

SPECTROSCOPIC AND PHASE TRANSITION STUDIES OF SOME HEXAFLUORO SILICATES AND TITANATES OF DIVALENT METALS

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S Y N O P S I S

Title : "Spectroscopic and Phase Transition Studies of Some Hexafluoro Silicates and Titanates of Divalent Metals"

Ph.D thesis

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There has been considerable interest in the study of metal hexahydrate compounds containing cations $[M(OH_2)_6]^{2+}$ and anions $[XF_6]^{2-}$, where M is a divalent metal ion and X stands for Si or Ti - a tetravalent element, in order to gain information about the bonding and dynamics of water molecules in these solids. Several of the hexahydrated fluorosilicates $[M(OH_2)_6SiF_6]$; where M = Fe, Mg, Mn, Co etc] and fluorotitanates $[M(OH_2)_6TiF_6]$; where M = Zn, Ni, Co, Mg etc] undergo structural phase transitions at low temperatures in which the high temperature rhombohedral phase generally changes over to a low symmetry phase. On the other hand, the Zn and Ni hexahydrated fluorosilicates are known to maintain room temperature structure down to 10k [Jenkins and Lewis, 1981] whereas Ni and Zn hexahydrated fluoro-titanates undergo structural phase transition at low temperatures [Choudhury et al, 1983].

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In most of the hexaquo-metal hexafluoro silicates, the $[\text{SiF}_6]^{2-}$ ion has a O_h molecular symmetry and, in the crystals of space group C_{3i}^2 , occupies a site of symmetry C_{3i} ; as for example the salts of Ni, Zn and Co fluorosilicate hexahydrates. The other salts of the series belong to the space group D_{3d}^5 and the site symmetry of the $[\text{SiF}_6]^{2-}$ ion in this type of crystals is D_{3d} [Ray et al, 1973]. Moreover, the $[\text{M}(\text{OH}_2)_6]^{2+}$ complex has the molecular symmetry T_h and occupies a site of symmetry C_{3i} or D_{3d} in the crystals of space group C_{3i}^2 or D_{3d}^5 . The water molecules of the system have C_{2v} molecular symmetry and also occupy sites of symmetry C_{2v} in both types of crystals. Most of the hexaquo metal hexafluoro silicates and titanates have a trigonally distorted CsCl type of structure and their unit cell has one formula unit. In all the salts of the series there is a disorder in the orientations of the $[\text{SiF}_6]^{2-}$ anions between two sites unrelated by any symmetry element and with unequal occupancy. In the Fe and Mg salts, there is a two-fold disorder in the $[\text{M}(\text{OH}_2)_6]^{2+}$ complex and for the $\text{Mg}(\text{OH}_2)_6\text{SiF}_6$ salt, the high temperature space group $R\bar{3}m (D_{3d}^5)$ changes to $P_2 1/c (C_{2h}^5)$ at low temperature during phase transition. The structure of the low temperature phase for most of the members of the series is unknown. Although a good deal of work has been reported on phase transitions in some members of the series by X-ray [Datta et al, 1979], specific heat [Karnezos et al, 1978], EPR [J. How et al, 1974 ; Rubins et al, 1976] and other techniques [Jenkins et al, 1981; Francis et al, 1977; Poulet et al, 1978], the understanding of the mechanism of phase

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transitions is still obscure in this series of salts. In particular one does not understand why among crystals of similar structure and parameters only a few show phase transitions while others do not? Moreover, some of the fluorotitanates of the series show two phase transitions while others show only one?

In order to understand the dynamics of structural phase changes in this family of salts, identify the low temperature phase, understand the bonding of water molecules and their role in the phase transition mechanism in these salts, we undertook systematic Laser Raman studies on oriented single crystals at different temperatures and infrared absorption measurements at room temperature on the following salts -

(i) $\text{CdSiF}_6 \cdot 6\text{H}_2\text{O}$ (ii) $\text{CdTiF}_6 \cdot 6\text{H}_2\text{O}$ and their deuterated analogues i.e. (iii) $\text{CdSiF}_6 \cdot 6\text{D}_2\text{O}$ and (iv) $\text{CdTiF}_6 \cdot 6\text{D}_2\text{O}$

We undertook systematic studies on these salts because, to our knowledge, no literature was available on the spectroscopic or the phase transition studies to arrive at a comprehensive picture of the mechanism of phase transitions in these systems. Although the process of growing single crystals of these salts is very difficult, we undertook the preparation of constituent materials and devised a method for growing single crystals in order to explore their properties by spectroscopic methods.

In order to elucidate the mechanism of phase transition, it is important to understand the vibrational characteristics of the system at both ends of phase transition and correct assignment of

the bands is very important. We, therefore, undertook measurements on single crystals of the above mentioned salts at various temperatures. Specifically we studied in depth the internal modes of the $[\text{SiF}_6]^{2-}$ and $[\text{TlF}_6]^{2-}$ octahedra, internal and librational modes of water molecules, variation of FWHM of some internal modes and lattice modes and the variation of peak intensities of some bands of these systems as a function of temperature. The work in this thesis is divided into the following chapters -

In Chapter I a brief review and discussion on various types of phase transitions, crystal hydrates, anharmonicity, Fermi Resonance, hydrogen bonding, isotopic substitution, previous vibrational studies (IR and Raman) on some other salts in this series and structural phase transitions on $\text{MXF}_6 \cdot 6\text{H}_2\text{O}/6\text{D}_2\text{O}$ single crystals have been given.

The experimental aspects relevant for the present investigation are given in Chapter II. A brief description of preparation and purification of samples, modification in the solution method for growing single crystals are discussed. A brief description of the techniques used for recording Raman spectra at room temperature as well as at low temperature, the Ramalog 1403 double monochromator, the Argon-Ion laser source, the helium cryo-cooler unit and the method of deuteration of the samples are given in this chapter [Thakur G, 1983].

The Chapter III deals with the pertinent theoretical details for understanding these systems. A brief description of the structure of the crystals, group theoretical analysis, Bhagavantam's method, local or site symmetry approach, correlation method etc are explained for determining the vibrational modes, their activity in the IR and Raman etc.

Chapter IV gives a detailed temperature-dependent Raman spectroscopic study on single crystals of $\text{CdTiF}_6 \cdot 6\text{H}_2\text{O}$. The Raman spectra at room temperature and at 10k in all the six polarization geometries are given. The IR spectrum at room temperature is also given in this chapter. The Raman spectral data at different temperatures at the intervals of 10k or 5k from room temperature to 10k are also given. The important findings on this system are summarized as follows [Thakur and Verma, 1986].

- (a) The room temperature space group of $\text{CdTiF}_6 \cdot 6\text{H}_2\text{O}$ is C_{3i}^2 ($R \bar{3}$).
- (b) There are two structural phase transitions, one at 200k and the other at 80k.
- (c) The space group of the crystal below 80k is C_{2h}^5 in monoclinic series.
- (d) The high temperature phase transition is triggered by distortions in the $[\text{Cd}(\text{OH}_2)_6]^{2+}$ octahedra.
- (e) The low temperature phase transition is triggered by similar distortions in the $[\text{TiF}_6]^{2-}$ octahedra.

Chapter V deals with the detailed study on $\text{CdSiF}_6 \cdot 6\text{H}_2\text{O}$ single crystals which can be summarized as follows -

- (a) The Raman spectra in all the six polarization geometries of the single crystals of the salt at room temperature and 10k.
- (b) IR spectra of the salt at room temperature.
- (c) Raman spectra of the single crystals at different temperatures at intervals of 10k or 5k from room temperature to 10k in the $\{x(yy)z\}$ polarization geometry.
- (d) Evaluation of peak intensity, measurement of FWHM of some isolated bands at different temperatures.
- (e) Assignments of bands at room temperature as well as at 10k.

From the above observations, the following conclusions are drawn in this chapter [Thakur and Verma, 1989] -

- (1) The space group of $\text{CdSiF}_6 \cdot 6\text{H}_2\text{O}$ at room temperature is C_{3i}^2 ($R \bar{3}$).
- (2) A structural phase transition at about 220k. There is no second phase transition as observed in case of $\text{CdTiF}_6 \cdot 6\text{H}_2\text{O}$.
- (3) The low temperature space group of the system is most likely C_{2h} in the monoclinic series.
- (4) The phase transition in this case is triggered due to distortions in the $[\text{Cd}(\text{OH}_2)_6]^{2+}$ octahedra.

The temperature dependent Raman study of single crystals of deuterated Cadmium fluoro silicate ($\text{CdSiF}_6 \cdot 6\text{D}_2\text{O}$) is discussed in Chapter VI. The Raman spectra at room temperature as well as at 10k in all the six polarization geometries are given.

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Frequency shift, peak intensity and FWHM as a function of temperature have been measured in this system. From the above observations, we discovered a phase transition in this system at 235k which shows a rise of 15k in the transition temperature compared to the hydrogenated system [Thakur and Verma, 1989].

The anomalous behaviour of $\Delta \nu_{\frac{1}{2}}$ of ν_s (O-D) stretching mode as a function of temperature from room temperature to 10k has been explained in terms of various dephasing mechanisms.

The low temperature space group of $\text{CdSiF}_6 \cdot 6\text{D}_2\text{O}$ is found to be C_{2h} which is the same as of its hydrogenated analogue $\text{CdSiF}_6 \cdot 6\text{H}_2\text{O}$.

Chapter VII contains the study of the **crystal of $\text{CdTiF}_6 \cdot 6\text{D}_2\text{O}$** at room temperature as well as at low temperatures in all the six polarization geometries. The temperature dependent Raman study of some bands including that due to the ν_s (O-D) mode has been given in this chapter. We discovered two phase transformations in this system, at 218k and 110k [Thakur and Verma]. This shows that there is a rise in the phase transition temperatures by 18k and 30k in the high and low temperature T_c 's with respect to the $\text{CdTiF}_6 \cdot 6\text{H}_2\text{O}$ salt. The space group at 10k is deduced C_{2h} which remains the same as of the hydrogenated analogue. It is concluded that the pure vibrational dephasing mechanism provides a major contribution to the width of the symmetric stretching mode ν_s (O-D).

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