

Pressure induced phase transition in mercurous chloride

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Abstract. Pressure induced phase transition in mercurous chloride has been studied by high pressure x-ray diamond anvil cell. The change in diffraction pattern started and ended at a pressure of about 5 kbar and 20 kbar respectively. The patterns recorded at 20 kbar could be indexed basing on an orthorhombic lattice, with lattice parameters $a=4.23$ Å, $b=4.54$ Å and $c=10.44$ Å.

Keywords. Mercurous chloride; phase transition; high pressure.

1. Introduction

Crystals of mercurous chloride (Hg_2Cl_2) possess some interesting properties. Hg_2Cl_2 crystallises in the space group $I4/mmm$ (D_{4h}^{17}) (Wyckoff 1948). Unit cell dimensions are $a=4.478$ Å and $c=10.914$ Å (Swanson and Tatge 1953). The structure contains chains of linear Cl–Hg–Hg–Cl molecules parallel to the c direction. The centres of the molecules of the nearest neighbour chains are displaced $c/2$ along c . Hg_2Cl_2 transforms to a phase of lower symmetry at low temperatures whose structure is uncertain. (Barta *et al* 1975; Boiko and Voilpolin 1977; Rosasco *et al* 1978). Richter *et al* (1977) studied the Raman spectra of mercurous chloride at room temperature and at pressures up to 16 kbar. They observed many bands that are forbidden by the crystallographic symmetry $I4/mmm$ under pressure. The weak band at 39 cm^{-1} of Hg_2Cl_2 splits progressively and intensifies under pressure. They report that the above changes in the Raman spectra may be explained on the basis of the change of structure, similar to the structure changes at low temperatures. To study the structural changes that occur under pressure, in situ x-ray diffraction studies were carried out. This paper presents the details of the transition.

2. Experimental procedure

The x-ray diffraction data of Hg_2Cl_2 at room temperature and at different pressures were obtained using a diamond anvil apparatus (XKB-100) supplied by Materials Research Corporation (USA). In this camera, pressure is generated between the opposed diamond anvils, and the load is applied by pneumatic loading cell. The diameters of opposing faces of diamond anvils are 0.5 and 0.8 mm. To facilitate the measurement of diffraction angle, a two film cassette (Singh 1972) was used to record

the diffraction patterns. MoK α radiation with Zr filter was used from a normal focus x-ray tube. The accuracy in the measurement of lattice parameter is 0.2%.

Mercurous chloride of 99% purity supplied by Sarabhai Chemicals, Baroda was used in this study. The lattice parameters at 30°C were determined using 19 cm Unicam high temperature powder camera and FeK α radiation. The lattice parameters are $a=4.4849 \pm 0.0001$ Å and $c=10.955 \pm 0.001$ Å. The value of a is comparable to the value reported by Swanson and Tatge (1949) and Boiko and Voilpolin (1977) ($a=4.479 \pm 0.001$ and $c=10.922 \pm 0.002$) but c is slightly more than their values. Two pressure runs were recorded—one with the pressure standard and one without the pressure standard. The exposure times range from 100 to 200 hr. Silver was used as internal standard. Silver was mixed in different proportions with the sample until it gave diffraction patterns of both the sample and silver. The diffraction lines (111), (200) and (220) of silver were used to calculate the lattice parameters at different pressures. Experimental equation of state for silver (Lin-gun Liu *et al* 1973) has been used to convert volumes into pressures.

3. Results and discussion

The phase transition was detected mainly by the blurring of 101 tetragonal line, appearance of two new lines and overlap of the 114 and 105 tetragonal lines at high pressures. At ambient pressure the lines 101, 110, 114 and 105 could be recorded very clearly. The blurring and decrease in the intensity of 101 and appearance of new lines could be seen in the pattern recorded at about a pressure of 5 kbar (This is the minimum pressure that can be obtained with the set-up and is a rough estimation made from the load applied on the anvils). The transition was complete at about a pressure of 20 kbar. Still the faint blurred 101 line could be seen. This pattern could be indexed on the basis of an orthorhombic lattice with parameters $a=4.23$ Å, $b=4.54$ Å and $c=10.44$ Å. The observed d -spacings and intensities along with the d -spacings and intensities of tetragonal phase are listed in table 1 for comparison. The

Table 1. Interplanar distances of tetragonal and orthorhombic phases of Hg₂Cl₂.

Tetragonal phase*			Orthorhombic phase (20 kbar)			
d (Å)	hkl	I/I_1	d_{obs}	I_{obs}	hkl^\dagger	d_{cal}
4.141	97	101	5.22	m	002	5.22
3.164	100	110	3.05	s	110	3.09
2.824	9	103	2.68	s	112	2.66
2.727	28	004	1.96	s	202	1.96
2.242	23	200	1.90	s	023	1.90
2.065	53	114				
1.970	38	211				
1.962	47	105				

*Data taken from ASTM data file No. 4-581.

†Indexing is made assuming an orthorhombic lattice with the lattice parameters $a=4.23$ Å, $b=4.54$ Å and $c=10.44$ Å and d_{cal} are the d -spacings calculated from these lattice parameters.

m: medium

s: strong

faint blurred 101 line persisted up to the highest pressure applied (about 80 kbar). The blurring of the 101 line may be its splitting when Hg_2Cl_2 transforms into a new phase. The overlap of the 114 and 105 reflections (indexed as 202 and 023 reflections in the new phase) could be observed in the patterns recorded at a pressure of 40 kbar. The overlap of the lines may be due to the anisotropic compressibility of the new phase. We could not determine the compressibilities of Hg_2Cl_2 above and below the transition. The reasons for this are that the transition starts at the minimum pressure that could be obtained with the set-up and overlap of the two lines in the new phase leaves us with only three lines from which it is difficult to calculate the lattice parameter. It has not been possible to determine the orthorhombic space group with the few lines available.

Compression measurements of Hg_2Cl_2 , carried out by Richter *et al* (1977) with a piston cylinder apparatus showed no discontinuity in volume change that might indicate a first order transition. Though we have found 9% decrease in volume at 20 kbar it could not be decided unambiguously that the transition is of the first order due to the following reasons.

1. Change of the lattice parameters of the tetragonal phase could not be studied below 5 kbar.
2. The pressures reported in our work involve large errors because of the inherent uncertainty in the pressure measurement at low pressures.
3. The lattice parameters of the new phase were calculated from a diffraction pattern which was not recorded in the vicinity of the transition point but at a higher pressure.

The new phase can be thought of as a distortion from the tetragonal to the orthorhombic lattice. The c axis is the same in the two phases and the tetragonal a splits into a and b . If the transition is of the second order its structural changes may be similar to the changes reported in the case of paratellurite (P4_12_12) (Skelton *et al* 1976) and nickel fluoride (rutile) (Jørgenson *et al* 1978).

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