

## Lattice thermal expansion of cesium plumbo chloride

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**Abstract.** The temperature variation of the lattice parameter of  $\text{CsPbCl}_3$  in the cubic phase has been studied by x-ray method, from a determination of the precision lattice parameter at various temperatures, ranging from 50°C to 400°C. The coefficient of thermal expansion of  $\text{CsPbCl}_3$  can be expressed by the quadratic equation,  $\alpha_T = 21.6 \times 10^{-6} + 2.44 \times 10^{-9} T + 5.90 \times 10^{-11} T^2$ .

**Keywords.** X-ray method; thermal expansion; phase transition; cesium plumbo chloride.

### 1. Introduction

As part of the general programme of evaluating accurate lattice parameters and coefficients of thermal expansion of some  $\text{ABX}_3$  halides in the high temperature range, we report the results of x-ray investigations on cesium plumbo chloride ( $\text{CsPbCl}_3$ ).

$\text{CsPbCl}_3$  perovskite undergoes successive structural phase transitions at 47°, 42° and 37°C (Cohen *et al* 1971; Yamada *et al* 1974; Plesko *et al* 1978). The presumably antiferroelectric transition at 47°C changes the cubic perovskite structure to tetragonal (Natarajan *et al* 1969).

Above 47°C this compound assumes a perovskite-type structure. All the transitions in  $\text{CsPbCl}_3$  are of reversible nature. In recent years many experimental investigations have been made on  $\text{CsPbCl}_3$  in order to understand the microscopic mechanism of these transitions. After the first report on the transitions on this compound by Moller (1959), Hirotsu and his collaborators have made significant contributions to the experimental study of various physical properties of  $\text{CsPbCl}_3$ . Mention may be made of their studies relating to conoscopic observations thermal expansion by a dilatometric method; far-infrared reflective spectra, x-ray and neutron diffraction studies effect of hydrostatic pressure and elastic constants (Hirotsu 1970, 1971, 1972; Hirotsu and Sawada 1969; Hirotsu and Suzuki 1978; Hirotsu *et al* 1974; Harada *et al* 1976; Ohta *et al* 1973).

It has been shown that the three phase transitions observed around the room temperature can be interpreted in terms of the condensation of soft phonon modes at the Brillouin zone boundaries in the cubic perovskite lattice (Yamada *et al* 1974). However, there appears to be contradictory opinion about the nature of the thermal expansion of this compound. While Moller (1959) who first detected the transitions, reported a decreasing value of the lattice parameter with increasing temperature in

phase I (cubic), Hirotsu and Suzuki (1978) using a dilatometric method, have observed that thermal expansion coefficient ( $\alpha$ ) between 50–80°C is temperature-independent. This study was coupled with the determination of  $S_{11}$  (the elastic compliance) and they concluded that the Pippard relation between  $S_{11}$  and  $\alpha$  does not hold good above  $T_I-T_{II}$  since the transition is of a first order.

The cubic phase in this compound is stable even above 80°C and due to the lack of data on the temperature variation of lattice parameter in the high temperature region, we have undertaken the present study using the x-ray method.

## 2. Experimental procedure and results

The powder sample of  $\text{CsPbCl}_3$  used in the investigation was kindly supplied by Dr S Hirotsu, Department of Physics, Oh-Okayama, Japan. The sample was filled in a quartz capillary tube having a diameter of 0.5 mm. The x-ray powder photographs were taken at six different temperatures using the General Electric high temperature camera and  $\text{CuK}_\alpha$  radiation. The camera is equipped with an automatic temperature controller capable of maintaining the temperature within  $\pm 2^\circ\text{C}$  accuracy. To get sharp lines in the high angle region it was found necessary to anneal the sample at 400°C for about 24 hr. The substance was heated a number of times and pictures were taken at orthorhombic, tetragonal and cubic phases and identified respectively, thus confirming the reversible nature of the phase transitions.

A picture taken at 44°C was measured and indexed. The results confirmed that the phase is tetragonal as reported earlier by Moller (1959) and later by Swanson *et al* (1967). The lattice parameters were calculated for phase II (tetragonal) by Cohen's (1935) method using the Bragg reflections  $523a_1$ ,  $206a_1$ ,  $424a_1$ ,  $514a_1$ ,  $226a_1$ ,  $504a_1$ ,  $603a_1$  and  $316a_1$  recorded in the  $\theta$  region between 55 and 68°C. The values of the lattice parameters are compared in table 1. It can be seen that all the three reports do not agree with each other.

Six different pictures were taken between 50°C and 400°C and the picture taken at 50°C was indexed as the space group and the structure of this phase is reported by Moller (1959). The reflections  $611a_1$ ,  $443a_1$ ,  $541a_1$ ,  $622a_1$ ,  $542a_1$  and  $631a_1$  recorded in the Bragg angle region 55 to 69°C were used to calculate the lattice parameter by Cohen's method. The lattice parameter at different temperatures (50–400°C) is calculated and the standard error in the value of the lattice parameter is evaluated by the method of Jette and Foote (1935) and is found to be  $\pm 0.0002 \text{ \AA}$ . The error at higher temperatures is of the same order.

The value of the lattice parameter at 50°C ( $5.6058 \pm 0.0002 \text{ \AA}$ ) obtained in the present study is in good agreement with the value of  $5.605 \text{ \AA}$  reported by Moller

Table 1. Lattice parameters of  $\text{CsPbCl}_3$  in phase II.

| Authors                     | $a$ (Å)             | $c$ (Å)             |
|-----------------------------|---------------------|---------------------|
| Moller (1959)               | 5.590               | 5.630               |
| Swanson <i>et al</i> (1967) | $5.584 \pm 0.001$   | $5.623 \pm 0.001$   |
| Present study               | $5.5799 \pm 0.0005$ | $5.6010 \pm 0.0007$ |

(1959). The temperature variation of the lattice parameter is shown in table 2. While the lattice parameter in table 1 pertaining to tetragonal phase as determined in the present study is very much smaller than those reported by either Moller (1959) or Swanson *et al* (1967), the difference in the value of  $a$  in cubic phase is about  $0.0008 \text{ \AA}$  with the only reported value of Moller (1959).

The coefficient of thermal expansion of CsPbCl<sub>3</sub> was evaluated by the graphical method of Deshpande and Mudholkar (1961). The coefficient of thermal expansion can be represented by the following quadratic equation

$$\alpha_T = 21.6 \times 10^{-6} + 2.44 \times 10^{-9} T + 5.90 \times 10^{-11} T^2.$$

Here  $T$  is the temperature in °C. The temperature variation of the thermal expansion is shown in figure 1.

### 3. Discussion

At 50°C the value of the true coefficient of thermal expansion is found to be  $21.93 \times 10^{-6}/^\circ\text{C}$ . The value of  $\alpha$  at 50°C reported by Hirotsu (1978), using a dilatometer, is  $30.0 \times 10^{-6}/^\circ\text{C}$ . According to Moller (1959) the lattice parameter in the cubic phase

Table 2. Lattice parameters of CsPbCl<sub>3</sub> at different temperatures in phase I.

| Temperature<br>(°C) | Lattice parameter<br>(Å) |
|---------------------|--------------------------|
| 50                  | 5.60580                  |
| 100                 | 5.61365                  |
| 150                 | 5.61800                  |
| 200                 | 5.62717                  |
| 300                 | 5.63987                  |
| 400                 | 5.65671                  |

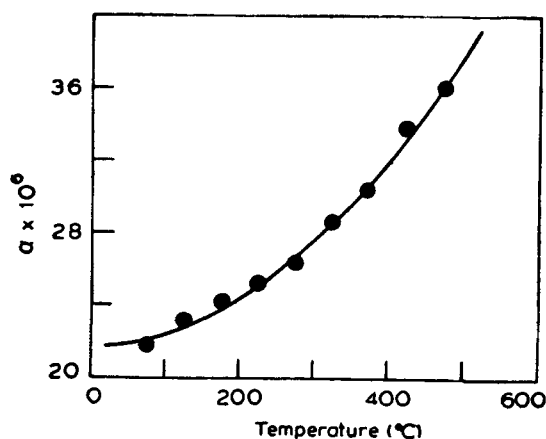


Figure 1. Temperature variation of coefficient of thermal expansion of CsPbCl<sub>3</sub>.

decreases with increasing temperature contrary either to the results in the present investigation or to the report of  $\alpha$  by Hirotsu (1971) using dilatometer. Further Hirotsu (1971) found  $\alpha$  to be independent of temperature in the range of 50–80°C. Our present investigation shows a very small variation of  $\alpha$  values from  $21.93 \times 10^{-6}/^{\circ}\text{C}$  at 50°C to  $22.32 \times 10^{-6}/^{\circ}\text{C}$  at 80°C.

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### References

- Cohen M U 1935 *Rev. Sci. Instrum.* **6** 68  
Cohen M I, Young K F, Te-Tsechang and Brower W S 1971 *J. Appl. Phys.* **42** 5267  
Deshpande V T and Mudholkar V M 1961 *Indian J. Phys.* **35** 434  
Harada J, Sakata M, Hoshino S and Hirotsu S 1976 *J. Phys. Soc. Jpn.* **40** 212  
Hirotsu S and Sawada S 1969 *Phys. Lett.* **A28** 762  
Hirotsu S 1970 *J. Phys. Soc. Jpn.* **28** S 185  
Hirotsu S 1971 *J. Phys. Soc. Jpn.* **31** 552  
Hirotsu S 1972 *Phys. Lett.* **A41** 55  
Hirotsu S, Harada J, Iisumi M and Gesi K 1974 *J. Phys. Soc. Jpn.* **37** 1393  
Hirotsu S and Suzuki T 1978 *J. Phys. Soc. Jpn.* **44** 1604  
Jette E R and Foote F 1935 *J. Chem. Phys.* **3** 605  
Moller C K 1959 *Mat. Fys. Medd. Kgl. Danske Videnskab. selskab* **32** No. 2, 1  
Natarajan M, Ramdas S and Rao C N R 1969 *Phys. Lett.* **A29** 528  
Ohta H, Harada J and Hirotsu S 1973 *Solid State Commun.* **13** 1969  
Plesko S, Kind R and Roos J 1978 *J. Phys. Soc. Jpn.* **45** 553  
Swanson H E, Mcmurdie H F, Morris M C and Evans H E 1967 *Natl. Bur. Std. (U.S.) Monograph* No. **25** 539  
Yamada Y, Fujii Y, Hoshino S, Axe J D and Shirane G 1974 *Ferroelectrics* **8** 591