipation that ZnO single crystals can be used as the materials of transducer or acoustic amplifier elements, and that large sound single crystals of ZnO can be grown. In view of the anticipation, the hydrothermal method with an autoclave to controlled impurities is more excellent than any other me-

thod.

ZnO single crystals were grown hydrothermally with 3~6 M KOH solutions in the autoclave, under nearly the same conditions as the temperature and the pressure used for quartz. Li, Cu, Mn and Fe were used as doped impurities, and in this study Li, Cu and Mn were doped intentionally. Namely, 1~2 M LiOH solvents were added to KOH solution as Li source and metallic copper powder (99.95% pure, 1.0 wt% to nutrient) or 0.1 M Cu(OH)₂ solvent was used with

sintered ZnO or to KOH solution as Cu source, and MnCO_3 reagent (0.6~6.0 wt% to nutrient) was mixed with sintered ZnO as Mn source. While, the source of the Fe impurity was brought about by Fe dissolved from the inner wall of the autoclave, when the silver lining tube was sealed defectively in previous study¹⁾. This report described the optical properties of those impurities-doped ZnO single crystals, from the view point of the impurity amount and crystal color, and of the absorption spectrum and photoconductive effect.

2. Experiments

The techniques of hydrothermal crystal growth were described in previous reports^{1~4)}. Grown crystals had prismatic and pyramidal shapes with size of about 10~25 mm. Specimens for absorption and photoconductive experiments were sliced with diamond cutter, polished with SiC powder (800 mesh) and with 9 N KOH solution at 90°C for a few minutes. The specimens were made up in thickness of 0.30 ± 0.02 mm.

To determine the contents of impurities, we used a few methods of a chemical analysis, of which were used a flame photometry for Li, a colorimetry for Cu and Mn, and a gravimetric analysis for Fe. For the absorption measurements, a "Shimadzu IV-50 A" automatic spectrophotometer and for the photoconductive measurements, a "Hitachi EPU-2 A" monochrometer were used. The dark resistivity of Li- and Cu-ZnO samples was about $10^4 \sim 10^8 \Omega$ at liquid nitrogen temperature, while the resistivity of Mn- and Fe-ZnO was about $10^1 \sim 10^2 \Omega$ at the same temperature. The photoconductive effects were carried out supplying a constant voltage of 30 V by an usual DC method.

3. Results and discussion

3.1 Impurity amount and crystal color

The impurity contents of the respective sample in this study were as follows: Li contents, 3~5 ppm; Cu contents, 10^2 ppm; Mn contents, 0.2~1.2 wt%; Fe contents, 0.5 wt%. Under the growth conditions of Li- and Cu-ZnO, even if the concentration of impurity source was increased,

Fig. 1. Doped Mn contents in hydrothermally grown ZnO vs. added Mn contents in nutrient.

the doped-impurity in grown crystal was little increased quantitatively. But in the cases of Mn- and Fe-ZnO, the contents of the doped-impurity were increased in proportion to the concentration on the impurity source. Fig. 1 shows the relation between the concentration of the impurity source and the contents of the doped-impurity in grown crystals, in the case of Mn-ZnO. This fact was corresponded with a color of the grown crystals, e.g., in the case of the smallest Li-doped ZnO, it was found hardly that the impurity, Li had influence on the color of the grown crystals. Although the color of Li-ZnO turned almost yellow, this color was caused possibly by having color centers under interstitial excess of Zn in hydrothermally grown ZnO, because the growth environment was brought to reducing condition⁴⁾. Cu contents in Cu-ZnO were a little larger than Li in Li-ZnO, but the influence on the color was shown similarly with Li-ZnO.

In the case of Mn-ZnO or Fe-ZnO, however, according as increasing each doped amount of impurity the change of the crystal color could be distinguished. The color of Mn-ZnO changed from reddish orange to deep red with increasing Mn contents from 0.2 to 1.2 wt%. The color of a natural ZnO crystal (zincite) turns to a similar red and changes with increasing or decreasing Mn contents⁵⁾.

Table 1. Summary of impurities-doped ZnO crystals. ($x=0\sim9$)

Properties	Crystals	Li-ZnO	Cu-ZnO	Fe-ZnO	Mn-ZnO		
					1	2	3
Crystal color		Pale yellow	yellow	dark green	reddish orange	red	deep red
Crystal habit		pyramidal	prismatic	prismatic		prismatic	
Impurity conc.		3~5 ppm	10^2 ppm	0.5 x %	0.1 x %	0.4 x %	1.2 x %
Conductivity ($\Omega \text{ cm}^{-1}$)		10^{-5}	$10^{-2} \sim 10^0$	10^2		$10^2 \sim 10^3$	
Absorption of impurity ($m \mu$)		398	440	490	510	530	550
Photoconductive effect		○	○	?		?	

The one of Fe-ZnO changed from green to dark green with Fe contents of 0.1~1. x ($x=0\sim 9$) wt%. Those results are shown in Table 1.

For Li- and Cu-ZnO, it was investigated previously by the electrical properties how each impurity was doped in the crystal⁴⁾. Since the crystals are grown with reduced environment, if the added impurity is ionized into the growth solution, this valency may be harmonized with the

smallest number of possible and variable valency. Therefore, Mn in Mn-ZnO and Fe in Fe-ZnO possibly become Mn^{++} and Fe^{++} .

3.2 Absorption spectrum and photoconductive effect

The absorption spectra of a pure ZnO, Zn- and Cu-ZnO crystals obtained by vapor phase method was described by Mollow⁶⁾. Fig. 2 shows an illustration of the absorption spectra of impurities doped hydrothermally grown ZnO. In all cases, it seem that the rise of the absorption constant in transition from the visible to the infrared is changed. For Mn- and Fe-ZnO, this phenomenon was distinguished especially. As the absorption constant was very small, of course, the curves were not indicated the fundamental absorption edge of ZnO crystal. Such the measurements had been made only on thin layers obtained by vapor growth. In Fig. 2, it was thought generally that the steep rise of the absorption constant at the short wavelengths was indicated by the proper absorption of each impurity. Because, Li- and Cu-ZnO samples showed the photoconductive effects at each wavelength (Fig. 3). In other hand, although Mn- and Fe-ZnO could not yet measure these effects due to the low dark resistivity of samples, the absorptions were believed to be shown by one of the impurity from the color of crystals. And that the absorption of this color was shifted toward longer

Fig. 2. Absorption spectra of various impurities-doped ZnO crystals (sample, plate 3×10^{-2} cm thick).

Fig. 3. Photoconductive effects of Li-ZnO and Cu-ZnO crystals. The wavelength of photoconductive effect is coupled with the steep rising position of the absorption constant at short wavelengths.

Fig. 4. Absorption spectra of Mn-ZnO with increasing Mn contents.

Fig. 5. Conductivity vs. Mn contents in Mn-ZnO crystal.

wavelengths with increasing doped impurity, e.g., Mn (Fig. 4). In all cases except Fe-ZnO and 1.2 % Mn-ZnO, the obvious peaks which could be regarded as a proper of ZnO crystal observed at the positions $\lambda=1420 \text{ m}\mu$ and $\lambda=2240 \text{ m}\mu$ (Fig. 2 and Fig. 4). Up to present time such the absorption peaks on the single crystal obtained by vapor growth were found only in more longer wavelength region, i.e., at $6700 \text{ m}\mu$ and $8100 \text{ m}\mu$, and on the ZnO powder or sintered ZnO such numerous ones were found in further long wavelength region⁶⁾. But any positive interpretation between them have not yet been obtained.

Mollow⁶⁾ has shown that the increase of color

centers may be concerned with the increase of the conductivity. For Mn-ZnO this relation is given very clearly in Fig. 4 and Fig. 5. If Fe^{++} and Mn^{++} with excess of Zn take the interstitial positions, they bring about the characteristic color centers and that form the donor levels. Therefore, according to increase the dopant, Mn^{++} or Fe^{++} , the color is concentrated gradually and the conductivity become of high. Since those donor impurities very decreased the dark resistivity of the crystal, in view of sensitization, it has need of a suitable compensative impurity, e.g., Li. A study of the compensators is presently under way.

Acknowledgement

The authors wish to express their sincere thanks to Dr. H. Konno and Mr. T. Koda for their valuable helps carrying out the experiments.

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[Received March 6, 1969]

不純物ドーピング水熱育成酸化亜鉛の光学的性質

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酸化亜鉛単結晶の圧電半導体としての性質を利用して、トランスジューサー、超音波増幅素子としての応用が考えられている。水熱条件下で得られる ZnO はその雰囲気還元性であるために、不純物無添加の場合は過剰 Zn が格子間位置を占めて暗抵抗を低下させる。そこで、筆者らは、その補償のために、 Li^+ , Cu^+ などを不純物として添加し、また、光学増感的な立場から Mn^{++} などの不純物添加を試みて、その波長吸収特性やドーピング量、色調などの光学的な検討を行なった。

Li-ZnO; 結晶中にドーピングされる Li 量は数 ppm~10 ppm までで、この範囲の濃度変化では結晶の色調、波長吸収には顕著な変化は認められない。しかし、電気抵

抗の変化は著しい⁴⁾。Li 吸収の位置は $398 \text{ m}\mu$ であり、光電導もこの近くに現われる。

Cu-ZnO; 10^2 ppm オーダーの量がドーピングされ、Cu 吸収と思われる波長は $440 \text{ m}\mu$ で光電導効果と一致する。

Fe-ZnO, Mn-ZnO; 共にドーピング量の変化により、色調、吸収の位置の変化が著しく、不純物量を増加して行くと色は濃くなり、吸収の位置も長波長側にずれ、電気抵抗の減少をみる。Mn 量の少ない Li-Mn-ZnO について、光学増感的な意味で目下検討中である。

(3/6/1969 受付)