

# FT-RAMAN STUDY OF THREE SYNTHETIC SOLID SOLUTIONS FORMED BY ORTHORHOMBIC SULFATES: CELESTITE-BARYTES, ANGLSITE-BARYTES AND CELESTITE-ANGLSITE

J.M. Alía<sup>1\*</sup>, H.G.M. Edwards<sup>2</sup>, S. López-Andrés<sup>3</sup>, P. González-Martín<sup>3</sup>, F.J. García-Navarro<sup>1</sup> and H.R. Mansour<sup>2</sup>

(1) E.U.I.T.A. - Dpto. de Química Física, Universidad de Castilla-La Mancha, 13071 Ciudad Real, Spain.

(2) Chemistry and Forensic Sciences, University of Bradford, Bradford BD7 1DP, United Kingdom

(3) Dpto. de Cristalografía y Mineralogía, Fac. de Geología, Universidad Complutense, 28071 Madrid, Spain

Our research group has recently undertaken the vibrational study of several solid solutions of geochemical and environmental interest [1,2]. In the present work, three different solid solutions whose end-members are the orthorhombic sulfates celestite ( $\text{SrSO}_4$ ), barytes ( $\text{BaSO}_4$ ) and anglesite ( $\text{PbSO}_4$ ) are studied using FT-Raman spectroscopy. The synthesis of these compounds was carried out by the method of Kornicker *et al.* [3] adding the corresponding cationic aqueous solutions (as nitrates) to a 6 M solution of sulfuric acid at room temperature. With this procedure, the precipitation of lead complex hydroxysalts is avoided.

Samples were analysed by powder X-ray diffraction and the crystal-structure cell dimensions were refined. The different unit cell parameters change linearly with the chemical composition of the solids expressed as mole fraction. Thus, Vegard's law is obeyed and the precipitation process is probably ideal because the chemical composition of the solid is identical to that corresponding with the mother solution. Figure 1 shows the linear plot of the unit cell volume against the composition of the samples. Similar results are obtained plotting the unit cell dimensions  $a$ ,  $b$  and  $c$ .

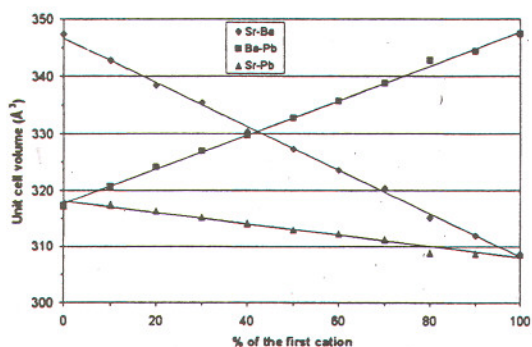


Fig. 1. Evolution of the unit cell volume ( $\text{Å}^3$ ) plotted against the composition of the solid solutions.

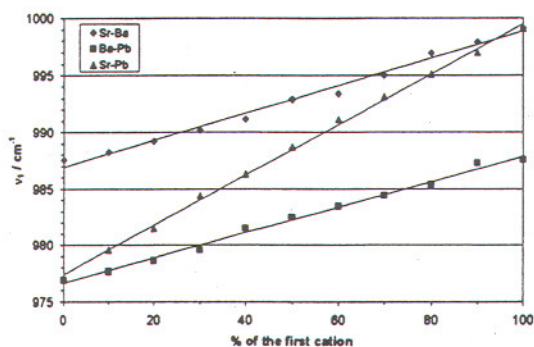


Fig. 2. Evolution of sulfate anion  $\nu_1(A_1)$  wavenumber plotted against the composition of the solid solutions.

Sulfate anion internal modes have been examined in detail by means of band-shape analysis and component fitting procedures. The symmetric stretching mode  $\nu_1(A_1)$

changes its wavenumber position linearly with the cationic composition of the samples, as can be observed in Figure 2, which further confirms the ideal character of the solid solutions studied. The corresponding full-width at half-height is strongly increased in the central components of the different solid solutions which can be understood as an effect of the positional disorder induced by random cationic substitution. Similar results are observed in the symmetric bending mode,  $\nu_2(E)$ .

The study of the low frequency spectral region permits to differentiate the vibrational behaviour of anglesite ( $\text{PbSO}_4$ ) from that corresponding to the alkaline-earth ( $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ ) sulfates. This finding is discussed in terms of the very different polarising power of  $\text{Pb}^{2+}$  and is parallel to that reported in the carbonates of these metal ions [1,4].

### References

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