

# Solubility of Sulphur in a Cadmium Borate Glass and Some Properties of the Sulphur Containing Glasses

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## Synopsis

The glass forming limit by substitution of CdS for CdO in a CdO-B<sub>2</sub>O<sub>3</sub> glass was determined by chemical analysis. When  $x$  CdS-(60- $x$ )CdO-40B<sub>2</sub>O<sub>3</sub> nominal mixtures in weight ratio were heated at 1100°C in flowing nitrogen gas for 1/2 hour, about 40~50% of mixed CdS and 10-15% of the mixed CdS were evaporated. The limit of nominal composition for glass forming was 10CdS-50CdO-40B<sub>2</sub>O<sub>3</sub> and the corresponding virtual composition after the above heat treatment was found to be 4.9CdS-46.4CdO-48.7B<sub>2</sub>O<sub>3</sub>. Further addition of CdS made the melt devitrified with CdS precipitation. D. C. conductivity measurements revealed that the current density was not linear with respect to the applied voltage, but the resistivity ranged around  $10^{12}\Omega\cdot\text{cm}$  for 4.1CdS-48.8CdO-47.1B<sub>2</sub>O<sub>3</sub> (virtual composition) glass and around  $10^{11.5}\Omega\cdot\text{cm}$  for 4.9CdS-46.4CdO-48.7B<sub>2</sub>O<sub>3</sub> glass. These sulphur containing glasses did not show photoconduction, although CdS-precipitated materials showed slight photoconductivity when disposed in ultra violet radiation. Apparent dielectric constant and  $\tan \delta$  were also measured as a function of frequency, revealing a moderate dispersion in the CdS-precipitated glasses.

## § 1. Introduction

Most of oxide glasses, such as silicate or borate glasses, are usually highly resistive to electric conduction, though a few kinds of glasses which contain high amount of vanadium oxide<sup>1)</sup> or a glass of the peculiar chemical composition in CdO-SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> system reported by chaslavska et al<sup>2)</sup> are semiconductive. On the other hand, many of glasses made of chalcogenide group have semiconductive character. A group of Se-Te-Si-Ge glass, discovered recently by Obsinsky<sup>3)</sup> and now famous for having possibility to be a new switching material, is a typical example.

It is interesting, in this point of view, to study how the conductive properties will change when oxygen ions in oxide glasses are gradually substituted by more large and more polarizable anions such as sulphur or selenium. The properties perhaps might approach to those of chalcogenide glasses as the substitution goes on.

The solubility of sulphur in any oxide glasses, however, has not been studied yet. One of the purposes of this report is to measure the

solubility in a borate glass. It is not easy to know, prior to experiments, what kind of borate glass will dissolve sulphur much, but it can be said that we should choose a network modifying cation which makes stable compound with sulphur in general. In this study a cadmium borate glass was chosen as a mother glass and the substitution limit of CdS for CdO was investigated.

It is also supposed that CdS crystals might precipitate in the matrix glass when the sulphur content exceeds the limit of solubility in the glass. The electric properties of this composite material are very interesting since CdS itself is well known photoconductive substance. So the electric properties of the sulphur containing glasses and CdS-precipitated composite material were measured.

## § 2. Glass preparation

The glass of a composition CdO/B<sub>2</sub>O<sub>3</sub>=60/40 in weight ratio was chosen as mother glass. Phase diagram of the CdO-B<sub>2</sub>O<sub>3</sub> system was reported by Subbarao and Hummel<sup>4)</sup> as is shown in Fig. 1. The glass region in this system was studied by Izumitani et al<sup>5)</sup>, the

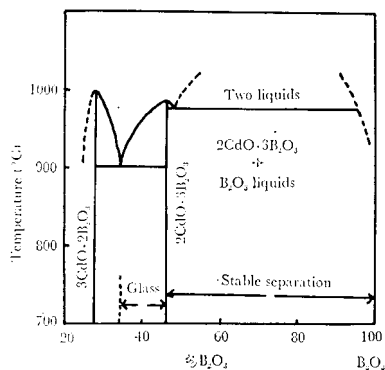


Fig. 1 Phase diagram and glass forming region in the CdO-B<sub>2</sub>O<sub>3</sub> system. (After Subbarao et al<sup>4)</sup> and Izumitani et al<sup>5)</sup>)

result of which is also shown in Fig. 1. It is seen in this figure that the 60CdO-40B<sub>2</sub>O<sub>3</sub> mixture makes glassy specimen when cooled down from more than 1000°C. The glass forming limit of  $x$ CdS-(60- $x$ )CdO-40B<sub>2</sub>O<sub>3</sub> composition was tried to be clarified. So the mixtures of the above composition, varying  $x$  value in weight ratio, were prepared with dried component oxides; CdO and B<sub>2</sub>O<sub>3</sub> of special grade reagents, and  $\alpha$ -CdS powder produced in Toda Ind. Co.

The mixtures were maintained in aluminium oxide crucibles in purified nitrogen gas flow at 750°C for a hour and then melted at 1100°C for 1/2 hour. Prolonged heating at this higher temperature was avoided in order to minimize the evaporations of component compounds. The melts were then cooled down in the same furnace quickly and taken out.

During these heating process three component compounds evaporated more or less, which made the glass composition differ from the corresponding nominal one. So chemical analysis of the obtained glass was necessary.

### § 3. Procedure of chemical analysis

#### (A) Gravimetric analysis of sulphur

A method of sulphur analysis in chalcogenide glasses was reported by Tsuchihashi et al<sup>6)</sup>. This method was applied in the present study with some modifications. Powdered specimens of 500 mg were added to a concentrated NH<sub>4</sub>OH solution with excess amount of H<sub>2</sub>O<sub>2</sub> and then heated. Subsequent addition of H<sub>2</sub>O<sub>2</sub> was necessary. The glass specimen dissolved in a few tenth of minutes, making sulphur in the glass oxidized to SO<sub>4</sub><sup>-</sup> ion

without evolution of H<sub>2</sub>S gas.

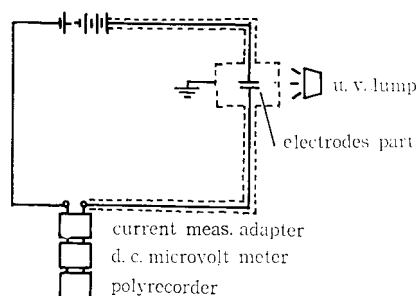
The liquid was then weakly acidified with HCl solution and then 0.05 M-BaCl<sub>2</sub> solution was added after warming up the liquid. The solution with BaSO<sub>4</sub> precipitate was left for a day. The precipitate was filtered and washed as usual way and calcined in a crucible. Thus sulphur in the glass specimen was weighed as BaSO<sub>4</sub>.

#### (B) Cadmium determination by electrolysis

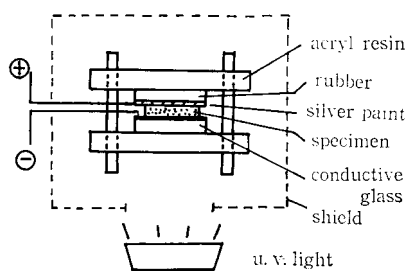
Glass powder of 200 mg was dissolved in 18N-H<sub>2</sub>SO<sub>4</sub> solution and then diluted to about 200 cc. Cd was electrically deposited on a platinum electrode with optimum current density 0.5~1.2A/cm<sup>2</sup> and with a voltage 4.8~5V. About 4 hours were enough to deposit all the Cd ions in the solution.

### § 4. Method of the conductivity and the dielectric measurements

The system of D. C. conductivity measurement used in present report is shown schematically in Fig. 2 (a), and the electrode part of it



(a)



(b)

Fig. 2 (a) Schematic diagram of the electric conductivity measurement system in the dark and in the exposure of a u.v. light.

(b) Magnified picture of the electrode part in the figure (a)

is pictured in magnified view in Fig. 2 (b). In order to measure photoconductivity of specimens, a  $\text{SnO}_2$  coated conductive silica glass which is transparent to ultra violet and visible light was used as the cathode. The anode was made of silver paste, which was rubbed and dried on a soft rubber plate. Since specimens had generally high electric resistivity, a more resistive acryl resin was used as the electrode holder, and electric screening was carefully established.

All the specimens including both the glasses and the CdS-precipitated materials were cut and polished into plates of about 1 mm thick and 1  $\text{cm}^2$  area. D. C. voltage of 1.5~300 V was applied with some dry batteries and Toshiba photochemical mercury lump H-400P was used as a light source for the photoconductivity measurement.

Dielectric properties were measured also for these specimens with a Yokogawa QM-102B Q-meter at room temperature in air as a function of wave frequency.

## § 5. Results and discussions

The mixtures of nominal composition  $x\text{CdS}$ -(60- $x$ )-40 $\text{B}_2\text{O}_3$  ( $0 \leq x \leq 10$ ), in weight ratio, yielded transparent yellow glasses, though the mixtures with  $x \geq 11.5$  became devitrified after the same heat treatment. X-ray analysis revealed that the precipitate was CdS in this case.

Results of quantitative analysis of sulphur and cadmium in these products were summarized in Table I and II, respectively. It is found that about 40~50% of initially mixed sulphur evaporated during the glass making treatment. It is also interesting that the loss of sulphur was not so serious when much CdS crystals remained as precipitate in glasses.

The results of cadmium analysis show that the evaporation of cadmium amounts to about 10~15% of the nominal content, which is not so large as that of sulphur.

Combining these analyses of the two components, the chemical composition of the obtained products were calculated, the results of which is shown in Table III. The amounts of

Table I Result of S analysis of the CdS-CdO- $\text{B}_2\text{O}_3$  products

nominal CdS CdS+CdO+ $\text{B}_2\text{O}_3$	nominal S weight*	analyzed S weight	mean value	fraction of evaporated S
1.0 wt %	1.110 mg	0.776 mg 0.788	0.782 mg	29.5 %
3.0	3.330	1.704 2.305	2.000	39.8
5.0	5.550	2.656 2.597	2.626	52.7
7.0	7.770	4.050 5.053	4.552	41.4
10.0	11.100	4.943 5.904	5.423	51.1
**11.5	12.762	8.414 9.604	9.001	29.4
**11.0	16.650	9.706 9.365	9.536	42.7
**25.0	27.744	23.049 23.286	23.167	16.5

\* nominal value in 500 mg specimens

\*\* makes CdS-precipitated composite material

Table II Result of Cd analysis of the CdS-CdO-B<sub>2</sub>O<sub>3</sub> products

nominal CdS CdS+CdO+B <sub>2</sub> O <sub>3</sub>	nominal Cd weight*	analyzed Cd weight	mean value	fraction of evaporated Cd
1.0 wt %	104.853 mg	93.703 mg 89.130	91.416 mg	12.8 %
3.0	104.464	89.744 89.780	89.762	10.1
5.0	104.074	85.873 85.211	85.542	17.8
7.0	103.684	90.304 93.394	91.849	11.4
10.0	103.100	88.861 88.802	88.832	13.8
**11.5	102.808	100.099 101.167	100.633	1.5
**15.0	102.164	91.038 90.389	90.739	11.1
**25.0	100.180	82.463 84.226	83.345	16.8

\* nominal value in 200 mg specimens

\*\* makes CdS-precipitated composite material

Table III Summarized result of the CdS-CdO-B<sub>2</sub>O<sub>3</sub> products

nominal composition			state	virtual composition (analyzed value)		
B <sub>2</sub> O <sub>3</sub>	CdO	CdS		B <sub>2</sub> O <sub>3</sub>	CdO	CdS
40.0 wt%	59.0 wt%	1.0 wt%	glass, light yellow, transparent	47.7 wt%	51.6 wt%	0.7 wt%
40.0	57.0	3.0		48.5	49.7	1.8
40.0	55.0	5.0		45.0	52.6	2.4
40.0	53.0	7.0		47.1	48.8	4.1
40.0	50.0	10.0		48.7	46.4	4.9
40.0	48.5	11.5	CdS-precipitated, yellow, opaque	41.6	50.3	8.1
40.0	45.0	15.0		47.4	44.1	8.5
40.0	35.0	25.0		41.0	38.1	20.9

B<sub>2</sub>O<sub>3</sub> were derived by the subtraction of the CdS and CdO, the amount of which were calculated by the analyzed amounts of sulphur and cadmium, from the whole weight of analyzed specimens. The limit of composition in the glass forming region in this series was thus found to be about 4.9CdS-46.4CdO-48.7B<sub>2</sub>O<sub>3</sub> in weight ratio.

The results of D. C. dark current-field strength measurement at room temperature are shown in Fig. 3. In this figure are shown

those for two glassy specimens, one of which has the highest sulphur content in this series of glasses. The relationship shown in Fig. 3 is not linear, and the slope changes from 1 to 2 in this log I-log V plot. Generally it is said that in the case with slope 1 the conduction of the specimen is ohmic and in the case of slope 2 the conduction is governed by the space charge limited current<sup>7)</sup>. The conduction mechanism of the present specimens is, therefore, a complex one which should be clarified

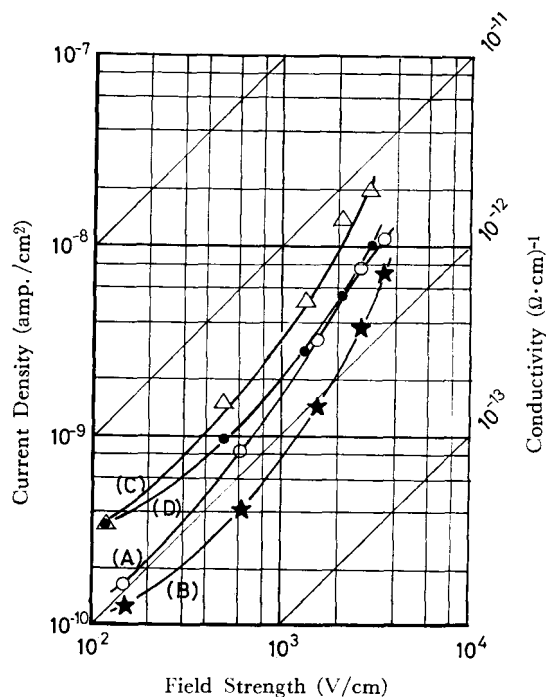


Fig. 3 Results of the dark current measurement for the glassy specimens as a function of the electric field.

(A), (B) ; 4.1CdS-48.8CdO-47.1B<sub>2</sub>O<sub>3</sub> glass.  
 (C), (D) ; 4.9CdS-46.4CdO-48.7B<sub>2</sub>O<sub>3</sub> glass.

with more experiments in future. Since the sulphur content is not so much even in these glasses, the electric resistivity is very high. Nor the glassy specimens of this system showed photoconductivity.

On the other hand, all the CdS-precipitated composite materials of different chemical composition were photoconductive, through the increment of D. C. current when the light was projected was about 30% of the dark current for all the specimens. The observed dark D. C. current-field strength relationship and the photoconductive effect in these materials was illustrated in Fig. 4. Dark current values were generally much higher than those for the homogeneous glassy specimens. The photoconductive efficiency of these materials is much low compared with other crystalline photoconductive materials that are being used in commercial grade.

It can be seen in Table III that in the composite bodies the fraction of all the CdS crystallites to the whole body is about 3~15% in weight. Therefore, it is surprising that these

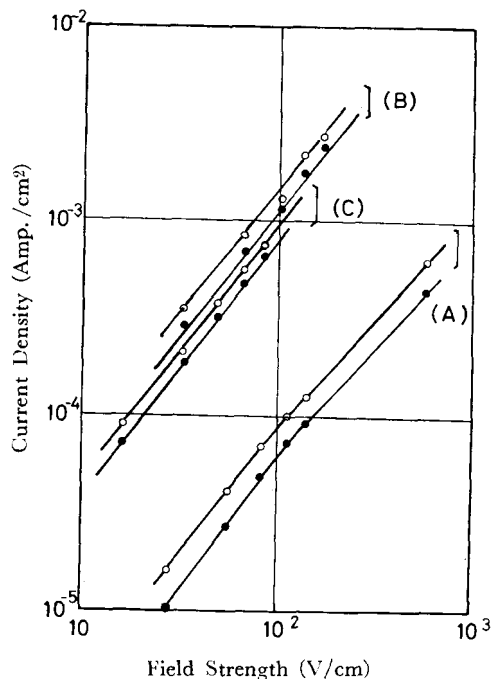


Fig. 4 Dark current (closed circles) and photocurrent (open circles) measured for the CdS-precipitated composite materials.

(A); the material of the 8.1CdS-50.3CdO-41.6B<sub>2</sub>O<sub>3</sub> virtual composition.  
 (B); that of the 8.5CdS-44.1CdO-47.4B<sub>2</sub>O<sub>3</sub> virtual composition.  
 (C); that of the 20.9CdS-38.1CdO-41.0B<sub>2</sub>O<sub>3</sub> virtual composition.

composite materials showed photoconductivity even when CdS crystallites are not considered to link together without being intervened by the glassy matrix, through the two electrodes.

The apparent dielectric constant and  $\tan \delta$  were measured, the results of which are shown in Fig. 5. The glassy specimens did not exhibit a dispersion in this frequency region. The CdS-precipitated ones showed a dispersion which can be explained with the help of a simple model of the material: there should be crystalline grains separated by layers of glassy matrix, as reported by C. G. Koops<sup>9)</sup> for a nickel zinc ferrite. For the homogeneous specimens the dispersion phenomenon is not expected and the experimental result confirmed that the two glassy specimens were homogeneous and did not include any second solid phase in any states. If our glassy specimens contain very small size of the second phase particles or colloidal ones which can not

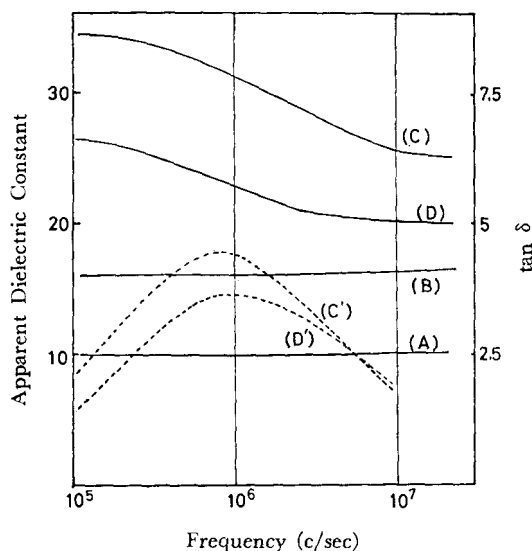


Fig. 5 Apparent dielectric constant (continuous lines) and  $\tan \delta$  (discontinuous lines) of the specimens. (A); 4.1CdS-48.8CdO-47.1B<sub>2</sub>O<sub>3</sub> glass. (B); 4.9CdS-46.4CdO-48.7B<sub>2</sub>O<sub>3</sub> glass. (C), (C'); 8.1CdS-50.3CdO-41.6B<sub>2</sub>O<sub>3</sub> composite material. (D), (D'); 8.5CdS-44.1CdO-47.4B<sub>2</sub>O<sub>3</sub> composite material.

be detected by the X-ray diffraction and the microscopic observation, the dielectric dispersion should be observed.

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