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The Synthesis of Single Crystals of $HgX_2 \cdot 2HgS$ (X=Halogen)

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Synopsis. Single crystals of $HgI_2 \cdot 2HgS$ ($3\times 1.2\times 0.2$ mm^3), $HgBr_2 \cdot 2HgS$ and $HgCl_2 \cdot 2HgS$ were prepared by means of a high-temperature vapor-phase reaction. X-Ray experiments showed that the crystal of $HgI_2 \cdot 2HgS$, the unit cell of which has dimensions of a=9.36 Å, b=9.69 Å, and c=18.5 Å, belongs to the rhombic system.

When powders of $HgI_2 \cdot 2HgS$ (yellow) and its related compounds are exposed to sunlight, they turn black in a few seconds; also, an absorption band is formed in all the visible regions. This process can be reversed, *i.e.*, bleaching occurs slowly in the dark after a few days or instantly when heated at 90 °C. The crystalline powders[1] of these compounds were easily prepared by the action of H_2S on the methanol solution of HgX_2. When a mixture of powdered HgX_2 and HgS (black) in a mole ratio of 1.1: 2 was heated at 170 °C for 1—2 h in an electric furnace, the same compounds as those of the hydrogen sulfide method were produced. In 1955, one of the present authors[2] synthesized a comparatively large single crystal by means of a vapor-phase reaction. About 30 g of a mixture of powdered HgI_2 and HgS (black) in a 1.1: 2 mole ratio were put into a glass tube (1 cm wide and 80 cm long) and placed in an electric furnace. After keeping the bottom of the tube at 520 °C for 30 min, the test tube was taken out and kept in the dark. Yellow crystals were observed inside the tube 40 cm from the bottom. These crystals were $HgI_2 \cdot 2HgS$, with rather small dimensions ($0.6\times 0.7\times 0.04$ mm^3). The purpose of the present investigation is to obtain a single crystal of $HgX_2 \cdot 2HgS$ as large as possible by using a more elaborate apparatus.

Vapor-phase Reaction between HgI_2, Hg, and S. A T-type glass tube (2 cm in inner diameter, 80 cm in length), whose two terminals were stopped with rubber stoppers, was put into a furnace consisting of two porcelain tubes (3 cm in inner diameter, 50 cm in length) and of 750 watts nicrom wires, as is shown in Fig. 1. The third terminal of the glass tube was connected to a water-stream pump in order to evacuate the inner air of the tube until the pressure became 748 mmHg. Asbestos was stuffed into the crevice between the furnace and the glass tube. The temperatures of the left and right parts of the furnace were kept at 280 °C and 500 °C respectively for 2 h by controlling the applied voltage at 50 V and 75 V with silidacs. Moreover, the temperatures at various positions of the two furnaces were measured by means of chromel–alumel thermocouples. The temperature of the B position (indicated in Fig. 1, 4—1 cm from the third terminal) was about 205—185 °C.

Next, a glass boat with 9 g of powdered HgI_2 was quickly placed into the left side of the glass tube, and another glass boat with 3 g of powdered black HgS was quickly put into the right side. The two terminals of the tube were closed again with rubber stoppers. HgI_2 molecules react in the vapor–phase with the Hg or S molecules produced by a decomposition of the HgS. These molecules also drive out oxygen in the tube. The reaction is as follows:

$$m\mathrm{HgI_2(g)} + n\mathrm{Hg(g)} + n\mathrm{S(g)} \longrightarrow \mathrm{HgI_2 \cdot 2HgS(s)} + (n-2)\mathrm{Hg(s)} + (n-2)\mathrm{S(s)} + (m-1)\mathrm{HgI_2(s)}$$

During the reaction, the temperature of the B part was higher than 180 °C. This shows that no crystals of $HgI_2 \cdot 2HgS$ were grown on the B position, because $HgI_2 \cdot 2HgS$ decomposes at 180 °C into HgI_2, Hg, and S. After the reaction had continued for 2 h, the applied voltage was slowly decreased and then cut off. It was observed that red and yellow crystals were deposited at the A and B cool parts respectively, and that gray powders were found at the C cool part, as is illustrated in Fig. 1. It is clear that the red crystals are HgI_2 and the gray ones are Hg and S. The yellow crystals ($3\times 1.2\times 0.2$ mm^3) show a phototropic character. The results of atomic light absorption analysis revealed the Hg content of this crystal to be 65.0% (calcd for $HgI_2 \cdot 2HgS$ 65.4%). These facts show that the crystals were $HgI_2 \cdot 2HgS$, which deposited upon cooling. In order to find the temperature which the crystal commences to deposit, the temperatures of the system while cooling were plotted against the time by using a big T-type glass tube (4 cm$\times$130 cm), two big furnaces, and 12 g of materials. When the temperatures of the left- and right-hand sides of the furnace were kept at 300 °C and 500 °C for 2 h and were then lowered at the rates of 5 °C and 7 °C per 10 min respectively, yellow crystals ($4\times 2\times 0.4$ mm^3) were found at a position corresponding to the C place in Fig. 1. In this case, the temperature of this position, which initially was 205 °C, was decreased at the rate of 2.5 °C per 10 min and then maintained between 175 °C and 150 °C for about 2 h.

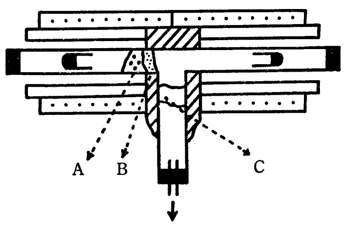

Fig. 1. Preparation apparatus for $HgI_2 \cdot 2HgS$.

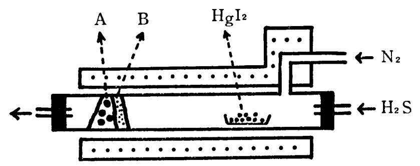

Fig. 2. Preparation apparatus for $HgI_2 \cdot 2HgS$.

It is certain that the crystals commenced to deposit in this temperature range.

High-temperature Reaction between HgI_2 and H_2S. Frerichs[3] prepared single crystals of CdS, CdSe, and CdTe by high-temperature reactions between Cd vapor and H_2S, H_2Se, or H_2Te. Crystals of $HgI_2 \cdot 2HgS$ could also be prepared by a similar method. As is shown in Fig. 2, a glass tube (2 cm in inner diameter, 2 m in length) was put into a horizontal electric furnace. At a point 20 cm from the entrance of the furnace, a glass boat with 5 g of HgI_2 powder was placed; a mixture of H_2S and N_2 was then introduced into the tube at a flow rate of 200 cm^3 per min. The temperature of the position near the glass boat was elevated up to 330 °C over a 1 h period and then kept at this condition for 2 h. After the electric source was cut off, it was observed that red and yellow crystals adhered to the A and B positions respectively, as is shown in Fig. 2. In the course of the reaction, the temperature of the B position was about 150 °C. The phototropy was observed from the yellow crystals deposited at the B place. These crystals are clearly $HgI_2 \cdot 2HgS$. By changing the experimental conditions, such a reaction was tried many times. It was found that $HgI_2 \cdot 2HgS$ crystals ($1.2 \times 0.5 \times 0.1$ mm^3) could also be obtained by this method.

Preparation of Single Crystals of $HgBr_2 \cdot 2HgS$ and $HgCl_2 \cdot 2HgS$. A glass tube (2 cm in inner diameter, 1 m in length) whose bottom had been sealed was placed in a vertical electric furnace. By putting into the bottom 5 g of a mixture of powdered $HgBr_2$ and HgS (black) in a mole ratio of 1 : 2 and by elevating temperature of the furnace, the temperature near the bottom was kept at 450 °C. A vapor-phase reaction was continued under their conditions for 30 h, as is shown in Fig. 3. The air in the tube was then evacuated by using a stream water pump. After the electric source had been cut off, yellow crystals ($1 \times 1 \times 0.5$ mm^3) were found inside the tube 25—29 cm from the bottom. It was easily confirmed by the curve between the temperature and the distance from the bottom that the temperature of this place was 160—200 °C. These crystals are clearly $HgBr_2 \cdot 2HgS$, because they showed phototropic behavior. When using a mixture of powdered $HgCl_2$ and HgS (black), white crystals ($1 \times 1 \times 0.5$ mm^3) were deposited 20 cm from the bottom. The temperature of this point was about 290 °C. These crystals correspond to $HgCl_2 \cdot 2HgS$. Their composition was confirmed by the atomic light absorption analysis; Hg content for $HgBr_2 \cdot 2HgS$: calcd 72.9%, obsd 72.5%; for $HgCl_2 \cdot 2HgS$: calcd 81.7%, obsd 81.3%.

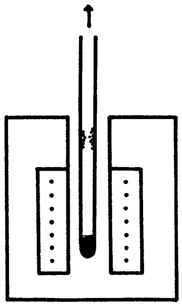

Fig. 3. Preparation apparatus for $HgBr_2 \cdot 2HgS$ or $HgCl_2 \cdot 2HgS$.

An investigation of the Laue photograph on a single crystal of $HgI_2 \cdot 2HgS$ showed that the Laue pattern is distributed with a 2-fold axis and that the symmetry planes of the spots are diagonal to each other. Observation of the single crystal by using a polarized microscope confirmed that this crystal has two light axes. The X-ray rotating-crystal method indicated the lattice constants of this crystal to be a=9.36 Å, b=9.69 Å, and c=18.5 Å. These facts established this crystal belongs to the rhombic system.

The X-ray experiments were carried out at the College of General Education, Kyushu University. The authors wish to express their hearty thanks to Professor Ikuhiko Ueda of Kyushu University for his continuous guidance and advice.

References

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