

INFRARED VIBRATIONAL SULPHATE BAND SHIFT CORRELATION IN ALKALINE SULPHATE MINERALS

L. A. GUIRGUIS

Nuclear Materials Corporation, Cairo, Egypt

ABSTRACT

Infrared spectra of anhydrite, celestine and barite minerals had been measured in the range 4000—400 cm^{-1} and discussed.

The shift of the SO_4^{2-} stretching modes to lower frequency on passing from anhydrite to barite minerals could be explained by the difference in the ionization potential of the cation.

INTRODUCTION

The absorption spectra of several sulphate minerals has been shown by WACHTER and LYON (1970). From a fundamental approach Ross (1972) has presented assignments of sulphate vibrations in anhydrous, hydrated, and hydroxyl containing sulphate minerals. Low frequency lattice vibrations for several sulphate minerals have been studied by MORANDAT *et al.*, (1966).

Differences of opinion exist between various authors dealing with the structural factors which influence molecular vibrations in sulphate minerals. Thus, ADLER and KERR (1965) have discussed the spectra of anhydrous sulphates MSO_4 ($\text{M} = \text{Sr, Ba, Pb}$) and band shifts of the stretching modes toward lower frequencies with increasing cation mass. On the contrary, the frequency shift of SO_4^{2-} stretching modes in a homologous hafnium and zirconium sulphate tetrahydrates is evidently caused by a slight change in ionic radius produced by cation substitution (ADLER, 1965). Lately POVARENNYKH (1978) summarized in a formula the main factors which affect the position of fundamental and characteristic absorption bands in IR spectra of minerals. These factors are as follows: valencies of cation and anion, coordination number of cation, interatomic distance cation—anion, the reduced mass of cation and the coefficient of relative bond strength.

The present work aims to correlate the value of the shift in absorption frequency observed in structurally related alkaline-earth minerals having a common functional ionic molecule.

MATERIALS AND METHOD

Three alkaline-earth sulphate minerals are collected from El Baharia area at the Western Desert of Egypt. These samples are anhydrite (CaSO_4), barite (BaSO_4), and celestine (SrSO_4), and denoted in this work by the letters A, B and C, respectively.

Each sample is prepared for infrared analysis using the pressed potassium bromide disc technique (FARMER, 1974). A known amount (2 mg) of the mineral was

carefully ground and mixed with 198 mg of spectroscopically pure dry potassium bromide for 10 sec in a vibrator, and this mixture pressed so as to give a disc of 12 mm diameter and about 0.2 mm thickness. The obtained KBr pellets were dried for four hours at 110 °C.

All spectra have been registered between 4000—400 cm^{-1} with a Perkin-Elmer 398 double-beam spectrophotometer. The maximum of absorption bands were reproducible within $\pm 0.5 \text{ cm}^{-1}$.

RESULTS AND DISCUSSION

IR spectra of the studied samples are shown in *Fig. 1*. The spectra are remarkably alike and appear to contain no anomalies except for small differences in the position of the absorption frequency.

In the spectrum of celestine, the strong frequencies at 1110, 1150 and 1200 cm^{-1} are due to triply asymmetric S-O stretching mode ν_3 in ionic sulphates while ν_1 occurs as a small ridge at 1015 cm^{-1} . Corresponding mode of barite are at 1100 1130 and 1190 cm^{-1} , respectively. Also its ν_1 occurs as a small ridge at 1020 cm^{-1} . The non degenerate S-O-S bending mode ν_4 occurs at 650 and 620 cm^{-1} in the spectrum of celestine. Corresponding value for barite occurs at 670 and 610 cm^{-1} .

The splitting of the fundamental sulphate stretching mode ν_3 in both the spectra of celestine and barite arises from the partial resolution of its triply degenerate vibrations of this mode, normally have exactly the same frequency when the SO_4^{2-} molecule is perfectly tetrahedron. However, they assume different frequencies if the molecular symmetry is lowered in conforming to the symmetry of the site. According to the relationships between molecular symmetry, site symmetry and vibrational activity of the sulphate ion, the three ν_3 bands and single ν_1 band for celestine and barite are indicative of C_{3v} or lower symmetry of the sulphate ion (ADLER, 1965).

In the spectrum of calcium sulphate (anhydrite) the bands due to ionic stretching vibrations ν_3 and its bending mode ν_2 and ν_4 differ in shape and/or position from that of celestine and barite. Thus the strong absorption band between 1120 and 1210 cm^{-1} are due to S-O stretching mode ν_3 in ionic sulphates, this band shows tendency of splitting to its three components at 1120, 1170 and 1210 cm^{-1} . The ν_1 mode occurs as small ridge at 1030 cm^{-1} . The O-S-O bending mode ν_4 occurs as a medium well defined peak at 670 cm^{-1} while ν_2 bending mode splits into two components at 610 and 559 cm^{-1} .

In going from one mineral to the other, there is a shift of 20 cm^{-1} between the ν_3 SO_4^{2-} stretching and from 20 to 10 cm^{-1} in the ν_4 SO_4^{2-} bending vibration. The following discussion is made in hopes of clarifying this problem.

All the studied sulphate minerals crystallise in the orthorhombic system. The space group for anhydrite is *Amma*, while that for barite and celestine is *Pnma*. Anhydrite got an anhydrite structure while celestine and barite got a barite structure. For anhydrite the *a*, *b* and *c* are 6.991, 6.996, 6.238 Å, while those for barite are 8.878, 5.450 7.152 Å, respectively, and for celestine 8.359, 5.352, 6.866 Å (DEER *et al.*, 1962).

It was found by VELDE and MARTINEZ (1981) that an increase in cell dimensions decreases the frequency vibrations of the Mg-OH vibrations in kaolinite. The value is about 7. cm^{-1} per 0.01 Å change in cell dimensions. However, in the present case there is no clear relation between the unit cell dimensions and the frequency shift.

Also, the shift to lower frequency observed for both ν_3 and ν_4 of the SO_4^{2-} ion on passing from anhydrite to barite minerals could not be explained by the difference

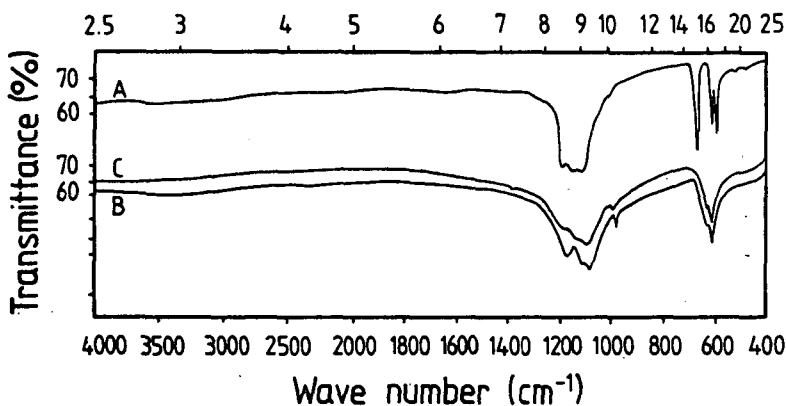


Fig. 1. Infrared absorption spectra of some alkaline earth sulphate minerals: anhydrite (A), barite (B) and celestine (C) in the range of 4000—400 cm^{-1}

in ionic radius (SHANNON and PREWITT, 1969) produced by Ca^{2+} (1.12 Å), Sr^{2+} (1.4 Å) and Ba^{2+} (1.60 Å) cation substitution, respectively. If the ionic radius of the cation were effective in producing a change in the frequency of the SO_4^{2-} vibration, the ν_3 and ν_4 mode would occur at higher rather than lower frequencies (ADLER, 1965).

The polarizing power of a cation is proportional to the ratio of its charge divided by its radius, and the charge of all the studied cations is +2 and their ionic radius appear to be a non functional property. Accordingly, the polarising power for Ca, Sr, and Ba is not useful in explaining the bathochromic shift, shown in the frequency, of the SO_4^{2-} vibration.

It is repeatedly mentioned in the literature (ADLER and KERR, 1965; FARMER 1974; SHANNON and PREWITT, 1969) that the frequency of valence stretching vibration varies inversely with the atomic mass. However, no evidence of a correlative shift obtained between the atomic weight of Ca^{2+} (40.08), Sr^{2+} (97.52), Ba^{2+} (137.34) and their sulphate frequencies.

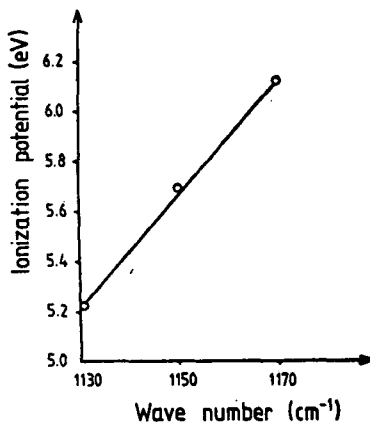


Fig. 2. Correlation of ionization potential and band frequency of SO_4^{2-} stretch ν_3 for anhydrite barite and celestine

The vibrational frequency is affected also by the force constant which was found to vary directly with electronegativity and inversely with the internuclear distance in some tectosilicates (MILKEY, 1960). The electronegativity values for Ca, Sr, Ba are 1.0, 1.0, and 0.9 respectively, as given by BLOSS (1971). It seems that the effect of the electronegativity change is not valid for the presently studied sulphate band shift.

According to POVARENENYKH (1978) the valency vibrations ν_3 in minerals shift to higher frequency with decreasing coordination number due to the increase in both atomic distances and quantum-mechanical interaction. The coordination number is 8 for anhydrite, 14 and 12 for celestine and barite (PHILLIPS and GRIFFEN, 1981). Definitely there should be another factor to account for the observed shift between celestine and barite, having the same coordination number.

Correlation of the ionization potential of the element atoms taken from OSLER (1972) appears to best account for the observed shifts shown in the frequency of the SO_4^{2-} vibration of the presently studied minerals. A relation which gives a straight line fits between the ionization potential of Ca (6.11), Sr (5.65), Ba (5.21) and the position of the sulphate vibration frequency ν_3 as shown in Fig. 2.

So the regularities in the frequency variation of this sulphate minerals could be attributed to the change in ionic character of the cation-oxygen bond with increasing covalency of the bonded polyatomic anions (SO_4^{2-}). This will possibly affects the relative bond strength between the adjacent atoms in their structure.

REFERENCES

- ADLER, H. H. (1965): Examination of mass radius effects, hydrogen bonding and splitting in infrared spectra of Zr-Hf homologs. *Amer. Miner.*, **50**, 1553—1562.
- ADLER, H. H. and KERR, P. F. (1965): Variation in IR spectra, molecular symmetry and site symmetry of sulphate minerals. *Amer. Miner.*, **50**, 132—147.
- BLOSS, E. D. (1971): *Crystallography and crystal chemistry*. Rinehart and Winston Inc., 194.
- DEER, W. A., HOWIE, R. A. and ZUSSMAN, J. (1962): *An introduction to the rock forming mineral*. John Wiley and Sons Inc., 462—472.
- EVANS, R. C. (1952): *An introduction to crystal chemistry*. Cambridge University Press. 258.
- FARMER, W. C. (1974): *The infrared spectra of minerals*. Adlard and Son Ltd. Dorking, Surrey. 12—15.
- MILKEY, R. G. (1960): Infrared spectra of some tectosilicates. *Amer. Miner.*, **45**, 990—1007.
- MORANDAT, J., LORENZELLI, V. and PAQUET, H. (1966): Far infrared absorption spectra of some metallic sulphates. *C. R. Acad. Sci., Paris, ser. A, B*, **263 B**, 697.
- OSLER, H. J. and LANGE, H. (1972): *Geochemical tables*. Elsevier Publ. Co., Amsterdam.
- PHILLIPS, W. R. and GRIFFEN, D. T. (1981): *Optical mineralogy of non-opaque minerals*. Freeman Co., San Francisco, 90.
- POVARENENYKH, A. S. (1978): The use of infrared spectra for the determination of minerals. *Amer. Miner.*, **63**, 956—959.
- ROSS, S. O. (1972): *Inorganic infrared and Raman-spectra*. McGraw-Hill, London, 414.
- SHANNON, R. D. and PREWITT, C. D. (1969): Effective ionic radii in oxides and fluorides. *Acta Cryst.*, **925—946**.
- VELDE, B. (1983): Infrared OH-stretch bands in potassic micas, talcs and saponites, influence of electronic configuration and site of charge compensation. *Amer. Miner.*, **68**, 1169.
- VELDE, B. and MARTINEZ, G. (1981): Effect of pressure on OH-stretching frequencies in kaolinite and ordered aluminous serpentine. *Amer. Miner.*, **66**, 196—200.
- WACHTER, B. G. and LYON, R. T. P. (1970): *Infrared mineralogical techniques for ore search*. Dept. Mineral. Eng. Stanford University, Stanford, California.

Manuscript received, 14 January, 1986.