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# Pressure-induced structural transformation in potassium stanichloride

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**Abstract.** Pressure-induced structural transformation in potassium stanichloride has been studied by x-ray diffraction at room temperature. The change in the diffraction pattern started at about a pressure of 15 kbar and continued upto 50 kbar. The pattern recorded at about 50 kbar could be indexed basing on an orthorhombic lattice, with lattice parameters $a$=7.32, $b$ = 7·02 and $c$ = 8·02 Å.

**Keywords.** Potassium stanichloride; structural transformation; x-ray diffraction; high pressure.

## 1. Introduction

Potassium stanichloride ($K_2SnCl_6$), a member of $A_2MX_6$-hexahalometallates, crystallises in the cubic face-centered antiflourite structure of space group $O_h^5$ [$Fm3m$] at room temperature and atmospheric pressure (Dickinson 1922; Brill *et al* 1974; Lerbscher and Trotter 1976; Ihringer 1977). The Sn atoms occupy an fcc lattice and are surrounded by $Cl_6$ octahedra, which are oriented according to the cubic symmetry. The $K$ atoms form a primitive cubic lattice with $a/2$, which is shifted 1/4 along the room diagonal. The crystal undergoes two structural phase transitions from its cubic room temperature phase to a lower symmetry at low temperatures (Morfee *et al* 1960; Sasane *et al* 1970; Jeffrey 1972; Winter and Rössler 1976; Winter *et al* 1976; Boysen *et al* 1976). Until recently, according to neutron-scattering and x-ray measurements (Boysen and Hewat 1978; Boysen *et al* 1976), phase transitions were considered to occur from the cubic room temperature phase $O_h^5$ to a tetragonal structure of space group $D_{4h}^6$ at $T_{c1}$ = 261°K and to a monoclinic structure of space group $C_{2h}^5$ at $T_{c2}$ = 255°K. More recent x-ray scattering experiments by Kugler *et al* (1979) and Brillouin-scattering experiments by Henkel *et al* (1980b), however, do not support this result. A symmetry change from $O_h^5$ to the orthorhombic structure of space group $D_{2h}^2$ at $T_{c1}$ and the monoclinic structure of space group $C_{2h}^5$ below $T_{c2}$ are found to be most compatible with their experimental results. Recent Raman-scattering experiments on $K_2SnCl_6$ under hydrostatic pressure by Henkel *et al* (1980a) showed that the crystal becomes orthorhombic at room temperature under a pressure of about 45 kbar. However, no x-ray studies on the structural changes of this compound under pressure at room temperature are reported so far. In an effort 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

$K_2SnCl_6$ single crystals were grown from aqueous solution by conventional methods. The high purity (99.99%) powder samples used for the single crystal growth of $K_2SnCl_6$ were kindly supplied by Dr. Henkel of Institut für Experimental Physik VI, Bochum, FRG. The lattice parameter of this compound determined from a Debye-Scherrer powder photograph at room temperature ($a=10.002\pm0.002$ Å) is comparable to the value reported by the NBS circular (Anon 1956) (10.002 Å). Lerbscher and Trotter (1976) (9.990Å) and Regelsberger and Pelzl (1979) (10.000 Å) at room temperature.

The x-ray diffraction data of $K_2SnCl_6$ at room temperature and at different pressures were obtained using a diamond anvil apparatus (XKB–100) supplied by the Materials Research Corporation (USA). In this camera, the pressure is generated between the opposed diamond anvils, and the load is applied by pneumatic loading cell. To facilitate measurements of diffraction angle, a two-film cassette (Singh 1972) was used to record the diffraction patterns. $MoK_\alpha$ radiation with Zr filter was used from a normal focus x-ray tube. Two pressure runs were recorded, one with the pressure standard and one without the pressure standard. Silver was used as the internal standard and was mixed in different proportions with the sample until it gave diffraction patterns of both the sample and silver. The exposure times range from 100 to 200 hr. The details of the experimental set-up and the method of estimating the true pressures on the sample were described in an earlier paper (Ranga Prasad *et al* 1979).

## 3. Results and discussion

At an ambient pressure the reflections 111, 200, 222, 400, 422, 511 and 531 could be recorded very clearly. As the pressure was increased the onset of the transition was evidenced in the diffraction data by a gradual blurring of 222, 400, 422 and 511 reflections coupled with slight displacement of some reflections from their correct cubic positions. Further the intensity of the reflections 111 and 200 gradually decreased with increasing pressure. The blurring of some reflections and the decrease in the intensity of the 111 and 200 reflections could be seen in the pattern recorded at about a pressure of 15 kbar. The pattern obtained at about a pressure of 50 kbar is completely different from that of the ambient pressure. The reflections 111 and 200 diminished very much in intensity. They could be hardly seen in the pattern obtained at about 50 kbar. The new phase was considered to be similar to the low temperature phase (Kugler *et al* 1979; Henkel *et al* 1980b) and the new phase indexed on this assumption with lattice constants $a=7.32$, $b=7.02$ and $c=8.02$ Å is in fair agreement with the predictions of the low temperature phase. The reflections 022, 301 and 004 (indexed in the new phase) could be recorded very clearly. Still some faint lines of cubic phase are seen in the pattern recorded at 50 kbar. The observed $d$-spacings and intensities along with the calculated values of the new phase (orthorhombic) are

**Table 1.** Interplanar distances of orthorhombic phase of $K_2SnCl_6$.

| $d_{obs}$ (Å) | $I_{obs}$† | *hkl** | $d^*_{cal}$ (Å) |
|---|---|---|---|
| 2·62 | ms | 022 | 2·64 |
| 2·34 | s | 301 | 2·33 |
| 2·01 | s | 004 | 2·01 |
| 1·41 | m | 431 | 1·42 |
| 1·22 | m | 350 | 1·22 |

† $I_{obs}$ are the visual estimated intensities.

* Indexing is made assuming an orthorhombic lattice with the lattice parameters $a = 7{\cdot}32$, $b = 7{\cdot}02$ and $c = 8{\cdot}02$ Å and $d_{cal}$ are the $d$-spacings calculated from these lattice parameters.

listed in table 1 for comparison. We could not determine the compressibilities of this compound above and below the transition. This is because the transition starts at a pressure which is slightly above the minimum pressure (about 7 kbar) that could be obtained with the set-up and in the new phase only three reflections have appreciable intensity. Further the transition is sluggish and it is not possible to separate the cubic and orthorhombic reflections in the intermediate pressures, where the two phases coexisted to calculate the volume at different pressures. The limited number of reflections in the new phase hampers conventional structural analysis. Hence it has not been possible to determine the orthorhombic space group with the few reflections available. Though a large discontinuity in the volume of the unit cell is found at the transition, it could not be decided unambiguously that the transition is of the first order. The reasons for this are that the change of the lattice parameter of the cubic phase could not be studied below 10 kbar and the lattice parameters of the new phase were calculated from a diffraction pattern which was not recorded in the vicinity of the transition but at a higher pressure.

The above information on the high pressure behaviour of $K_2SnCl_6$ does not allow us a very detailed discussion of the phase transformation. However, from the Brillouin scattering study of Henkel *et al* (1980b) on this compound it was found that the effective elastic constant $\frac{1}{2}(C_{11}-C_{12})$ exhibits a pronounced softening as $T_{c1}$ is approached from the room temperature. This is similar to the behaviour in the case of nickel fluoride (Jorgensen *et al* 1978) in which a pressure-induced structural phase transition was reported by Jamieson and Wu (1977). If this is true the phase transformation in the case of potassium stanichloride may be a pressure-induced strain transition, as in the case of nickel fluoride (Jamieson and Wu 1977).

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## References

Anon 1956 National Bureau of Standards Circular **6** 539
Boysen H and Hewat A W 1978 *Acta Crystallogr.* **B34** 1412
Boysen H, Ihringer J, Prandl W and Yelon W 1976 *Solid State Commun.* **20** 1019
Brill T B, Gearhart R C and Welsh W A 1974 *J. Mag. Reson.* **13** 27
Dickinson R G 1922 *J. Am. Chem. Soc.* **44** 276
Henkel W, Hochheimer H D, Pelzl J and Höck K H 1980a Proceedings of the VII International Raman Conference (Ottawa)
Henkel W, Pelzl J, Höck K H and Thomas H 1980b *Z. Phys.* **B37** 321
Ihringer J 1977 *Röntgenographische Untersuchung der Hochtemperaturstruktur and Phasenumwandlungen von* $K_2SnCl_6$ Dissertation, Univ. München
Jamieson J C and Wu A Y 1977 *J. Appl. Phys.* **48** 4573
Jeffrey K R 1972 *J. Mag. Reson.* **7** 184
Jorgensen J D, Worlton T G and Jameison J C 1978 *Phys. Rev.* **B17** 2212
Kugler W, Knorr K, Ihringer J and Prandl W 1979 Diskussionstagung der AGKP, Aachen. 19.3 and Priv. Comm.
Lerbscher J A and Trotter J 1976 *Acta Crystallogr.* **B32** 2671
Morfee R G S, Staveley L A K, Walters S T and Wigley D L 1960 *J. Phys. Chem. Solids* **13** 132
Ranga Prasad T, Sathyanarayana Murthy K, Leela Iyengar and Krishna Rao K V 1979 *Pramana* **12** 523
Regelsberger M and Pelzl J 1979 *Solid State Commun.* **28** 001
Sasane A, Nakamura D and Kubo M 1970 *J. Mag. Reson.* **3** 76
Singh A K 1972 *Rev. Sci. Instrum.* **43** 1311
Winter J and Rössler K 1976 *J. Phys. (Paris)* **37** 265
Winter J, Rössler K, Bolz J and Pelzl J 1976 *Phys. Status Solidi* **74** 193