

STUDY OF THE INFRARED SPECTRA OF SOME INORGANIC SULPHATES

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Abstract. IR spectra of the anhydrous sulphates, CaSO_4 , MgSO_4 , MnSO_4 , $\text{Al}_2(\text{SO}_4)_3$ and $\text{Cr}_2(\text{SO}_4)_3$ have been recorded and discussed. In connection with the preparation of the anhydrous sulphate samples, the dehydration temperature of the hydrated compounds and the decomposition temperature of the anhydrous ones have been mentioned.

IR absorption studies of complex inorganic compounds, mainly phosphates and sulphates, were not made systematically. Only in recent years some studies have been made. Bentley and Freeman¹ have listed the IR absorption data of some inorganic sulphates. The data for the above anhydrous sulphates are not available.

Experimental

Anhydrous sulphates have been prepared by heating chemically pure hydrated salts at different temperatures. Dehydration temperatures have been determined by differential thermal analyses² of the hydrated compounds. Differential thermal analyses have been made by raising the temperature $10^\circ\text{C}/\text{min}$. So for complete dehydration the substances were heated for certain period of time at the temperature below the dehydration temperature indicated by the differential thermal analysis to avoid the decomposition of the sulphates to oxides. For recording the IR spectra small amount of the anhydrous substances (1.50–2 mg) were mixed thoroughly with finely powdered KBr (0.25 g). The mixtures were pressed to a disk by applying appropriate pressure. The spectra were then recorded on a Beckman spectrophotometer Model IR9.

Results and Discussions

The dehydration and decomposition temperatures of the above sulphates have been shown in the Table 1. The differences between the dehydration and decomposition temperatures of the sulphates are sufficient enough to allow safe dehydration of the hydrated compounds without decomposition to respective oxides. In all the cases the dehydration and de-

TABLE 1. DEHYDRATION AND DECOMPOSITION TEMPERATURES OF THE SULPHATES.

Substances	Dehydration ($^\circ\text{C}$)	Decomposition ($^\circ\text{C}$)
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	560	~ 1000
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	558	~ 1000
$\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$	570	924
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	580	850
$\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	298	710

composition processes are endothermic.² The complete dehydration is indicated by the absence of the IR absorption band in the region $1640\text{--}1660\text{ cm}^{-1}$ due to O—H bending.

The IR spectra of the above compounds have been shown in Fig. 1. In the spectrum (Fig. 1a) of CaSO_4 there is one very strong and broad absorption band at 1140 cm^{-1} . At 1012 cm^{-1} there is one very weak band. There are three very strong absorption bands at 665, 612, and 595 cm^{-1} respectively. These bands are very sharp and well-defined. It is very likely that Ca^{+2} has 6 coordination in CaSO_4 by oxygen and sulphur and the absorption band at 612 cm^{-1} may be an indication of octahedral structure of calcium sulphate. At 512 cm^{-1} there is one weak but well-defined band. The spectrum (Fig. 1b) of MgSO_4 is similar to that of CaSO_4 . Here in this spectrum also there is one very strong and broad band at 1150 cm^{-1} , and there is one very weak band at 1015 cm^{-1} . There are three very strong, sharp, and well-defined absorption bands at 667, 616 and 598 cm^{-1} respectively. It seems that the absorption band at 616 cm^{-1} is showing the 6 coordination of Mg^{+2} by oxygen and sulphur. At 515 cm^{-1} there is one very weak absorption band. The stretching frequencies of XO_4 (X= divalent or trivalent metal ion) tetrahedra are higher than those of corresponding XO_6 octahedra.³ The substances having octahedral coordination absorbing the region round about 600 cm^{-1} range.⁴

In the spectrum (Fig. 1c) of MnSO_4 there is one valley in the region $1300\text{--}900\text{ cm}^{-1}$. The valley contains four absorption bands at 1200, 1135, 1050 and 995 cm^{-1} respectively. These bands are not so well-defined. Rest of the absorption bands lie in the region $700\text{--}450\text{ cm}^{-1}$. There are three strong and well-defined bands at 675, 665 and 620 cm^{-1} . Like calcium and magnesium sulphates, the absorption band at 620 cm^{-1} in the spectrum of MnSO_4 may be an indication that there is 6 coordination of Mn^{+2} by oxygen and sulphur. There is one strong, well-defined absorption band at 470 cm^{-1} which is absent in the spectra of CaSO_4 and MgSO_4 .

In the IR spectrum (Fig. 1d) of $\text{Al}_2(\text{SO}_4)_3$ there is a very strong valley in the region $1400\text{--}1050\text{ cm}^{-1}$. The valley contains several absorption bands. Among them the band at 1122 cm^{-1} is well-defined. There is one ill-defined band at 715 cm^{-1} . The three absorption bands at 685, 652 and 610 cm^{-1} respectively are all very strong and very well-defined. Here it appears that the absorption band at 610 cm^{-1} is the characteris-

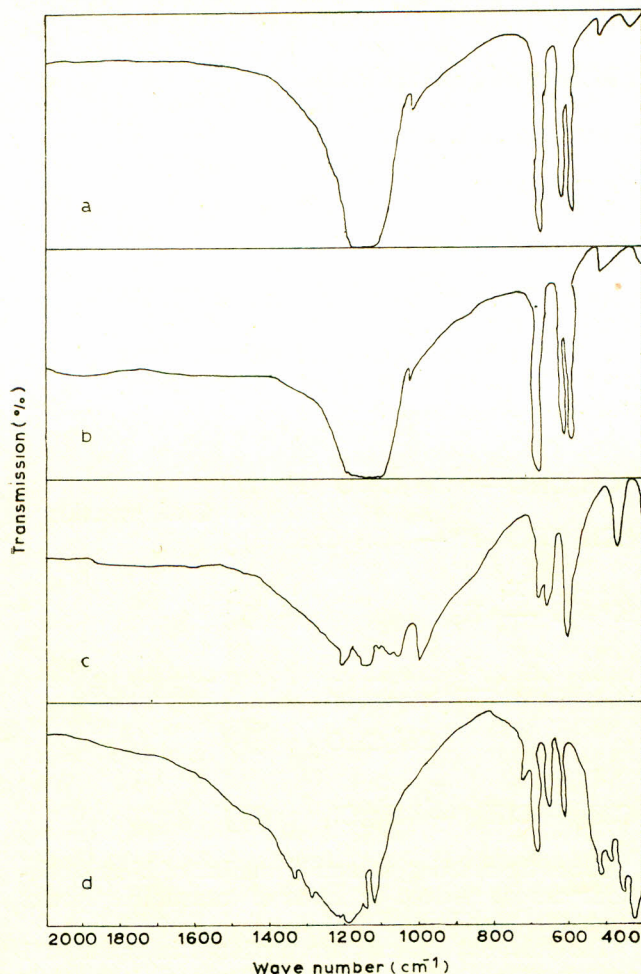


Fig. 1. IR spectra for (a) CaSO_4 , (b) MgSO_4 , (c) MnSO_4 and (d) $\text{Al}_2(\text{SO}_4)_3$.

tic band showing the 6 coordination of Al^{3+} by oxygen and sulphur. In the case of Al_2O_3 the shift in Al—O stretching frequencies from around 800 cm^{-1} in $\text{Ca}_3\text{Al}_2\text{O}_4$ to below 650 cm^{-1} in its hydration product indicates a change in the coordination of aluminium from 4 to 6.⁵ There are four absorption bands at 505 , 485 , 450 and 425 cm^{-1} respectively. These bands are not well-defined. In the spectrum of $\text{Cr}_2(\text{SO}_4)_3$,⁶ there is a valley in the region $1350\text{--}900\text{ cm}^{-1}$, this valley contains several absorption bands. They are rather well-defined. There is one very strong and very well-defined band at 705 cm^{-1} . At 670 cm^{-1} the band is well-defined. There is one weaker band at 625 cm^{-1} . The band at 600 cm^{-1} is very well-

TABLE 2. IONIC PROPERTIES OF THE CATIONS IN THE ABOVE SULPHATES.

Ions	Charge	Ionic radii (Å)
Ca^+	2	0.99
Mg^+	2	0.65
Mn^+	2	0.80
Al^+	3	0.50
Cr^+	3	0.63

Ionic radii correspond to 6 coordination

defined and very strong. It seems that the absorption band at 600 cm^{-1} is showing the 6 coordination of Cr^{3+} by oxygen and sulphur. In normal chromium oxide⁷ this characteristic band is at 640 cm^{-1} and in the case of delta chromium oxide⁸ the band is at 635 cm^{-1} . Perhaps due to some bonding with sulphur ion the band in the case of $\text{Cr}_2(\text{SO}_4)_3$ has been shifted to 600 cm^{-1} . There are three very well-defined absorption bands at 497 , 465 and 450 cm^{-1} respectively.

It is noteworthy here that in the region $500\text{--}400\text{ cm}^{-1}$ there is no absorption band in the spectra of CaSO_4 and MgSO_4 ; in the spectrum of MnSO_4 there is one, in the spectra of $\text{Al}_2(\text{SO}_4)_3$ and $\text{Cr}_2(\text{SO}_4)_3$ there are three absorption bands in each spectrum. Calcium and magnesium ions have different ionic radii, but their charge is the same. So size of the cation has no effect on the IR spectra of the compounds. On the other hand magnesium and chromium ions do not differ much in radii but they have different charges. As a result the structural complexity of MgSO_4 and $\text{Cr}_2(\text{SO}_4)_3$ is different. And hence their IR spectra have different number of absorption bands.

References

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