Crystal Structure Transformations in Inorganic Sulfates, Phosphates, Perchlorates, and Chromates

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Foreword

The National Standard Reference Data System provides access to the quantitative data of physical science, critically evaluated and compiled for convenience and readily accessible through a variety of distribution channels. The System was established in 1963 by action of the President's Office of Science and Technology and the Federal Council for Science and Technology, and responsibility to administer it was assigned to the National Bureau of Standards.

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Reliable data on the properties of matter and materials are a major foundation of scientific and technical progress. Such important activities as basic scientific research, industrial quality control, development of new materials for building and other technologies, measuring and correcting environmental pollution depend on quality reference data. In NSRDS, the Bureau's responsibility to support American science, industry, and commerce is vitally fulfilled.

Ernest Ambler

Ernest Ambler, ***Acting Director***

Preface

Earlier in this series, we presented critical reviews of phase transitions in binary halides (NSRDS–NBS 41), transition metal oxides (NSRDS–NBS 49), and inorganic nitrites, nitrates, and carbonates (NSRDS–NBS 53). In this monograph, we review crystal structure transformations in inorganic sulfates, phosphates, perchlorates, and chromates based on the literature up to 1974. A review on transition metal sulfides is due to appear in Progress in Solid State Chemistry (Vol. 10) this year. We believe that these five reviews would adequately cover most of the important facets of crystal structure transformations in inorganic solids and indicate the nature of problems in this area. These reviews could not have been prepared but for the support and encouragement of the National Bureau of Standards.

Contents

Crystal Structure Transformations in Inorganic Sulfates, Phosphates, Perchlorates, and Chromates*

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Literature dealing with crystal structure transformations of simple inorganic sulfates, phosphates, perchlorates and chromates has been critically reviewed. Data on thermodynamic, crystallographic, spectroscopic, dielectric and other properties are given. Experimental techniques employed to obtain the data are indicated and comments on the data are made wherever necessary. All pertinent references to the published literature (up to 1974) are listed.

Key words: Chromates; crystal structure; crystal structure transformations; perchlorates; phase transformations; phosphates; sulfates; thermodynamic data; x-ray diffraction data.

1. Introduction

The study of crystal structure transformations is of great importance in understanding the structure and properties of inorganic solids. As part of our programme in preparing critical reviews on the crystal structure transformations of various types of inorganic solids, we have presently carried out a survey of the transformations of inorganic salts containing tetrahedral oxy-anions such as sulfates, phosphates, perchlorates and chromates. This review is a sequel to our monograph on the crystal structure transformations in inorganic nitrites, nitrates and carbonates [1].[1] In earlier monographs we have presented the transformations in binary halides [2] and transition metal oxides [3].

Of the various systems reviewed in this article, the most extensive studies have been on the crystal structure transformations of inorganic sulfates. Accordingly, we have discussed this system at length. Stern and Weise [4] have reviewed the high temperature properties and decomposition of inorganic sulfates. In view of the limited information available on the crystal structure transformations in inorganic phosphates, perchlorates and chromates, we have presented the available data in tabular form.

The general theory and other aspects of phase transformations in inorganic solids have been reviewed in the literature [5, 6] and some aspects were briefly presented in our earlier publications from NSRDS–NBS [2, 3]. We shall, therefore, not resort to any discussion of a general nature in this review. The present review covers the material published in the literature up to 1974 and lists most of the important references. All the available crystal structure data of the different phases have been given. Results of studies employing a variety of methods and properties of solids are also presented.

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2. Units, Symbols, and Abbreviations

Å = Angstrom (10^{-8} cm)
bar = Unit of pressure = 10^6 dyn/cm^2 = 10^5 pascal
cal = Thermochemical calorie = 4.1840 Joule

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[1] Figures in brackets indicate literature references which appear after each section.

*Supported by the National Bureau of Standards through the Special International Ptogram (NBS–G–77). Earlier publications by Rao and coauthors on crystal structure transformations in this series are NSRDS–NBS 41, 49, and 53.

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C =Coulomb
eV =Electron volt
Hz =Hertz (cycle/second)
O_e =Oersted
χ =Magnetic susceptibility
ϵ' =Dielectric constant
ϵ'' =Dielectric loss
A =Curie constant
α =Seebeck coefficient
P_s =Spontaneous polarization
T_c =Curie temperature
T_N =Neél temperature
T_t =Transition temperature
T =Temperature in kelvin (K)
ΔH_{tr} =Enthalpy of transformation
ΔS_{tr} =Entropy of transformation
ΔT =Thermal hysteresis
ΔV_{tr} =Volume change
Z =Number of molecules per unit cell
DTA =Differential thermal analysis
EPR =Electron paramagnetic resonance
IR =Infrared
NMR =Nuclear magnetic resonance
TGA =Thermo-gravimetric analysis

3. The Sulfates

3.1. Alkali Metal Sulfates

All the alkali metal sulfates undergo reversible polymorphic transformations [1, 2]. With the exception of lithium sulfate where the transformation is from a monoclinic to a cubic structure, the other alkali metal sulfates show transformations from an orthorhombic to a hexagonal phase [3] and there is a progressive increase in transition temperature and decrease in heat of transformation as we go from sodium to cesium sulfate. In table 1, we have summarized the data on the crystal *structure transformations of alkali metal sulfates.* Table 2 gives crystal structure data on the various phases. The II–I phase transition in alkali metal sulfates seems to have features of both first and second order transitions as revealed by the thermodynamic and structural data as well as electrical conductivity measurements [4].

Some special features of the transitions in individual alkali metal sulfates are described in the following paragraphs.

Lithium sulfate. The value of ΔH_{tr} in lithium sulfate is very high compared to other alkali metal sulfates [7] and is even higher than the heat of fusion of Li_2SO_4. This abnormality is possibly due to the high degree of disorder in the high temperature phase [3]. Substitution by ^6Li isotope lowers the T_t by 0.7 K [24].

Bridgman [25] did not find any high pressure transformation in Li_2SO_4 up to 50 kbar. Pistorius [26] has, however, identified three new high pressure forms III, IV, and V. The phase diagram of Li_2SO_4 shows the triple points at the pressures and temperatures listed below:

TABLE 1 *Crystal structure transformations of alkali metal sulfates*

Sulfate	Transformation	T_t, K	ΔH_{tr}, kcal mol^{-1}	ΔS_{tr}, cal mol^{-1}K^{-1}	References
Li_2SO_4	$II \rightleftharpoons I$	859	6.5	7.6	[3, 5–8]
Na_2SO_4	$V \rightleftharpoons IV$	443	0.7	1.6	[5, 9–13]
	$IV \rightleftharpoons III$	458			
	$III \rightarrow I$	515	1.8	3.5	
	$I \rightarrow II$ (on cooling)	509			
K_2SO_4	$II \rightleftharpoons I$	858	1.94	2.27	[5, 6, 14, 15]
Rb_2SO_4	$II \rightleftharpoons I$	930	0.35		[15–17]
			2.11		[6]
Cs_2SO_4	$II \rightleftharpoons I$	940	0.600 ± 0.13		[6, 7, 15]
			0.50		[6]
		986			[18]
		993			[16]

TABLE 2. *Crystal structure data of alkali metal sulfates*

Sulfate (phases) 1	Crystal system 2	Space group 3	Z 4	Cell dimensions 5	References 6
Li_2SO_4					
II (298 K)	monoclinic	$P2_1/a$	4	$a=8.2390$ Å, $b=4.9536$ Å, $c=8.4737$ Å, $\beta=107.98°$	[19]
I	cubic	F23 or $F\bar{4}3m$	4	$a=7.07$ Å	[3]
Na_2SO_4					
V (298 K)	orthorhombic	D_{2h}^{24}-Fddd	8	$a=5.863$ Å $b=12.304$ Å $c=9.821$ Å	[9]
I (514 K)	hexagonal	—	–	$a=5.405$ Å $c=7.215$ Å	[15]
K_2SO_4					
II (298 K)	orthorhombic	D_{2h}^{16}-Pmcn	4	$a=5.772$ Å $b=10.072$ Å $c=7.483$ Å	[20]
I (858 K)	hexagonal	—	–	$a=5.85$ Å $c=8.03$ Å	[15]
Rb_2SO_4					
II (298 K)	orthorhombic	D_{2h}^{16}-Pmcn	4	$a=7.801$ Å $b=5.965$ Å $c=10.416$ Å	[21]
I	hexagonal	D_{3d}^{3}-$P\bar{3}m1$	2	$a=6.151\pm0.005$ Å $c=8.467\pm0.003$ Å	[22]
Cs_2SO_4					
II (298 K)	orthorhombic	D_{2h}^{16}-Pmcn	4	$a=6.264$ Å $b=10.95$ Å $c=8.242$ Å	[23]
I	hexagonal			$a=6.485$ Å $c=8.980$ Å	[18]

I/III/II	10.7 ± 0.5 kbar	877 ± 3 K
III/IV/II	14.8 ± 0.5 kbar	871 ± 3 K
III/V/IV	20.1 ± 0.7 kbar	943 ± 4 K
I/V/III	21.5 ± 0.8 kbar	986 ± 6 K

Lithium sulfate monohydrate shows endothermic transformations at 443, 853, and 1133 K due to dehydration, polymorphic transformation, and fusion, respectively [27], the last two effects being reproducible. The 853 K transformation is akin to that in anhydrous Li_2SO_4 with a ΔH_{tr} of 6531 cal mol^{-1} [28]. DTA and x-ray diffraction studies by Gruver [29] confirm the reversible phase transformation around 873 K with a ΔT of 30 K.

Sodium sulfate. Na_2SO_4(IV), stable above 443 K and below 458 K is monoclinic [9]. Above 458 K the stable phase is Na_2SO_4(III). Frevel [30] found Na_2SO_4 (III) to have an orthorhombic unit cell with space group Pbnn and dimensions $a=5.59\pm0.02$ Å, $b=8.93\pm0.02$ Å, $c=6.98\pm0.02$ Å and $Z=4$. Dasgupta [31] has, however, reported that Na_2SO_4 (III) is tetragonal and belongs to a space group $D_{2d}^{12}I\bar{4}2$, $Z=16$, $a=13.45$ Å and $c=7.879$ Å. Fischmeister [15] has shown Na_2SO_4 (III) to possess an orthorhombic unit cell at room temperature with cell dimensions close to those by Frevel [30]. Fischmeister has also reported the cell parameters for the metastable orthorhombic Na_2SO_4 (II) to be

$a = 5.775$ Å, $b = 10.073$ Å and $c = 7.481$ Å at room temperature. DTA studies of Kreidl and Simon [32] show only one high temperature transition (V → I) a 511 K which occurs directly and reversibly in presence of water. According to Bird [33] the high temperature transition in dry Na_2SO_4 is irreversible. Rao and Gregor [34], have shown the V → I transition to be reversible even in dry Na_2SO_4. Moreau [14] found only three of the five previously observed forms in his DTA and x-ray diffraction investigations of Na_2SO_4. Dialatometric studies by Kracek and Gibson [11] have given the volume changes in the various transitions of Na_2SO_4 as follows: $V \rightleftharpoons IV$, $+0.0005\ cm^3g^{-1}$; $IV \rightleftharpoons III$, $-0.0034\ cm^3g^{-1}$; $III \rightleftharpoons I$, $+0.007\ cm^3g^{-1}$. Kracek and Gibson point out that Na_2SO_4 (II) has no region of stability at low temperatures, but if the reaction I → III is inhibited, the I → II transformation takes place reversibly at 509 K with a volume decrease of $0.004\ cm^3g^{-1}$. High temperature x-ray diffraction and thermographic studies of Khlapova [35] reveal two hexagonal phases between 723 and 873 K. This supports Wyronboff [36] who had reported a high temperature transition in Na_2SO_4 around 773 K. Simanov and Kirkina [37] have found a new orthorhombic form of Na_2SO_4 at 993 K. A departure from linearity in the enthalpy versus temperature curve above 837.4 K was observed by Popov and Ginzburg [38]. The effect was more clear in their mean specific heat versus temperature curve which was interpreted as evidence for yet another polymorphic transformation. High temperature specific heat investigations of Schmidt and Sokolov [39] showed an anomaly between 963 and 993 K, with a ΔH_{tr} of 0.01 kcal mol^{-1}. This transformation is given as Na_2SO_4 (I) → $\delta - Na_2SO_4$.

Bridgman [40] studied Na_2SO_4 at pressures up to 50 kbar and temperatures up to 448 K. He encountered sluggish transitions around 10 kbar and 27 kbar, corresponding to V/III and III/VI transformations, respectively. High pressure DTA studies by Pistorius [41] up to 45 kbar and 723 K have revealed two new phases VII and VIII. The phase diagram shows the triple points at the pressures and temperatures indicated below:

V/IV/III	1.5 ± 1.5 kbar	446 ± 13 K
I/III/VII	13 ± 1 kbar	603 ± 8 K
III/VI/VII	22.5 ± 1 kbar	548 ± 8 K
I/VII/VIII	23 ± 1 kbar	678 ± 8 K

Potassium sulfate. Pannetier and Gaultier [42] reported expansion discontinuities at 533 K in a and c parameters, at 633 K in a and b parameters and at 733 K in a, b, and c parameters. These variations, however, did not affect the orthorhombic structure of K_2SO_4.

K_2SO_4 was found to undergo some changes at 573, 623, 723 K, and possibly at 663 K [43–45]. Moreau [14] however, detected only two transformations at 623 K and 723 K, respectively. The electrical conductivity measurements of Ramasastry and Acharyulu [46] show an anomaly at 678 K. Watanabe et al. [47] have found the dielectric constant of K_2SO_4 to increase with increasing temperature resulting in a maximum around 873 K. The electric conductivity shows an ionic behaviour above 740 K with an activation energy of 0.8 eV. On heating K_2SO_4, significant changes of the relative intensities of the diffuse and Laue maxima take place well below the transition temperature [48]. It seems that the transition is preceded by a pretransition in a broad temperature interval. Structural changes observed are not caused by the nuclei of the new phase, but by a structural intermediate between the low and high temperature modification. There is very little indication of the pretransition effect in K_2SO_4 immediately below T_t, as shown by the calorimetric measurements of Dworkin and Bredig [49]. According to them ΔH_{tr} is 2020 ± 80 cal mol^{-1} and ΔS_{tr} is 2.3 cal mol^{-1} deg^{-1}.

Up to 1 kbar the results of Majumdar and Roy [45] and Pistorius [50] are almost identical. The transition line rises linearly with pressure to 22.6 kbar and 1263 K where the slope undergoes a sharp change. This change in slope indicates a splitting of the II/I phase boundary and the appearance of K_2SO_4 (III). Pistorius and Rapoport confirm that K_2SO_4 (II) at 853 K differs crystallographically from the room temperature phase. They, however, do not observe the higher order transformations around 573, 623, and 723 K in the high pressure DTA.

Rubidium sulfate. The discontinuities observed in the thermal coefficients of the lattice parameters and volume indicate the existence of two new low energy transitions around 648 K and 848 K and a very low energy transformation at 548 K besides the usual $II \rightleftharpoons I$ transformation [51].

Cesium sulfate. DTA, dilatometric and crystallographic investigations by Auby et al. [52] have established a weak transformation probably of first order around 593 K with $\Delta T \sim 30$ K. They also found a second order transformation around 733 K. The II → I transformation at 933 K was accompanied by a slight change in volume [52]. With increasing temperature the *a* parameter was found to undergo a much larger dilation (8.264–8.882 Å) than the *b* (10.977–11.152 Å) and the *c* (6.276–6.433 Å) parameters [53]. The electrical conductivity of Cs_2SO_4 was found to be enhanced above 723 K [54] possibly due to the II → I transition.

3.2. Ammonium Sulfate

The room temperature phase of $(NH_4)_2SO_4$ has an orthorhombic unit cell space group Pnam, $Z = 4$, $a = 7.73$ Å, $b = 10.50$ Å, and $c = 5.95$ Å [55]. Ammonium sulfate undergoes a polymorphic transformation around 223 K as shown by various techniques [56–63]. Mathias and Remeika [64] discovered that below 223 K $(NH_4)_2SO_4$ is ferroelectric parallel to the *a*-axis, P_s and E_c at 215 K being 0.254 μC cm^{-2} and 2.0 kV cm^{-1}, respectively. Kamiyashi and Miyamoto [65], however, reported the transformation to occur in the temperature range 237–244 K for single crystals and around 220 K for polycrystalline material. Singh [66] has studies the crystal structures of the room-temperature as well as the low-temperature phases of $(NH_4)_2SO_4$. The refinement of the room-temperature structure indicates that the actual crystal is a statistical mixture of two enantiomorphic states, the true symmetry being $Pna2_1$ rather than Pnam. Neutron diffraction studies of Singh [66] have shown that two ammonium ions which are crystallographically unrelated also have different surroundings. NH_4^+(I) involves a hindered rotation at room temperature about the polar *c*-axis and its rotation persists below the T_t. NH_4^+(II) is disordered around the plane at $Z = \frac{1}{4}$ above the T_t and is ordered below. In the low temperature phase, NH_4^+(II) shows five H-bonds of normal strength which are responsible for the dielectric polarization of ammonium sulfate. Numerous experimental results [67–69] lead to the conclusion that the transformation in $(NH_4)_2SO_4$ is of first order.

Results of dielectric measurements on $(NH_4)_2SO_4$ by different workers are not entirely in agreement. Hoshino et al. [67] notice an unusual shape of the dielectric constant versus temperature curve. The dielectric constant measured in the direction of the ferroelectric *c* axis was found not to depend on temperature in the paraelectric phase. Koptsik et al. [68], however, show the dielectric constant to have a weak linear temperature dependence above T_t. On the contrary, Unruh [70] and Oshima and Nakamura [71] have observed that the behaviour of dielectric constant is governed by the Curie-Weiss law above T_t (T_c). Couture-Mathieu et al. [62] and Freymann [61] find a normal behaviour at high frequencies (i.e., the dielectric behaviour shows a radical change at some frequency between 10 kHz and 24 GHz); the lower limit of frequencies at which $(NH_4)_2SO_4$ exhibits a normal type of dielectric behaviour occurs in MHz region [67]. The rate of warming and cooling the crystal near T_t markedly affects the shape of the low frequency ϵ versus temperature curve. Thus, with an extremely slow rate of temperature variation, normal dielectric behaviour is observed [72]. Bodi et al. [73] have studied the behaviour of the complex dielectric constant of unirradiated and gamma-irradiated ferroelectric ammonium sulfate in the microwave region as a function of temperature. They find T_t to shift from 238 K to 226 K for the irradiated sample. T_t is also affected by the application of a dc electric field along the [110] direction of the crystal [74] and by the pressure under which the study is made [75]. Hoshino et al. [67], however, could not detect any noticeable shift of T_t by any of the above effects. These authors report spontaneous polarization below T_t not to depend on temperature. Ikeda et al. [76] show that the anomalous temperature dependence of the dielectric constant, spontaneous polarization, spontaneous strain and elastic compliance can be explained in terms of the temperature dependence of the order parameter. Unruh [77] has found the spontaneous polarization to strictly depend on temperature. The NH_4^+ ions in the paraelectric phase oscillate with large amplitudes and this continues even in the ferroelectric phase. At lower temperatures than T_t, NH_4^+ ions show dual behaviour [78]. Consequently, changes in the orientation of dipoles are related to NH_4^+ (I) and NH_4^+ (II) ions and they can possibly affect the orientation of SO_4^{-2} ion with change in temperature. This leads to a temperature dependent P_s [79]. The lattice parameters and birefringence of $(NH_4)_2SO_4$ also show anomalous dependence on temperature [67, 80]. Anistratov and Martynov [81] show that the anomalies in birefringence at the T_c (or T_t) are due to the spontaneous deformation of the crystal. Around T_t, electrical conductivity increases possibly because of the formation of cracks in the crystal near the transition [82].

Blinc and Levstek [83], from their studies of NMR and IR spectra have suggested that above 173 K the NH_4^+ groups reorient about random axes with a frequency higher than 10^5 Hz. There is no change at T_t, but a line-width transition occurs below 163 K. Below T_t, two components can be resolved, which have been interpreted as being due to "frozen in" and rotating NH_4^+ ions, respectively. In the IR spectrum of $(NH_4)_2\ SO_4$ [84], the splitting of the wide band at 3235 cm^{-1} into a doublet (with components at 3190 and 3290 cm^{-1}) below 223 K is probably due to the tunnelling of a proton along the N—H . . . 0 bond. A very narrow band at 963 cm^{-1} also appears when $(NH_4)_2SO_4$ transforms to the ferroelectric state. These results and the absence of Curie point shift on dueteration [67] do not permit the ferroelectric properties of the crystal to be atributed to hydrogen bonding. Schutte and Heyns [85] find that the $2\nu_2$ line at $\sim 3300\ cm^{-1}$ disappears at T_t. In this mode of vibration, the H-atoms move on the surface of a sphere whose radius is the N—H bond distance.

Raman studies by Bazhulin et al. [86] show that the intensity of bands depend on the orientation of the cyrstals during excitation of the spectra by natural and polarized light. Some additional bands besides those corresponding to the internal vibration of SO_4^{2-} ion are also seen. Stekhanov and Gabrichidze [87] report that the band maximum due to valence vibrations of NH_4^+, is displaced toward the smaller frequencies by 150 cm^{-1} at the transformation of the crystal through the Curie point. These authors are of the view that hydrogen bonds play an important role in the appearance of the ferroelectric effect in $(NH_4)_2SO_4$. Recently Jain et al. [88] from their IR studies reported that the ferroelectric phase transition in $(NH_4)_2SO_4$ is primarily due to sudden distortion in the SO_4^{-2} ions.

Inelastic neutron scattering investigations by Rush and Taylor [89] show the rotational freedom of the ions to undergo only a very small change in passing through the transition. Bajorek et al. [90] found a jump in the variation of the elastic intensity at the T_t in their neutron scattering study. Schlemper and Hamilton [91] have arrived at the same conclusion from their neutron diffraction study. They report that the transition is not of the order-disorder type, but rather involves a change in the hydrogen bonding of the ammonium groups to the SO_4^{2-}—prime which in turn results in stronger hydrogen bonds in the ferroelectric phase. This becomes possible by a structural change in the crystal where the symmetry plane perpendicular to the ferroelectric axis is lost in the low-temperature phase. In the high-temperature phase, while each of the NH_4^+ ion has only one H—O bond of 2 Å, there are bonds of 1.9 Å in the ferroelectric phase.

From proton and deutron magnetic resonance measurements, O'Reilly and Tsang [92, 93], on the other hand, find a definite change in the dynamical behaviour of NH_4^+ ions. They conclude that the phase transition in $(NH_4)_2SO_4$ is of the order-disorder type and is caused by the ordering of distorted tetrahedral NH_4^+ ions which carry a dipole moment of 0.11 D relative to the crystallographic plane. Dahlborg et al. [94] commenting on the controversy of the findings of Hamilton [95] and O'Reilly and Tsang [92, 93] held that the methods used were sensitive to different intervals of time. The characteristic time of a neutron-diffraction measurement is considerably different compared to the frequency of the oscillating field (42 MHz) employed by O'Reilly and Tsang [92]. Thus, the different results can be explained on the basis of the different time scales; further, the measurements were made at different temperatures. Dahlborg et al. [94] find the transition to be of dynamic nature. The change in the dynamics of NH_4^+ ions is related to the structural change in the lattice. The transition is not sharp, but extends over some twenty degrees in the time scale seen by the neutron. Far below T_c, the ions perform translational and torsional oscillations during a time longer than 10^{-10} s. Above T_c, due to thermal fluctuations in the system, the ions are capable of performing rotational motions during a considerable length of time ($> 5 \times 10^{-11}$ s). The rotational motions of adjacent groups are believed to be coupled. These authors support the view of O'Reilly and Tsang [92, 93] that the transition is of order disorder type.

Nuclear spin-lattice relaxation studies of $(NH_4)_2SO_4$ reveal a definite change in the proton relaxation behaviour in the neighbourhood of the Curie point (T_t) indicating a change in the state of motion at the transition. The results suggest that the ferroelectric transition in $(NH_4)_2SO_4$ is accompanied by a change in lattice structure which alters the potential in which the nuclei move, but does not involve an important change in the degree to which nuclei must cooperate in order to surmount the potential barriers [96]. Jain and Bist [79] recently developed a point charge model to compute the spontaneous polarization (P_s) $\sim 0.42\ \mu C\ cm^2$ which agrees well with the experimental value reported by Hoshino et al. [6]. According to them [79] SO_4^{-2} ions also contribute to the total spontaneous polarization of $(NH_4)_2SO_4$.

The crystal structure as well as the physical properties of $(ND_4)_2SO_4$ are similar to $(NH_4)_2SO_4$ [67, 97, 98].

3.3. Alkaline Earth Metal Sulfates

Among the alkaline earth metal sulfates, $BeSO_4$ exhibits two polymorphic transformations while all the other sulfates undergo one transformation. The size of the ions seems to be the major factor controlling these transformations [99]. The available data on the phase transformations of alkaline earth metal sulfates are shown in the table 1. Table 2 gives the crystal structure data of the various phases.

Relevant data on some of the individual alkaline earth sulfates are presented below.

Magnesium sulfate heptahydrate. $MgSO_4 \cdot 7H_2O$ has an orthorhombic unit cell with the space group D_2^4–$P2_12_12_1$, $Z=4$, and $a=11.86$ Å, $b=11.99$ Å and $c=6.858$ Å at 298 K [111] Chihara and Seki [112] reported a phase transformation without dehydration in $MgSO_4 \cdot 7H_2O$ at 362–368 K. The T_t is sensitive to external conditions and sample history. Employing radioactive isotopes, Purkayastha and Sarkar [113] reported the dehydration transition $MgSO_4 \cdot 7H_2O \rightarrow MgSO_4 \cdot 6H_2O$ to occur at 298 ± 0.5 K. $MgSO_4 \cdot 6H_2O$ has a monoclinic unit cell with the space group A2/a, $Z=8$, and $a=24.34$ Å, $b=7.15$ Å, $c=10.04$ Å, $\beta=98°34'$ [114].

Calcium sulfate. Naturally occurring calcium sulfate is found in two forms, gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$). By heating gypsum at successively high temperatures, four modifications can be prepared [115]: 1, $CaSO_4 \cdot 0.5H_2O$ (hemihydrate); 2, an extremely hygroscopic anhydrous form (soluble anhydrite, $CaSO_4$(III)) which changes rapidly to hemihydrate in the presence of water vapor; 3, anhydrous modification identical to anhydrite ($CaSO_4$(II)), and 4, at ~ 1473 K, a stable high temperature form ($CaSO_4$(I)) which decomposes afterwards.

$CaSO_4$(III) is a metastable phase and under equilibrium conditions, transformation takes place directly to $CaSO_4$(II). Flörke [108] and Newmann [115] have shown that $CaSO_4$(I) cannot be quenched at room temperature. A number of workers have confirmed the presence of a high temperature thermal anomaly in $CaSO_4$ [101, 116, 117, 118]. Deer et al. [117] have pointed out that the high temperature heat effect might be associated with the onset of rotation of SO_4^{-2} ions and not with a transition to another distinct crystal structure. Gutt and Smith [102] observed a sudden lowering of birefringence on heating $CaSO_4$ around 1473 K leading to an isotropic state. This inversion was fully reversible and reproducible provided the specimen was not heated to a temperature far exceeding the T_t. The II → I transformation is accompanied by a considerable volume increase. Gutt and Smith [102] have concluded that the high temperature microscopic observations of a sudden change in birefringence cannot be explained by the rotation of SO_4^{-2} ions.

DTA investigations of gypsum have shown an exothermic heat effect at ~ 623 K possibly due to III → II transformation [119, 120]; Berry and Kuntze [121] have reported the T_t to be 665 K. This transformation does not involve a simple monotropy, but represents the precipitation of anhydrous $CaSO_4$ with the loss of interstitial water from the phase III solid solution [122]. The decrease in volume (~ 10 Å^3) per $CaSO_4$ formula group prohibits the subsequent rehydration of the anhydrous compound.

TABLE 1. *Phase transformation data*

Sulfate	Transformation	T_t, K	ΔH_{tr}, kcal mol^{-1}	ΔS_{tr}, cal mol^{-1}K^{-1}	References
$BeSO_4$	III → II II → I	863–883 908–913	3.3		[8, 100]
$MgSO_4$	II → I	1283 ± 10			[101]
$CaSO_4$	II ⇌ I	1453 1486	5.0	3.4	[5] [102]
$SrSO_4$	II → I	1425 ± 5			[5, 103]
$BaSO_4$	II → I	1422			[5]

TABLE 2. *Crystal data of the stable phases*

Sulfate	Phase (temperature)	Crystal system	Space group	Z	Cell dimensions	References
$BeSO_4$	III (room temperature)	Tetragonal (body centered)	$I\bar{4}$	2	$a=4.485$ Å $c=6.90$ Å	[104]
	II (883 K)	Orthorhombic (pseudo tetragonal)		2	$a=6.58\pm0.01$ Å $b=4.606\pm0.005$ Å $c=4.675\pm0.005$ Å	[8]
	I (923 K)	Cubic (face centred)			$a=6.65\pm0.03$ Å	[8]
$MgSO_4$	II (below T_t)	Orthorhombic	D_{2h}^{17}–Cmcm	4	$a=5.182$ Å $b=7.893$ Å $c=6.506$ Å	[105]
	I (above T_t)	Orthorhombic	D_{2h}^{16}–Pbnm	4	$a=4.742$ Å $b=8.575$ Å $c=6.699$ Å	[106]
$CaSO_4$	II (299 K)	Orthorhombic	D_{2h}^{17}–Cmcm	4	$a=6.238$ Å $b=6.991$ Å $c=6.996$ Å	[107]
	I (above T_t)	Cubic (face centred)			$a=7.82$ Å*	[108]
$SrSO_4$	II (299 K)	Orthorhombic	D_{2h}^{16}–*Pnma*	4	$a=8.359$ Å $b=5.352$ Å $c=6.866$ Å	[109]
	I (above T_t)	Cubic			$a=7.11$ Å*	[108]
$BaSO_4$	II (299 K)	Orthorhombic	D_{2h}^{16}–*Pnma*	4	$a=8.878$ Å $b=5.450$ Å $c=7.152$ Å	[110]
	I (above T_t)	Cubic			$a=7.21$ Å*	[108]

*Changed from kx units where 1kx = 1.00202 Å.

Barium sulfate. Flörke [108] has observed the II→I transformation in the range 1343–1383 K. Hahn emanation technique has revealed T_t to be in the range 1393–1453 K on heating and 1373–1343 K on cooling [123].

3.4. Thallium Sulfate

The room temperature phase of Tl_2SO_4(II), has an orthorhombic unit cell, with space group D_{2h}^{16}–Pmcn, $Z=4$ and $a=5.923$ Å, $b=10.66$ Å, $c=7.828$ Å [124]. Tl_2SO_4(II) transforms to Tl_2SO_4(I) at 765±4 K [125]. In their dilatometric studies, Samen and Tammann [126] had observed in 1903 that Tl_2SO_4 goes through a sharp volume change in the vicinity of 703 K. Fischmeister [127] has found that the volume change at 703 K is not accompanied by any change in enthalpy. Urazov and Bashilova [128] in their thermographic investigations have observed the II→I transition at 773–778 K. DTA and high temperature x-ray diffraction studies of Majumdar and Roy [45] show a hexagonal modification to be the stable polymorph above T_t, at atmospheric pressure. They report an irregular volume expansion near T_t. Majumdar and Roy [45] find the behaviour of Tl_2SO_4 to be similar to that of K_2SO_4. Dworkin and Bredig [49] disagree with Majumdar and Roy in this regard. While in K_2SO_4 most of the transformation occurs isothermally at ~857 K ($\Delta H_{tr} \sim 2$ kcal mol^{-1}), the corresponding transformation in Tl_2SO_4 has a very small isothermal part ($\Delta H_{tr} \sim 160$ cal mol^{-1} at 774 K) and is predominantly a gradual pretransitional process. The difference might be attributed to the high polarizability of the Tl^+ ion.

3.5. Lead Sulfate

DTA investigations of Gruver [29] reveal a single endothermic peak at 1158 K, apparently representing an inversion temperature in $PbSO_4$ described earlier [129].

3.6. 3*d* Transition Metal Sulfates

At ordinary conditions, the sulfates of divalent 3*d* transition metals do not show any clear thermal phase transformations except for those of cobalt and zinc. Most of these sulfates undergo magnetic transitions at very low temperatures. Some of the compounds especially $MnSO_4$, $CoSO_4$, $NiSO_4$, and $ZnSO_4$, exhibit high pressure transformations. Table 1 and table 2 give the phase transformations and crystal data of the 3*d*-transition metal sulfates.

Trivalent 3*d* transition metal sulfates like $Cr_2(SO_4)_3$ do not undergo any phase transitions in the anhydrous state in the temperature range 100–295 K [130]. The hydrated sulfate $Cr_2(SO_4)_3 \cdot 18H_2O$, however, shows possibly a second order transition around 195 K. This transition has a marked effect on the dielectric properties due to the freeing of the polar molecular groups [131]. Ferric sulfate exists in two modifications [132], one crystallizing in the rhombohedral space group $R\bar{3}$, $Z = 2$, $a = 8.791 \pm 0.004$ Å, $\alpha = 55°52'$ and the other in the monoclinic space group, $P2_1/n$, $Z = 4$, with $a = 8.296 \pm 0.002$ Å, $b = 8.515 \pm 0.002$ Å, $c = 11.600 \pm 0.002$ Å, $\beta = 90°30'$. Thermodynamic data for $Fe_2(SO_4)_3$ indicate a minor transition at 800 K with ΔH_{tr} of 540 cal mol^{-1} [133].

Additional information regarding the phase transformation of these sulfates is given below:

Manganese sulfate. $MnSO_4$ shows a magnetic phase transition at 11.5 K which is the Neél temperature (T_N) [143]. Specific heat measurements [144] have confirmed this value of T_N and in addition show three other peaks between 5 K and 11.5 K. Two of these peaks correspond to the two phase transitions theoretically predicted by Solyom [145].

$MnSO_4 \cdot H_2O$. The Neél temperature for $MnSO_4 \cdot H_2O$ has been reported to be 16 K [143]. Date [146] has reported some anomalies in the measurements of paramagnetic resonance and susceptibilities. This sulfate showed no resonance absorption in the liquid helium temperature region but showed a strong paramagnetic resonance above liquid nitrogen temperature. The monohydrate exhibits strong exchange interaction as seen from the narrowness of the paramagnetic resonance lines [147].

The curve of electric resistance with pressure up to 59.5 kbar at 353 K shows a sharp change in slope at 17.1 ± 1 kbar. This has been attributed to freezing of a saturated aqueous solution of $MnSO_4$ [134].

Iron sulfate. $FeSO_4$ undergoes a transformation to an antiferromagnetic state at 21 K [148] and Curie-Weiss law is valid in the range 45–90 K. Specific heat measurements on $FeSO_4 \cdot 7H_2O$ reveals a maximum at 2.3 K [149]. In the heptahydrate, Curie law is applicable between 64 and 290 K. Between 20 and 14 K, however, the susceptibility increases much less rapidly than the high temperature Curie constant would require.

Cobalt sulfate. In addition to the two well known phases, a third phase $CoSO_4$(III) was found to exist along with the form $CoSO_4$(I). $CoSO_4$(III) is possibly monoclinic ($P2_1/m$) with dimensions $a = 4.71$ Å, $b = 6.70$ Å, $c = 4.75$ Å and $\beta = 66.2°$ [150]. Borovik-Romanov et al. [148] measured the magnetic susceptibility of $CoSO_4$ in the temperature range 13 K–300 K and observed a maximum typical of an antiferromagnetic transition near 15.5 K. Curie-Weiss law is obeyed at temperatures appreciably higher than T_t, but at lower temperatures, the temperature dependence of the magnetic susceptibility deviates widely from the Curie-Weiss law in the paramagnetic range and displays an anomalously large decrease in the antiferromagnetic range. This is possibly due to the splitting of the ground state of the Co^{+2} ion by the crystalline field. Kreines [151] measured the magnetic susceptibility in the temperature range 1.3–300 K. In magnetic fields up to ~4 kOe, the susceptibility was independent of the field intensity. The χ-value reached a maximum along the 3 crystal axes at 12 K. Below this temperature, χ along each axis was different. The magnetic moment reached its maximum value at 4.2 K. Borovik-Romanov and Kreines [152] showed that $CoSO_4$ undergoes a ferromagnetic-antiferromagnetic transformation around 12 K (T_N). Brown and Frazer [153] and Ballestracci et al. [154] reported the structure of the low and high temperature phases of $CoSO_4$ by neutron diffraction studies, confirming the earlier x-ray diffraction results.

Nickel sulfate. Borovik-Romanov et al. [148] found a maximum in magnetic susceptibility at ~37 K characteristic of an antiferromagnetic transition. Curie-Weiss law was found to be obeyed in the temperature range 45–300 K. In the 14–34

TABLE 1. *Phase transformation data*

Sulfate	Transition at atmospheric pressure	Transition at high pressures	Remarks	References
$MnSO_4$		I → II 55.2 ± 3 kbar (771 K)		[134]
		II → III 73.5 ± 3 kbar (771 K)		
		III → IV 96.6 ± 6 kbar (771 K)		
$FeSO_4$		I → II 5 kbar (1073–1123 K)	A polymorph obtained by quenching $FeSO_4$ at 1073–1123 K	[135]
$CoSO_4$	T_t, 705 ± 8 K	I → II 6.1 ± 1 kbar (773 K)		[5, 134]
	ΔH_{tr}, 1.6 ± 0.1 kcal mol^{-1}	I → III 25 ± 1 kbar (773 K)		
	ΔS_{tr}, 2.3 ± 0.2 cal mol^{-1} K^{-1}	I → IV 31 ± 2 kbar (623 K)		
		II → III 20.6 ± 1 kbar (973 K)		
		III → IV 37.7 ± 2 kbar (773 K)		
		IV → V 40.6 ± 2 kbar (773 K)		
		V → VI 48.8 ± 2 kbar (773 K)		
		VI → VII 98 ± 5 kbar (773 K)		
$NiSO_4$		I → II 19 ± 1 kbar (773 K)		[134]
		I → III 25 ± 2 kbar (573 K)		
		II → III 29 ± 1.5 kbar (773 K)		
		III → IV 41.8 ± 2 kbar (773 K)		
		IV → V 65 ± 3 kbar (773 K)		
		V → VI 94 ± 5 kbar (773 K)		
		VI → VII 106.5 ± 6 kbar (773 K)		
		VI → VIII 108 ± 7 kbar (943 K)		
		VII → VIII 112.3 ± 6 kbar (773 K)		
		VIII → IX 123 ± 6 kbar (773 K)		
$CuSO_4$		I ⇌ II ~ 50 kbar	At all temperatures between 523 K and 775 K	[134]
$ZnSO_4$	II → I	I → II 22.8 ± 2.5 kbar (773 K)		[5, 29, 134]
	T_t, 1013 K	I → III 10 kbar (1053 K)		
		I → IV 15 kbar (1063 K)		
		I → V 28.0 ± 1.5 kbar (773 K)		
		II → VI 37.0 ± 2 kbar (773 K)		
		III → IV 16.0 ± 2 kbar (1123 K)		
		VI → VII 50.1 ± 3 kbar (773 K)		
		VII → VIII 73.2 ± 3.5 kbar (773 K)		
		VIII → IX 86.7 ± 4 kbar (773 K)		
		IX → X 96.8 ± 5 kbar (773 K)		
		X → XI 102.6 ± 6 kbar (773 K)		

TABLE 2. *Crystal data for known phases*

Sulfate	Phase	Crystal system	Space group	Z	Cell dimensions	References
$MnSO_4$	room temperature	orthorhombic	D_{2h}^{17}–Cmcm	4	$a=5.248$ Å $b=8.048$ Å $c=6.842$ Å	[134]
$MnSO_4 \cdot H_2O$	room temperature	monoclinic	A2/a–C_{2h}^{6}	4	$a=7.758$ Å $b=7.612$ Å $c=7.126$ Å $\beta=115°42.5'$	[136]
$FeSO_4$	room temperature	orthorhombic	D_{2h}^{17}–Cmcm	4	$a=5.261$ Å $b=8.013$ Å $c=6.454$ Å	[137]
$FeSO_4 \cdot 7H_2O$	room temperature	monoclinic	C_{2h}^{5}–$P2_1/c$	4	$a=14.072$ Å $b=6.503$ Å $c=11.041$ Å $\beta=105°34'$	
$CoSO_4$	room temperature	orthorhombic	D_{2h}^{17}–Cmcm	4	$a=5.191 \pm 0.002$ Å $b=7.864 \pm 0.002$ Å $c=6.516 \pm 0.002$ Å	[139, 140]
	high temperature	orthorhombic	D_{2h}^{16}–Pnma	4	$a=4.738 \pm 0.002$ Å $b=8.603 \pm 0.002$ Å $c=6.699 \pm 0.002$ Å	
$NiSO_4$	room temperature	orthorhombic	D_{2h}^{17}–Cmcm	4	$a=6.338 \pm 0.002$ Å $b=7.842 \pm 0.001$ Å $c=5.155 \pm 0.001$ Å	[114]
$CuSO_4$	room temperature (299 K)	orthorhombic	D_{2h}^{16}–Pmnb	4	$a=6.6982 \pm 0.0006$ Å $b=8.3956 \pm 0.0006$ Å $c=4.8291 \pm 0.0004$ Å	[141]
$CuSO_4 \cdot 5H_2O$	room temperature	triclinic	—	2	$a=6.113$ Å $b=10.712$ Å $c=5.958$ Å $\alpha=97°58'$ $\beta=107°17'$ $\gamma=77°26'$	[114]
$ZnSO_4$	room temperature (298 K)	orthorhombic	D_{2h}^{16}–Pnma	4	$a=8.588$ Å $b=6.740$ Å $c=4.770$ Å	[142]

K range, the susceptibility of $NiSO_4$ in the antiferromagnetic state varies with temperature according to a quadratic law.

Copper sulfate. Anhydrous copper sulfate shows an abrupt break at 35 K in the molar susceptibility versus temperature curve [148,155] possibly due to the formation of an antiferromagnetic array in half of the Cu^{+2} ions. The other half of the ions remains disordered and causes an increase in the susceptibility. Curie-Weiss law is valid in the temperature range 40–300 K. Kido and Watanabe [156] have found the Curie-Weiss law to be valid in the temperature range 90–600 K.

$CuSO_4 \cdot 5H_2O$. Taylor and Klug [157] discovered three polymorphic transformations at 302, 308, and 326.7 K, respectively. Expansion coefficient and

DTA measurements [158, 159] confirmed all these transitions to be second order. High temperature DTA investigations between 548 and 998 K [160] show no thermal anomaly. A number of workers [161–164] have observed DTA peaks related to the dehydration of pentahydrate. Kiriyama and Ibamoto [165] measured the temperature dependence of the dielectric constant and losses of $CuSO_4 \cdot 5H_2O$ in the temperature range 93–393 K and found distinct dispersion of the dielectric constants at temperatures higher than 343 K. Geballe and Giauque [166] showed that the magnetic system orients under the restraining influence of directional crystal forces causing changes in internal energy. The heat capacity curve has a maximum at 1.35 K, a minor maximum at 0.75 K and possibly a third maximum at 0.25 K. Dehaas and Gorter [167] measured the magnetic susceptibility in the temperature range 14.3–290 K, and found Curie-Weiss law to hold good. The measurements of magnetic anisotropy of $CuSO_4 \cdot 5H_2O$ at different temperatures from 83 K to 299 K [168] revealed the crystal to be nearly magnetically uniaxial with its two principal susceptibilities conforming roughly to the Curie law with different Curie constants. Magnetic measurements down to 1.6 K [169] show this salt to approximately follow Weiss law with $\theta = -0.7°$ over the whole temperature range. Benzie and Cook [170] found that the susceptibilities measured in different directions with respect to the crystallographic axes follow a Curie-Weiss law. The discrepancy between these and previous results [168] were attributed to temperature independent paramagnetism.

Zinc sulfate. DTA investigations of Gruver [29] on $ZnSO_4 \cdot 7H_2O$ (natural) show two endothermic effects at 473 K and 623 K, possibly due to the loss of water of hydration. A reversible inversion is reported for anhydrous $ZnSO_4$ at 1013 K.

3.7. 4*d* Transition Metal Sulfates

Silver sulfate exhibits a polymorphic transformation (II →I) while $CdSO_4$ is reported to have two polymorphic transformations (III→ II→ I). Data on phase transformations as well as the crystal structures of known phases are given in tables 1 and 2.

TABLE 1. *Phase transformation data*

Sulfate	Transformation	T_t, K	ΔH_{tr}, kcal mol^{-1}	ΔS_{tr}, cal mol^{-1} K^{-1}	References
Ag_2SO_4	II $\rightleftharpoons$ I	685	1.9	2.8	[5]
$CdSO_4$	III $\rightleftharpoons$ II	773			[171]
	II → I	1073			[172]

Additional information regarding these sulfates is given below.

Silver sulfate. Hedvall et al. [175] reported a higher T_t (703 ± 3 K) from their DTA measurements, the T_t being independent of the heating rate. On cooling, the high temperature form could be supercooled up to 20° below T_t. Johansson's studies [176] indicate a heterogeneous process of nucleation during this transition. Once started, the

TABLE 2. *Crystal data for known phases*

Sulfate	Phase (temp)	Crystal class	Space group	*Z*	Cell dimensions	References
Ag_2SO_4	II (298 K)	orthorhombic	D_{2h}^{24}–Fddd	8	$a = 5.8167$ Å $b = 12.704$ Å $c = 10.269$ Å	[173]
$CdSO_4$	III (298 K)	orthorhombic	D_{2h}^{13}–Pmmn	2	$a = 4.7174$ Å $b = 6.5590$ Å $c = 4.7012$ Å	[174]
$CdSO_4$	I	orthorhombic			$a = 5.310$ Å $b = 8.157$ Å $c = 7.180$ Å	[172]

transition proceeds very fast in a given crystal. The transition could not be induced by contact with the low temperature form above 698 K. At the II → I transition, the electrical conductivity of Ag_2SO_4 was found to increase rapidly by approximately one decimal power [177]. Vesnin [178] reported an enantiotropic transformation around 843 K. He found this transformation to be rather slow.

Cadmium sulfate. Maksimova [171] detected two peaks in the DTA heating curves for $CdSO_4$. Specimens prepared by different methods produce different thermograms possibly due to difference in crystal structure. Maksimova found that $CdSO_4(III)$ is non-homogeneous and consists of two types of aggregates with different refractive indices. Heterogeneity was observed only in specimens whose thermograms show the double thermal effects. From the heating and cooling curves of $CdSO_4$ Sholokovich and Zvorykina [179] showed a new transformation in the range 1119–1125 K.

3.8. Rare Earth Metal Sulfates

Thermal anomalies in hydrated rare earth metal sulfates have been reported by a number of workers [180–185] which are mostly attributed to the loss of water of hydration. Zaitseva [186] from thermographic, thermogravimetric, spectroscopic and x-ray diffraction studies, showed $Eu_2(SO_4)_3 \cdot 8H_2O$ to have one polymorphic transformation in the temperature range 678–738 K which could not be related to the loss of water of hydration. Around 573 K, the hydrated sulfate was found to change to an anhydrous cubic modification ($a = 6.63 \pm 0.01$ Å), which on further heating changed to an equilibrium macrocrystalline state (678 K). TGA thermograms did not show further weight loss in the 573–873 K range. There appeared another transformation in the crystal structure (as found from x-ray studies) above 873 K, which was not accompanied by any thermal effects. Thermograms for $Gd_2(SO_4)_3 \cdot 8H_2O$ and $Tb_2(SO_4)_3 \cdot 8H_2O$, differ from that of $Eu_2(SO_4)_3 \cdot 8H_2O$ in not having the exothermic effect in the temperature range 678–738 K. At 473 K the crystalline hydrates apparently possess cubic structure with $a = 6.36 \pm 0.02$ Å. Heating the octahydrate up to 573 K, leads to formation of compounds isostructural with anhydrous Eu-sulfate. For anhydrous Gd-sulfate two more polymorphic modifications were found at 823 K and 923 K, respectively. Anhydrous Tb-sulfate shows two polymorphic modifications, the first, stable over the wide temperature range, 573–873 K, having a cubic structure. The second modification at 903 K has a relatively complex crystal structure.

Room temperature crystal data for the Eu, Gd, and Tb sulfate octahydrates are given in table 1.

TABLE 1. *Crystal data for some monoclinic rare earth metal sulfates* [186]

Sulfate	*a* ±0.003	*b* ±001	*c* ±0.004	*β* ±1°	*Z*
$Eu_2(SO_4)_3 \cdot 8H_2O$	13.566	6.781	18.334	102°14′	4
$Gd_2(SO_4)_3 \cdot 8H_2O$	13.544	6.774	18.299	102°11′	4
$Tb_2(SO_4)_3 \cdot 8H_2O$	13.502	6.751	18.279	102°09′	4

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4. The Phosphates

Substances	Measuring technique	Observations	Remarks	References
Lithium phosphate Orthorhombic, Pcmn $a = 6.07$ Å, $b = 10.26$ Å, $c = 4.86$ Å (stable phase)	Crystallographic studies	T_t, 775 K Low Li_3PO_4 has the $\beta_{\|\|}$ structure while high Li_3PO_4 has the $\gamma_{\|\|}$ structure. The β-phase is stable at RT.	High temperature γ-phase can be preserved metastably at ambient conditions by rapid cooling.	[1, 2]
Sodium phosphate tetragonal $a = 10.81$ Å $c = 6.84$ Å (stable phase)	Crystallographic and dielectric measurements	T_t, 473–573 K Low temperature form (α) transforms to high temperature form (γ). Between 110 and 180 K very rapid increase of c'' occurs.	The γ-phase is cubic with $a = 7.56$ Å at 873 K.	[3, 4]
Ammonium phosphate $(NH_4)_3PO_4$	NMR	T_t, 193 K The spectrum changes from a single line at RT to two components at temperatures below T_t.	These components belong to frozen in and rotating NH_4^+ ions.	[5]

4. The Phosphates—Continued

Substances	Measuring technique	Observations	Remarks	References
	Dielectric constant and loss	At 262 K, an abrupt, almost discontinuous increase is observed.		[4]
	High pressure studies up to 40 kbar	Details not available		[6]
Calcium phosphate α-$Ca_3(PO_4)_2$, monoclinic, $P2_1/a$, $Z=8$, $a=13.07$ Å, $b=9.11$ Å, $c=12.86$ Å, $\beta=108°9'$ (stable phase)	Crystallographic studies	T_t, 1453 K	High temperature form β-$Ca_3(PO_4)_2$ is hexagonal, $R\bar{3}c$, $Z=8$ with $a=10.345$ Å and $c=36.905$ Å.	[7, 8]
	Luminescence and calorimetric measurements	Anomalies at 233 and 308 K appear in these measurements.		[8]
Boron phosphate BPO_4, hexagonal $a=4.332$ Å $c=6.640$ Å (low cristobalite form, stable phase)	High pressure studies	BPO_4 transforms from a cristobalite to a quartz form at 46 kbar	High pressure form is quartz like hexagonal with $a=4.470\pm 0.005$, $c=9.926\pm 0.01$ Å and and $Z=3$.	[9–11]
		Investigations up to 85 kbar at temperature range 1273–1473 K show a dense modification of BPO_4.	The dense modification has the cell dimensions $a=7.75\pm 0.02$ Å, $c=9.95\pm 0.02$ Å and $Z=9$.	
Aluminium phosphate $AlPO_4$, hexagonal, $P3_1$, $Z=3$, $a=4.92$ Å $c=10.91$ Å (berlinite form, stable phase)	Crystallography and TGA	T_t, 854 (rhombohedral to hexagonal) T_t (rev) 847 K; ΔH_{tr}, 2.64 cal g^{-1}; ΔV_{tr}, $+0.88$ Å^3	The transformation involves dilation in the c-direction as in quartz. The crystal data for other forms are as follows: *low cristobalite:* orthorhombic, $C222_1$ $Z=4$, $a=7.099\pm 0.003$ Å $b=7.099\pm 0.003$ Å $c=7.006\pm 0.003$ Å tetragonal, $I\bar{4}$, $Z=2$, $a=4.99$ Å $c=6.90$ Å *Cristobalite*, cubic, $Z=4$, $a=7.11\pm 0.01$ Å at 623 K.	[1, 10, 12]
	Crystallographic and DTA studies	Three distinct modifications of $AlPO_4$ are obtained; tridymite, cristobalite and berlinite (quartz structure). The T_t's are 363 K, 493 K, and 853 K, respectively.	The tridynite and cristobalite forms were not found to convert back to the berlinite on prolonged heating.	[13–15]
	EPR of $AlPO_4$:Fe^{+3}	The transformation is confirmed.		[16]
	Raman spectroscopy	Confirmed the transformation.	$AlPO_4$ has a complicated soft mode lying at reciprocal lattice points in $AlPO_4$. These are Raman active. One such mode is at 158 cm^{-1} and is totally symmetric.	[17]

Substances	Measuring technique	Observations	Remarks	References
	High pressure investigations	Pressure-temperature curve for the quartz-tridymite transformation, determined up to 1 kbar gave ΔH_{tr}, ~262 cal mol^{-1}. Polymorphic transformation near 55 kbar and 723 K. At 1173 K and 60 kbar two new forms entirely different from the known forms were obtained.		[10, 18, 19]
		The 1273 K and 100 kbar, a third form was found.	The third new form at 1273 K and 100 kbar has the crystal data: $a = 5.11$ Å, $b = 7.48$ Å, $c = 6.09$ Å.	
Gallium phosphate $GaPO_4$, hexagonal, $P3_1$, $Z = 1$, $a = 4.902$ Å, $c = 11.05$ Å (stable phase)	Crystallographic studies and DTA	$GaPO_4$ was found to exhibit three phases: 1. berlinite (low quartz) 2. low cristobalite 3. high cristobalite Two phase transformations were detected corresponding to DTA peaks.	The cristobalite form of $GaPO_4$, can be easily converted to the berlinite type by proper heat treatment.	[1, 20, 21]
		a. berlinite → high cristobalite (a slow change) at 1243–1253 K. b. low-cristobalite → high cristobalite (a rapid and reversible change) at 886–896 K on heating and 843–	The low cristobalite form is orthorhombic $C222_1$, $Z = 4$ $a = 6.967 \pm 0.003$ Å $b = 6.967 \pm 0.003$ Å $c = 6.866 \pm 0.003$ Å	
Lead phosphate $Pb_3(PO_4)_2$ monoclinic, C_{2h}^6-C2/c $Z = 4$ $a = 13.816$ Å $b = 5.692$ Å $c = 9.429$ Å	Crystallographic studies.	Low temperature monoclinic phase transforms to the high temperature around 473 K.	The high temperature form (I) has orthorhombic unit cell, $D_{3d}^5-R\bar{3}m$ $Z = 1$, $a = 5.53 \pm 0.02$ Å $c = 20.30 \pm 0.05$ Å at 473 ± 15 K.	[22, 23]
and = 102.36° (stable phase)	Heat capacity	Measurements between 15 and 300 K did not show any anomaly.		[24]
Bismuth phosphate $BiPO_4$, monoclinic $P2_1/n-C_{2h}^5$, $Z = 4$ $a = 6.74 \pm 0.02$ Å $b = 6.92 \pm 0.02$ Å $c = 6.46 \pm 0.02$ Å $\beta = 103°30'$ (monazite type, stable phase)	Crystallographic studies	Two phases monoclinic as well as hexagonal are the stable forms at room temperature.	The room temperature hexagonal phase has the cell dimensions $a = 6.966 \pm 0.001$ Å $c = 6.460 \pm 0.002$ Å	[25, 26]
		A third phase stable at high temperatures was also discovered.	The high temperature phase is monoclinic with the cell dimensions $a = 4.88 \pm 0.03$ Å $b = 7.06 \pm 0.02$ Å $c = 4.71 \pm 0.03$ Å $\beta = 96.3 \pm 0.5°$ space group: $P2_1-C_2^2$ or $P2_1/m$	
		The monazite type is the stable form of $BiPO_4$ over a wide temperature range.		

4. The Phosphates—Continued

Substances	Measuring technique	Observations	Remarks	References
		The high temperature structure slowly converts to the monazite type at ordinary temperatures. No spontaneous change from the hexagonal to the monazite type has been detected.		
Chromium phosphate $CrPO_4$ (crystal data not available)	Crystallographic, DTA and hydrothermal studies	T_t, 1448 K ($\beta \rightarrow \alpha$) An amorphous form exists up to 1073 K. The reflections for the β-phase appear at 1223 K	β=phase is an unstable phase and converts to α-phase gradually.	[27, 28]
Manganese phosphate $Mn_3(PO_4)_2$, hexagonal $a = 4.94$ Å $c = 5.48$ Å (stable phase)	DTA	T_t, 1086 ± 5 K (Quartz type phase converts to the cristobalite type)	Cristobalite type phase has the cell dimensions: $a = 4.97$ Å, $c = 6.97$ Å	[29]
	High pressures	At the pressure ~ 55 kbar and temperature 723 K, a new phase has been reported.		[10]
Iron phosphate	Crystallographic studies	Four varieties, orthorhombic, triclinic, monoclinic (dull red) and orthorhombic (pale green) forms were reported. The last three were, however, later found to be identical with no apparent points of transformation among themselves.	In nature $FePO_4$ is found as strengite (orthorhombic) and phosphosiderite (monoclinic). Quartz type modification has the dimensions: $a = 5.035$ Å $c = 5.588 \times 2$ Å	[30–32]
	X-ray diffraction and DTA	T_t, 973–983 K (reversible transformation)	Several inversions reported earlier were not confirmed.	[29, 33]
	High pressure studies	Around 55 kbar and 723 K, $FePO_4$ is reported to transform to a new form.		[10]
Zinc phosphate $Zn_3(PO_4)_2$ monoclinic C^6_{2h}–C2/c, $Z = 4$ $a = 8.14 \pm 0.02$ Å $b = 5.63 \pm 0.01$ Å $c = 15.04 \pm 0.04$ Å $\beta = 105°08' \pm 05'$ (stable phase)	Crystallographic studies	α-$Zn_3(PO_4)_2$ transforms to the β-$Zn_3(PO_4)_2$ at 1215 K	β-$Zn_3(PO_4)_2$ is also monoclinic with space group $P2_1/c$, $Z = 4$, $a = 9.393 \pm 0.003$ Å $b = 9.170 \pm 0.006$ Å $c = 8.686 \pm 0.003$ Å $\beta = 125.73° \pm 0.10$	[34. 35]
Rare earth metal phosphates	Crystallographic studies	La, Ce, Pr, Nd, Sm, Eu, Gd, and Tb-phosphates have monazite type structure. Some of them also possess a hexagonal structure at RT. This hexagonal α-phase transforms to β-phase on heating between 673 and 1073 K. Dy-, Ho-, Er-, Tin-, Yb-, and	*Crystal data* (hexagonal) $Z = 3$, space group $P3_121(D^4_3)$ *Phosphate* *a* *c* La- 7.081 ± 0.005 Å 6.468 ± 0.008 Å Ce- 7.055 ± 0.003 Å 6.439 ± 0.005 Å Nd- 7.00 6.39	[36–39]

4. The Phosphates – Continued

Substances	Measuring technique	Observations	Remarks	References
		Lu-phosphates have zircon type structure (tetragonal, space group C_{2h}^{19}). Tb-phosphate also exists in zircon type structure.	±0.01 Å ±0.03 Å Gd- 6.89 6.32 ±0.01 Å ±0.02 Å *Monoclinic monazite type,* $P2_1/n$–C_{2h}^5, $Z=4$ *Phosphate* *a* *b* *c* β La 6.83 7.05 6.48 103°34′ Ce 6.76 7.00 6.44 103°38′ Pr 6.75 6.94 6.40 103°21′ Nd 6.71 6.92 6.36 103°28′	
	Crystallographic studies	Phase transformations in $SmPO_4$ and $PrPO_4$ have been found at 873 K. Above 773 K, $YbPO_4$ undergoes a phase transition like $SmPO_4$ and $PrPO_4$.	The x-ray diffraction pattern of $YbPO_4$ after being heated at 1273 K is different from the corresponding patterns of $SmPO_4$ and $PrPO_4$. This high temperature phase is tetragonal, space group $I4_1/amd$ (D_{4h}^{19}) with $a=6.812$ Å, $c=5.973$ Å.	[40]
	Magnetic measurements	The T_t's in magnetically ordered rare-earth compounds, which have no conduction electrons, are considerably low because of the weak exchange interactions between rare-earth ions.	The Gd-, Tb-, and Dy-phosphates were found to have extremely high Neél temperatures of 225 K, 415 K, and 505 K respectively. Saji et al. [42], however, differ from earlier results of Wang et al. [41] suggesting antiferromagnetic transitions.	[41–43]
Erbium phosphate	Magnetic measurements	From the temperature dependence of the susceptibility in the low temperature region where only the lowest doublet is populated, a Curie temperature of −1 K is extrapolated. This would place a transition to an antiferromagnetically ordered state below 1 K.	A similarly low T_t of 0.8 K has been calculated from the estimated dipole interaction, indicating that the exchange interaction is very small or negligible compared to the dipole interaction. $ErPO_4$, therefore, may be a good example of a pure dipolar magnetic ordering.	[44]
Terbium phosphate	Specific heat and magnetic measurements	The plot of the specific heat versus temperature shows two λ-type anomalies. One at the Neél point (T_N), 2.20±0.05 K and the other at Curie point (T_c), 3.5±0.1 K, which has to be atrributed to a crystallographic phase transition from tetragonal to some lower symmetry. The magnetic measurements on single crystals show that there is a strong magnetic anisotropy in the plane perpendicular to the optical axis at temperatures below T_c.	With external fields more than 7 kOe the weak and strong directions can be interchanged, giving rise to a very sharp $\pi/2$ periodicity of the magnetization perpendicular to the optical axis, if the crystal is rotated around the *c*-axis by 2π.	[45]

4. The Phosphates—Continued

Substances	Measuring technique	Observations	Remarks	References
Dysprosium phosphate	Magnetic measurements	$DyPO_4$ is found to order antiferromagnetically at approx. 3.5 K. The transition from the antiferromagnetic to the paramagnetic state is first order, below a critical temperature T_c near 0.75 K. This transition at higher temperatures is of higher order.	This appeared to be an ideal 3-dimensional Ising antiferromagnet.	[46–49]
		T_t (paramagnetic-antiferromagnetic) in case of $DyPO_4$ has been reported to be 2.8 K.		[50]
Holmium phosphate	Specific heat and magnetic measurements	At 1.39 K, a magnetic phase transition is observed.		[51]

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5. The Perchlorates

Substance	Measurement technique	Observations	Remarks	References
Lithium perchlorate $LiClO_4$ Orthorhombic, Pmnb, $Z=4$ $a=6.926$ Å $b=8.659$ Å $c=4.836$ Å (stable phase)	Crystallography and DTA	No polymorphic transformation at normal pressures.		[1–4]
	High pressure studies	A high pressure phase transition is seen around 16.4 kbar		[5]
Sodium perchlorate $NaClO_4$ orthorhombic, Amma, $Z=4$ $a=7.06\pm0.02$ Å $b=7.08\pm0.02$ Å $c=6.48\pm0.02$ Å (stable phase)	Crystallography and DTA	T_t, 577–586 K (orthorhombic → cubic) The transformation is accompanied by a volume increase ΔV_{tr} of 14.27 Å^3 per molecule. There is not much hysteresis accompanying the transformation.	High temperature phase is cubic, space group: $F\bar{4}3m$, $Z=4$ $a=7.09$ Å at 587 K.	[1–4, 6, 7]
	Dielectric constants	A sharp increase in the dielec constant at T_t, is observed. ϵ/Tcurve has a small maxima slightly before the T_t.	Small anomaly just before T_t is possibly due to the prerotation caused by the loosening of the lattice structure. The sharp increase in ϵ at T_t must be corresponding to the onset of free rotation of ClO_4^- during the disordering of the lattice to the cubic structure.	[7, 8]
	Electrical conductivity	Thermal anomaly at T_t is observed.	In $NaClO_4$, the large difference in the ionic radii and a very high value of the ϵ in the cubic phase suggests a Frenkel type disorder.	[7]
	Thermoelectric power	A break in the α versus T is noticed at the T_t. An abrupt increase in α is found.		[7]
	IR spectroscopy and micro projection measurements	T_t, 581 K A band around 935 cm^{-1}, the symmetric stretching frequency of ClO_4^-, disappears at the T_t.	The transformation is reversible.	[4, 8, 9]

5. The Perchlorates—Continued

Substance	Measurement technique	Observations	Remarks	References
	High pressure studies	$NaClO_4$ has two high pressure transitions up to 50 kbar.	$NaClO_4$ phase III, the phase stable at >30 kbar probably has a structure similar to $BaSO_4$.	[5, 10]
Potassium perchlorate orthorombic, Pbnm, $Z=4$ $a=7.2401\pm0.0023$ Å $b=8.8373\pm0.0030$ Å $c=5.6521\pm0.0040$ Å (stable phase)	Crystallographic, DTA and dilatometric studies	T_t, 573–579 (orthorhombic→cubic) with ΔT, 5.6 K. ΔH_{tr}, 3.29 kcal mol^{-1} The transformation is accompanied by a large volume change.	The cubic phase has the crystal data as follows: space group: $F\bar{4}3m$ $Z=4$ $a=7.52$ Å at 583 K	[1–3, 6, 11–13]
	Dielectric measurements	An increase in ϵ is observed at the T_t.	Rotation of ClO_4^- is indicated by the results. Transformation is an order-disorder type.	[7, 8]
	Electrical conductivity	An increase in conductivity is reported at the T_t.	The activation energy for the cubic phase is less than that in orthorhombic phase.	[7]
	Thermoelectric power	A break in the curve α vs T is noticed at T_t.	$KClO_4$ indicates an increase in α followed by a sharp decrease.	[7]
	IR spectroscopy and microprojection	A band around 935 cm^{-1}, observed in orthorhombic form, disappears at T_t.	The transition is reversible.	[4, 8, 9]
	High pressure studies.	Orthorhombic→cubic transition line rises from 569 K at atmosperic pressure to 839 K at 11.3 kbar, where it is found to decompose explosively.	No high pressure phase exists in $KClO_4$.	[5, 14]
Rubidium perchlorate $RbClO_4$, orthorhombic, Pbnm, $Z=4$ $a=7.53$ Å $b=9.27$ Å $c=5.81$ Å (stable phase)	Crystallographic and DTA studies.	T_t, 551–554 K	High temperature phase is cubic with space group $F\bar{4}3m$, $Z=4$ and $a=7.72\pm0.01$ Å at 573 K.	[1, 2, 6]
	Dielectric constant	A sharp increase is observed at the T_t.	The transformation is an order-disorder type.	[8]
	Electrical conductivity	An increase in conductivity is observed at the T_t.	Energy of activation for conduction is less in cubic phase as compared to that of orthorhombic phase.	[7]
	Thermoelectric power	$RbClO_4$ shows an increase in α followed by a sharp decrease after the transformation.		[7]
	IR spectroscopy and micro projection technique	T_t, 552 K A band around 935 cm^{-1} disappears at the T_t.	Transformation is found to be reversible.	[4, 8]

5. The Perchlorates—Continued

Substance	Measurement technique	Observations	Remarks	References
	High pressure studies.	$RbClO_4$ has a high pressure transformation near 15 kbar with a volume change of less than 1.3 $cm^3\ mol^{-1}$.		[5, 15]
Cesium perchlorate $CsClO_4$, orthorhombic, Pnma, $Z=4$ $a=7.79$ Å $b=9.82$ Å $c=6.00$ Å (stable phase)	Crystallographic, DTA and dilatometric measurements	T_t, 492–497 K (orthorhombic→ cubic) The transformation is accompanied by a large volume change.	The high temperature cubic phase has the space group F$\bar{4}$3m, $Z=4$ and $a=8.00\pm0.02$ Å at 503 K.	[1, 2, 6, 11, 13
	Dielectric constant	$CsClO_4$ shows a sharp increase of ϵ at T_t.	Order-disorder type transition is suggested.	[8]
	Electrical conductivity	An increase in conductivity of $CsClO_4$ is noticed at the T_t.	The energy of activation in the cubic phase is less than that in the orthorhombic phase.	[7]
	Thermoelectric power	$CsClO_4$ shows an anomalous behaviour as α changes sign from negative to positive value.	α increases with increase in temperature in cubic $CsClO_4$.	[7]
	High pressure studies (DTA, crystallography and volumetric technique)	$CsClO_4$ is found to have two transitions with a volume change of 3.5 $cm^3\ mol^{-1}$ in the former. The high pressure transition III→ IV occurs near 1 kbar. The transitions from II and IV phases to I take place at 6.4 kbar, 692 K, and 17.1 kbar, 813 K, respectively.	*Triple points* IV/III/II 4.5 kbar 587 K I/IV/II 7.0 kbar 684 K	[5, 16]
Ammonium perchlorate NH_4ClO_4, orthohombic, Pbnm, $Z=4$, $a=7.449\pm0.005$ Å $b=9.202\pm0.006$ Å $c=5.816\pm0.004$ Å (stable phase)	Crystallography	T_t, 513 K (orthorhombic-cubic) NH_4ClO_4 seems to undergo a phase transformation near 83 K also.	The cubic phase has the crystal data: space group F$\bar{4}$3m, $Z=4$, $a=7.69\pm0.02$ Å at 516 K. The transformation is presumably occasioned by the onset of free rotation of ClO_4^- ion. In addition NH_4^+ ion has also been reported to undergo free rotation.	[1, 17–21]
	DTA	T_t, 513 K ΔT, 15 K	DTA thermograms change with the thermal history of the sample, and even with aging at ambient temperature.	[22]
	Heat capacity measurements	The measurement do not support earlier results showing a phase transformation at 83 K.	NH_4^+ ion has been found to freely rotate.	[23, 24]
	Crystallography, IR, Raman spectra	No phase transformation in 120 K–300 K range. Anomalies are seen in the temperature ranges, 20–50 K and 100–110 K.	The free rotation of NH_4^+ ion is also reported.	[25, 26]

5. The Perchlorates—Continued

Substance	Measurement technique	Observations	Remarks	References
	NMR	The results are interpreted in terms of reorientation of the NH_4^+ ion about random or nearly random axes.	The relaxation times are consistent with a barrier hindering reorientation of 2.0 ± 0.6 kcal.	[27]
	Cold neutron studies	This also supports the principle of essentially unrestricted rotational motion of the NH_4^+ ion in the crystal lattice.		[28]
	Optical microprojection technique	T_t, 513 K		[4]
	High pressure studies	NH_4ClO_4 is found to have a transformation accompanied by a volume change of < 1.3 cm^3 mol^{-1}. The usual orthorhombic→ cubic transition was followed to 4 kbar and 573 K. NH_4ClO_4 explodes violently in the range 603–623 K at 2–3.6 kbar although at atm. pressure it explodes only at 713 K.	The anomalous curvature of Bridgman's NH_4ClO_4 II/III transition line near 373 K is due to a triple point involving the phase found at atmospheric pressure below 83 K. The explosion in NH_4ClO_4 may be due to large volume change upon transition which causes local pressure increase at the sample. No other transitions could be detected down to 123 K at atmospheric pressures.	[5, 29]
Thallium perchlorate $TlClO_4$, orthorhombic, Pbnm, $Z=4$ $a=7.50$ Å $b=9.42$ Å $c=5.88$ Å (stable phase)	Crystallographic studies	T_t, 539 K (orthorhombic→ cubic)	High temperature phase is cubic, space group: $F\bar{4}3m$, $Z=4$ and $a=7.63$ Å	[1]
	Optical microprojection technique	T_t, 539 K	The Thallium salt is particularly more suited for microprojection demonstration as the orthorhombic form is strongly birefringent.	[4]
	High pressure studies	A high pressure phase III is found with the initial volume change ΔV_{tr}, 5 cm^3 mol^{-1} The triple point I/III/II is at 0.7 kbar and 553 K.	Earlier, Bridgman reported the transition to accompany ΔV_{tr}, < 1.3 cm^3 mol^{-1}.	[5, 30]
Silver perchlorate $AgClO_4$, orthorhombic	Crystallographic	T_t, 428 K (orthorhombic-cubic)	The high temp. cubic phase has the space group $F\bar{4}3m$, $Z=4$ and $a=7.01 \pm 0.01$ Å at 433 K.	[1]
	Optical microprojection studies	T_t, 428–432 K Another transition appears to take place at 375–383 K.	The silver salt begins decomposing near T_t	[4, 31]

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6. The Chromates

Substance	Measurement technique	Observations	Remarks	References
Sodium chromate Na_2CrO_4, orthorhombic, Amam, $Z=4$ $a=7.138$ Å $b=9.259$ Å $c=5.861$ Å (stable phase)	Crystallographic and thermal measurements	T_t, 686 K (orthorhombic → hexagonal) II → I		[1, 2]
	High pressure studies	Three new phases III, IV, and V appear at pressures up to 45 kbar	The triple points are given as follows: Pressure, kbar / Temperature, K I/II/IV 11.3±1 745±5 II/III/IV 14.6±1 694±7 I/IV/V 20.4±1 809±7	[3]
Potassium chromate K_2CrO_4, orthorhombic space group, Pnam $Z=4$ $a=7.61$ Å $b=10.40$ Å $c=5.92$ Å (stable phase)	Crystallographic and thermal measurements	T_t, 952 K	The transformation is accompanied by change in color from yellow to red.	[1, 4]
	Thermal analysis	T_t, 939 K ($\alpha \rightarrow \beta$)	Color change is attributed to some gradual change in $\beta-K_2CrO_4$ and not due to polymorphic transformation. $\beta-K_2CrO_4$ is hexagonal with $a=6.125$ Å $c=8.245$ Å at 978 K.	[1, 5–7]

6. The Chromates – Continued

Substance	Measurement technique	Observations	Remarks	References
	Specific heat between 80 and 300 K	No transformation		[8]
	Magnetic susceptibility (89–723 K)	χ is independent of temperature.		[9]
	Dielectric permitivity and loss	From the behaviour of ϵ' and ϵ the development of the transformation process in time can be followed and transition rate can be determined.	The effect of different variables on the polymorphic transformation can also be determined.	[10]
	High pressure studies	No indication of polymorphism in the temperature range 293–473 K up to 12 kbar, but there appear three new high pressure polymorphs of K_2CrO_4 between 20 and 100 kbar. A triple point between the phases α, γ, and δ is near 923 K at 28.5 kbar.		[11, 12]
Strontium chromate $SrCrO_4$, monoclinic $P2/n\text{–}C_{2h}^5$ $Z=4$ $a=7.081$ Å $b=7.388$ Å $c=6.771$ Å $\beta=103°25' \pm 5'$ (stable phase)	Crystallographic study	A possible orthorhombic high temperature phase at 1148 K, has been reported.		[13]
Thallium chromate Tl_2CrO_4, Orthorhombic, Pmcn $a=5.910$ Å $b=10.727$ Å $c=7.910$ Å (stable phase)	Crystallographic, DTA and elec. conductivity studies	T_t, 638 K, ΔH_{tr}, 15 cal mol^{-1} (I) T_t 795 K (774 K on cooling) (II) ΔH_{tr}, 70 cal mol^{-1} The trend in variation of lattice constants also shows an anomaly in Tl_2CrO_4 between 523 and 623 K.	The second order phase transformation around 638 K was disputed by Sladky [12]. The high temperature hexagonal phase has cell dimensions: $a=10.04 \pm 0.04$ Å $c=16.28 \pm 0.08$ Å at 803 K.	[14–17]
Lead chromate $PbCrO_4$, monoclinic space group: $P2_1/n\text{–}C_{2h}^5$, $Z=4$ $a=7.118 \pm 0.004$ Å $b=7.434 \pm 0.004$ Å $c=6.794 \pm 0.004$ Å $\beta=102°25.5' \pm 2'$ (stable phase)	Crystallography and thermal analysis	T_t, 980 K–1056 K	$PbCrO_4$, however, has also been found to evolve oxygen around 873 K due to decomposition to Pb_2CrO_5 and Cr_2O_3.	[13, 18–20]

6. The Chromates—Continued

Substance	Measurement technique	Observations	Remarks	References
Silver chromate Ag_2CrO_4, orthorhombic, space group: Pnma $Z=4$ $a=10.063\pm0.011$ Å	DTA and electrical conductivity	T_t, 762–766 K $\underset{(II)}{\text{orthorhombic}} \rightarrow \underset{(I)}{\text{hexagonal}}$	At lower temperatures Ag_2CrO_4 is an *n*-type semiconductor, which transforms to a *p*-type semiconductor at higher temperatures.	[21–23]
$b=7.029\pm0.004$ Å $c=5.540\pm0.002$ Å (stable phase)	High pressure studies	The II → I transition temperatures to 40 kbar were fitted as $t(°C)=479+2.3\,P-0.020\,P^2$		[24]

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