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X- ray Determination of thermal expansion of Calcium Fluoride

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ABSTRACT: *Calcium Fluoride has the fluorite structure with four molecules per unit cell. It is the prominent representative of the material known as super ionic conductors which develops high electrical conductivity at high temperatures. Because of this it has attracted considerable attention. In recent years numbers of properties were investigated. We are interested in Thermal Expansion of Caf_2. The lattice Constant and coefficient of expansion Caf_2 has been determined over the range of 300- 700k. Coefficient of expansion at room temperature is calculated as it increases with temperature where as the Gruneisen parameter decreases with temperature.*
Keynote*: X –ray diffraction, Lattice Constants, Thermal Expansion Coefficient and Gruneisen constant.*

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I. Introduction

Calcium Fluoride crystallizes as fluorite structure. Each Ca^{2+} has eight coordinates for eight F^- centers. Each F^- center is Coordinated to four F^- centers. The unit cell of CaF_2 is known as fluorite

Calcium Fluoride has cubic structure with space group Fm3m and four molecules per unit cell by virtue of its structure it is very stable, insoluble in water and have high melting points. Caf_2 has useful transmission characteristics in the infrared region. It may be used as epitaxial dielectric film in thin film devices.

X- Ray studies of Weiss etal (1957) and Togowa (1964) revealed that Caf_2 is built of ions with low density of electrons between them. The bonding is mainly ionic with no sign of covalence.

The temperature variation of the wavelength intensity and line shape of Raman lines in Caf_2, Srf_2, Pbf_2 and Baf_2 has been studied by Elliot etal (1978) at high temperatures. Such studies have revealed the existence anharmonicity and disorder in these crystals at high temperature.

The specific heat of Fluorite structure have been measured by Dowrkin and Bredig (1968) and Derring etal (1976) over wide range of temperature almost up to the melting points. The Debye temperature has been calculated from Specific heat and elastic constants.

Thermal expansion is the basic physical property represents the dimensional change of the solid induced by a change of temperature. It is being the property of technical as well as lattice dynamical interest. We are interested in thermal expansion of solids by X- ray diffraction technique.

Among the Fluorides and Fluorites Caf_2 has received maximum attention. Kopp (1852), Pfaff (1858) and Fizeau (1868) made measurements of thermal expansion near room temperature using mineral samples of Fluorite. Sharma (1952) studied the temperature variation using the optical method. Krukooska – Fudle and Niemy Ski (1967) determined the thermal expansion

Experimental

Fine powder supplied by Reidel de Hahn was used. The powder was so fine that the lines showed some broadening. Firing the powder at 1000 K helped in improving the quality of the diffraction photographs. For recording the X – ray diffraction a high temperature Seeman Bohlin systematic focusing camera designed in our laboratory was used with CuK radiation. It is known that camera with this geometry $\Phi\tan\Phi$ is the appropriate error function (Φ being the compliment of Bragg angle). The lattice parameters were determined accurately by a least square extrapolation to $\Phi = 0$. Fifteen photographs were obtained at different temperatures in the range 300-600 K. Four α_1 α_2 doublets appeared at high angels.

The valves of the lattice constants at different elevated temperatures are given in table-1. These values are also shown in figure-1. The temperature variation has a very slight degree of nonlinearity. The data on lattice constants at different temperatures was fitted to a three term polynomial in temperature and the following equation was obtained.

$$\mathbf{a_T = 5.4353 + 0.964 \times 10\text{-}4T + 0.649 \times 10^{-8}T^2}$$

By differentiation of this equation, the following equation is obtained for the coefficient of thermal expansion.

$$\mathbf{\alpha = 17.63 \times 10^{-6} + 0.237 \times 10^{-8}\ T}$$

values of α calculated from this equation are given in table-2 along with the values from other sources.

The values of lattice parameters calculated from above equation is presented in the table 1. The room temperature values of lattice constants are in fair agreement with those in the ASTM files. The values of α at some select temperatures are included in the table. The accuracy in the measurements of various quantities is as follows.

a: ±0.0002; T: ± 0.5 ; α: ± 0.5 × 10^{-6} K^{-1}

II. Results And Discussion

Values of the lattice constants of calcium fluoride at room temperature are available in several earlier reports. Values of 5.4640 and 5.4637 A were reported by Sirdeshmukh and Deshpande (1964) and Batchelder and Simmons (1964). Values of 5.4629 and 5.4626 A are quoted by Wyckoff (1965) and in the ASTM file. Hazen and Finger (1981) and Schumann and Neumann (1984) obtained values of 5.4632 and 5.466 A for the lattice constant of CaF_2. In the present experiments, a value of 5.4654 A is obtained at room temperature which agrees with the above values in general but is very close to the value obtained by Schumann and Neumann in particular.

Several investigators have reported the value of the coefficient of thermal expansion of calcium fluoride in the vicinity of the room temperature. Sharma (1950), Murat and Chatelut (1971), Rao and Maiti (1977) and Kuzmin et al., (1979) obtained values of 19.2, 20.3, 22.6 and 18.6 (10^{-6} K^{-1}): respectively from measurements of bulk crystals. Sirdeshmuk and Deshpande (1964) and Schumann and Neumann (1984) obtained values of 20.2 and 19.3 (10^{-6} K^{-1}) from x-ray measurements. A value of 18.35 x 10^{-6} K^{-1} has been obtained at room temperature in the present work. This value is close to the values quoted above from other sources.

The temperature variation of thermal expansion is shown in figure-2. For comparison the low temperature results of Bailey and Yates (1967) and White (1980) are also included. The low temperature results from these sources lie on a common curve and are quite consistent with one another. Bailey and Yates (1967) commented that the results of Sirdeshmukh and Deshpande (1967) do not form a smooth continuation of their low temperature results. This was one of the reasons for undertaking a redetermination. As is to be expected from equation-3, equation-4 yields values of thermal expansion which show a very slight linear temperature variation of α. Over the range of temperature studies, α rises by about 1 x 10^{-6} K^{-1} which is just larger than that error limits. Sharma's (1950) results show a very high nonlinear temperature variation. The results of Kuzmin et al., (1979) yield values which increase with temperate. Schumann and Neumann's (1984) results show a linear increase with temperature. The increase in the α with temperature is very small in the presents results, moderate in the results of Kuzmin et al., (1979) and in the results of Schum,an and Neumann (1984) and is very large in the results of Sharma (1950). The temperature variation of the lattice constant and thermal expansion of calcium fluoride is presented in the following tables.

Table-1
Lattice constants (a) of calcium fluoride at elevated temperatures

Temperature (K)	a (A)	Temperature (K)	a (A)
300	5.4654	443	5.4797
323	5.4662	463	5.4814
343	5.4687	503	5.4853
363	5.4709	523	5.4872
403	5.4751	563	5.4922
423	5.4775	583	5.4938
		603	5.4954

Table-2
Values of the coefficient of thermal expansion (α) of calcium fluoride at elevated temperatures

Temp K	α (10^{-6} K^{-1})				
	Present work	Sharma (1951)	Sirdeshmukh and Deshpande (1964)	Kuzmine et al. (1979)	Schumann and Neumann (1984)
300	18.36	19.1	20.25	18.6	19.3
350	18.48	-	-	-	-
400	18.60	23.9	22.6	20.7	21.1
450	18.72	-	-	-	-
500	18.84	32.9	24.1	22.1	22.9
550	18.96	-	-	-	-
600	19.08	46.3	24.7	23.2	24.9
600	19.32	64.0	-	-24.0	27.0

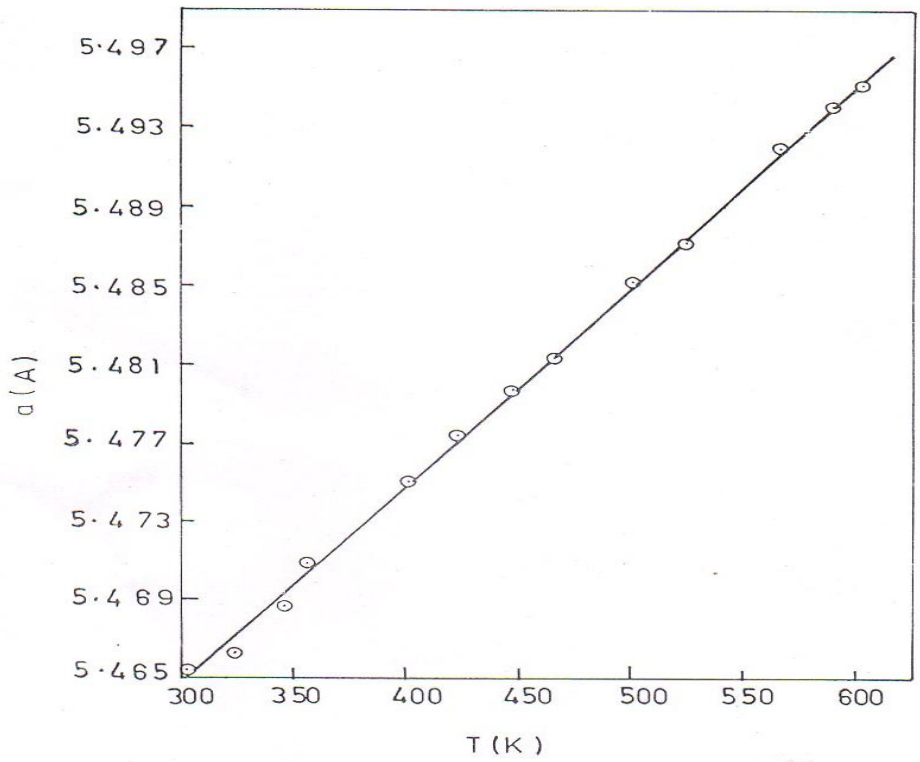

Figure 1: Temperature variation of lattice constant of CaF_2

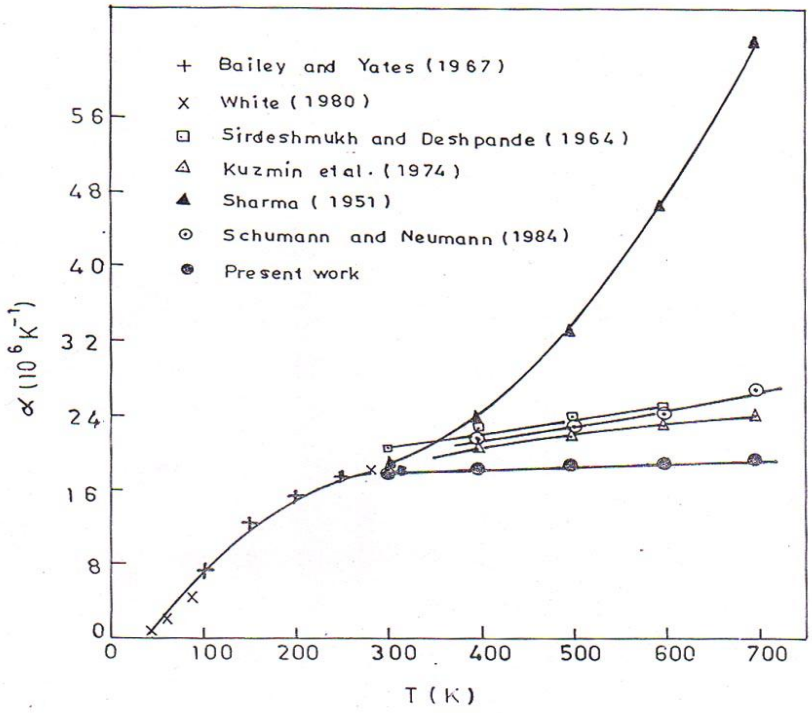

Figure 2: Temperature variation of thermal expansion of CaF_2

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