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Hexagonal High Pressure Phase of Copper(I)tetraiodomercurate (Cu_2HgI_4)

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Summary. Using a high pressure X-ray camera Cu_2HgI_4 was subjected at room temperature to pressures up to about 8 GPa. A hexagonal high pressure phase ($a = 8.28$ (2) Å, $c = 3.40$ (0) Å, space group P$\bar{3}$1m, $Z = 1$) could be detected. This phase shows a reversible transformation with pressure hysteresis. The transition occurs at 7 GPa when the pressure is increased but at 6 GPa when the pressure is decreased.

Keywords. Cu_2HgI_4; High pressure phase; X-ray-investigation.

Hexagonale Hochdruckphase von Kupfer(I)tetraiodomercurat (Cu_2HgI_4)

Zusammenfassung. Cu_2HgI_4 wurde in einer Hochdruckkamera bei Raumtemperatur mit einem Druck bis zu 8 GPa belastet. Dabei bildete sich eine hexagonale Hochdruckmodifikation ($a = 8.28$ (2) Å, $c = 3.40$ (0) Å, Raumgruppe P$\bar{3}$1m, $Z = 1$). Für diese Phase wurde eine reversible Umwandlung mit Druckhysterese festgestellt. Mit steigendem Druck findet die Umwandlung bei 7 GPa mit sinkendem Druck jedoch bei 6 GPa statt.

Introduction

Copper(I)tetraiodomercurate, Cu_2HgI_4, and silver(I)tetraiodomercurate, Ag_2HgI_4, were among the first examples of thermochromic materials investigated. When heated Cu_2HgI_4 changes its colour at 69 °C, and Ag_2HgI_4 at 52 °C. These compounds were originally studied by Ketelaar [1], [2] and Hahn [3]. The structures of these compounds are ordered at lower temperatures, both cations occupy specific sites within the unit cell and each divalent cation is associated with a vacancy. Above the transition temperature the structures are partially disordered, both cations and vacancies are randomly distributed over the cation sites. The thermochromic behavior is due to this order – disorder transition of the cations.

It was shown by Ketelaar [4] that there is a change in electrical conductivity when the ordered low temperature compound is transformed to the disordered high temperature form. Further studies dealt with pressure experiments on Ag_2HgI_4 only but some of them should be discussed here because the two substances may behave similar. Weil and Lawsen [5] studied the electrical conductivity of Ag_2HgI_4 under pressure and found a phase transition above about 0.6 GPa; they suggested the possible existence of still another new phase between 0.4 and 0.6 GPa. The authors paid special attention to the silver compound because of the complex behavior of the copper compound. In Webb's [6] study of Ag_2HgI_4 the reported transitions at 0.4 and 0.6 GPa [5] were confirmed and additional ones were found at 0.75, 4.4, and 7.5 GPa. The results of optical observations in a diamond anvil cell agreed only approximately with those of the pressure measurements.

Baranowsky, Friesel, and Lundén [7] described the phase diagram of Ag_2HgI_4 in the range up to 1 GPa and from 278 to 440 K using differential scanning calorimetry data. Their phase diagram is characterized by four phases. At room temperature a transition of the ordered β phase is found at 0.62 GPa when the pressure is increased and at 0.47 GPa when the pressure is decreased. The authors reported a transition between two ordered phases.

Experimental Method

For the investigations a high pressure X-ray camera (model XKB 100, MRC) was used. A supply tank of nitrogen is fitted to a pneumatic loading cell on which one of the diamonds, the "piston diamond", is mounted directly. The "anvil diamond" is in opposition to the piston diamond. The substance is placed between the polished flats of piston and anvil. The polished face of the anvil diamond is larger than that of the piston diamond to achieve pressure magnification. This magnification factor and the pressure given by the gas source can be directly read from a pressure gauge, and it is equal to the pressure at the interface between the piston and the anvil diamond where the sample is placed. To keep the specimen between the diamonds when pressure is applied a simple copper disk with a central hole is used as gasket.

The X-ray beam passes the collimating system of the camera, the piston diamond, the sample, and the anvil diamond. Behind the anvil diamond there is a flat filmholder which is used for taking X-ray diagrams with unfiltered Mo K_α-radiation. The distance between sample and filmholder was determined by experiments with substances of known lattice parameters. Using a micrometer screw behind the filmholder it was ensured that this distance ($d = 75.2$ mm) between sample and filmholder was kept constant during all the experiments. The pressure was changed in steps of 0.5 GPa and at each pressure value an X-ray exposure was made. The pressure scale of the pressure gauge was calibrated by some known phase transformations [8]: RbCl (0.5 GPa), KCl (2 GPa), and CdS (3 GPa). The pressure readings have an accuracy of about 0.5 GPa. Cu_2HgI_4 was obtained by mixing of freshly prepared CuI and HgI_2 [9]. X-ray films were made to ascertain that the powder had only the β-structure, no additional lines could be detected.

Results and Discussion

The β phase of Cu_2HgI_4 was used as starting material for the investigations at normal pressure and room temperatur. When pressure was increased the first time X-ray patterns up to about 1 GPa always showed this β phase with its ordered tetragonal structure ($a = 6.08$ Å; $c = 12.22$ Å). On raising the pressure up to about 5 GPa the reflexes of the β phase which may coincide with the reflexes of the cubic disordered α phase ($a = 6.103$ Å) increased in intensity. At about 5.5 GPa the reflexes of the β phase with $l = 2n + 1$ lost in intensity and when they disappeared at about 6 GPa weak reflexes of a new phase appeared. At about 7.5 GPa a new arrangement of reflexes could be observed. The corresponding phase was found to be hexagonal (Table 1) with $a = 8.28$ (2) Å, $c = 3.40$ (0) Å, with the space group $P\bar{3}1m$, and $Z = 1$. In this structure both mercury and copper ions are randomly distributed over the position (3 f). They occupy the edges and the center of the planes at the bottom and the top of the unit cell. The four large iodide anions have a close packed hexagonal arrangement within the unit cell. The volume of the hexagonal unit cell

Table 1. Powder diffraction data for the high pressure modification of Cu$_2$HgI$_4$; unfiltered Mo K$_\alpha$-radiation; space group: D$^1_{3d}$−P$\bar{3}$1m, No. 162; (1 Hg + 2 Cu) in 3 f) 1/2, 0, 0; B = 0; 4 I in 4 h) 1/3, 2/3, z; with z = 0.166, B = 0; r/mm: distance of a given diffraction halo measured from the film center

hkl	*r*/mm	*d*/Å (obs)	*d*/Å (calc)	*I* (obs)	*I* (calc)
100	–	–	7.1	–	–
110	c., 12	4.51	4.13	st (diff)	(32)
001 (β)	14.2	β	–	vw	–
200	15.0	3.60	3.59	vw	0.3
001	16.0	3.40	3.40	st	14.9
101	17.7	3.08	3.07	st	12.4
210	20.0	2.739	2.708	m-w	9.4
111	20.7	2.653	2.624	m-w	4.0
201	22.3	2.474	2.467	m	4.9
300	23.1	2.394	2.387	m	8.2
220 (β)	23.8	β	–	vvw	–
211; 220	26.8	2.084	2.118; 2.070	vst	29.4 (8.6 + 20.8)
310	28.2	1.991	1.988	vw	4.4
301	–	–	1.954	–	1.3
400	–	–	1.793	–	0
221; 311	c., 32.5	1.753	1.769; 1.716	m	19.4 (15.4 + 4.0)
002	–	–	1.700	–	0
102	–	–	1.653	–	0
320	c., 35.0	1.643	1.644	vvw	5.1
401	–	–	1.585	–	1.3
112; 410	c., 37	1.566	1.572; 1.564	vvw (diff)	7.3 (2.2 + 5.1)

is 201.97 Å^3. Compared with half the tetragonal unit cell of the β-modification (V = 225.86 Å^3) and the cubic cell of the α-modification (V = 227.32 Å^3) there is a decrease in unit cell volume of 10.6 and 11.2%, respectively.

By decreasing the pressure the hexagonal phase disappeared at about 5 GPa, and another phase – very similar to the β phase – could be detected on the X-ray films. This β-like phase was stable at about 4 GPa. The weak reflexes of the β phase with $l = 2n + 1$ could not be seen on the X-ray films. It is therefore suggested that this phase has the same a- but half the c-parameter of the β-modification possibly with a = 6.08 Å and c = 6.11 Å. By decreasing the pressure to about 3 GPa very weak reflexes of the β phase with $l = 2n + 1$ reappeared on the X-ray films. By decreasing pressure down to normal pressure conditions this β-like phase seemed to be stable, and even 100 hours after releasing the pressure the X-ray pattern was different from that of the starting material. In their investigations about the silver compound Baranowsky et al. [7] reported to have found after pressing metastable mixtures of the β phase and some high pressure phase which could exist for a long time at normal pressure and room temperature. Webb [6], too, reported that samples of Ag$_2$HgI$_4$ after pressure experiments were different from the original ones. So perhaps the copper compound has some similar behavior.

For the second cycle the above mentioned two-component material was set under pressure again, and it remained stable up to about 5.5 GPa. At this pressure up to about 6 GPa the above mentioned reflexes of the β phase lost in intensity but it was not possible to find the one-phase region of the β-like phase by increasing the pressure because the first weak lines of the hexagonal phase had again appeared on the X-ray films. Above 7 to about 8 GPa the X-ray patterns showed only the hexagonal phase. By decreasing the pressure the hexagonal phase was stable to about 6 GPa. Below this value weak lines of the β-like phase were seen on the X-ray films and by further decreasing the pressure these lines increased in intensity, while the lines of the hexagonal modification grew fainter, and at about 5 GPa the lines of the hexagonal phase had disappeared. X-ray films taken at about 4 GPa showed the one-component region of the β-like phase again, and below 3.5 GPa down to normal pressure conditions the two-component region of the β and the β-like phase could be supposed.

This behavior of Cu_2HgI_4 – with exception of the first pressure experiment – was confirmed by several cycles and it could be shown that at room temperature the hexagonal modification is found at about 7 GPa when increasing the pressure and to about 6 GPa when decreasing the pressure. The pressure hysteresis of this reversible transformation is in the range of about 1 GPa. It was recognizable, too, that with further cycles after releasing the pressure the amount of the β-like phase had increased.

As it is very difficult to see the transformation from the β to the β-like phase on X-ray films attention in this work was paid only to the unit cell of the hexagonal phase and to the transition between the β-like phase and the hexagonal one. In addition the one- and the two-component regions of the β, the β-like, and the hexagonal phases could be estimated by X-ray investigations.

Finally it should be mentioned that X-ray patterns taken from a freshly prepared Cu_2HgI_4 and a product stored at ambient temperature for about three years showed no significant difference but the transformation to the hexagonal modification occurred at much lower pressure values when the stored copper compound was used as starting material. This might well be the case for the complex behavior of the copper compound.

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References

[1] Ketelaar J. A. A. (1931) Z. Kristallogr. **80**: 190

[2] Ketelaar J. A. A. (1934) Z. Kristallogr. **87**: 436

[3] Hahn H., Frank G., Klingler W. (1955) Z. Anorg. Allgem. Chem. **279**: 271

[4] Ketelaar J. A. A. (1938) Trans. Faraday Soc. **34**: 877

[5] Weil R., Lawson A. W. (1964) J. Chem. Phys. **41**: 832

[6] Webb A. W. (1973) J. Phys. Chem. Solids **34**: 501

[7] Baranowsky B., Friesel M., Lundén A. (1986) Phys. Rev. **B33**: 7753

[8] Basset W. A., Takahashi T., Stook P. W. (1967) Rev. Sci. Inst. **38**: 37

[9] Palmer W. G. (1954) Experimental Inorganic Chemistry. University Press, Cambridge, p. 192

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