

# STUDY OF MIXED CRYSTALS OF THE BARIUM-STRONTIUM SULPHATE SYSTEM USING INFRARED SPECTROSCOPY AND X-RAY DIFFRACTION

I. KŘIVÝ, J. MORAVEC and O. VOJTĚCH

*Institute of Nuclear Research, 250 68 Prague - Řež*

Received March 7th, 1974

The  $\text{BaSO}_4$ — $\text{SrSO}_4$  mixed crystals were prepared by the coprecipitation and heat treatment of mixtures of both components. In the heat-treated samples the distribution of alkali earth cations was much more homogeneous as compared with that of coprecipitated samples. Infrared frequency shifts of the  $\text{SO}_4^{2-}$  absorption bands are discussed as a function of composition of the crystals. The  $\nu_1(\text{SO}_4^{2-})$  vibration was found to be least sensitive to the homogeneity of the crystals. The behaviour of the  $\nu_4$  vibration bands agreed with theoretical predictions. The X-ray powder diffraction revealed that the unit cell parameters of the mixed crystals increase with rising  $\text{BaSO}_4$  content according to the Vegard's rule.

In last years, both the sorption properties and the structure characteristics of binary systems of alkali earth sulphates have been studied in our laboratory. A special attention has been paid to the formation of metastable  $\text{BaSO}_4$ — $\text{CaSO}_4$  mixed crystals with structure of the barite and also the anhydrite types<sup>1-3</sup>. The crystals possessing the barite-type structure proved to be efficient sorbents for selective capture and fixation of  $^{90}\text{Sr}$  from liquid radioactive wastes.

In this paper, the experimental results of a study of  $\text{BaSO}_4$ — $\text{SrSO}_4$  mixed crystals are given, indicating the important role of thermal treatment in homogenizing the crystals with respect to  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  distributions. The effect of a long-time contact of the crystals with redistilled water is also briefly discussed.

## EXPERIMENTAL

The samples of the  $\text{BaSO}_4$ — $\text{SrSO}_4$  mixed crystals containing 20, 40, 60, and 80 mol %  $\text{BaSO}_4$  were prepared by coprecipitation<sup>4,5</sup> as well as by a thermal treatment of mixtures of the pure components (solid state diffusion), the pure sulphates being synthesized by precipitation.

Concerning the heat-treatment, the mixtures of  $\text{BaSO}_4$  and  $\text{SrSO}_4$  were homogenized by grinding them in a mechanized agate mortar and pressed into tablets of a cylindrical form. The tablets were heated in an electrical resistance furnace at about 1200°C for 20 min and afterwards slowly cooled to room temperature. In addition to densification, the phase transition to a high-temperature modification also occurred during the heating-up. The thermal cycle described was repeated ten times to obtain samples with a sufficiently homogeneous distribution of both alkali earth cations. The degree of the tablet homogeneity was checked by microprobe analysis.

Small portions ( $\approx 300$  mg) of the samples prepared by both methods in a suspension with 1 ml redistilled water were sealed in glass ampoules and shaken for 43 days. After removing water and washing with ethanol and diethyl ether, the samples were dried to a constant weight. These particular samples, subjected to long-time contact with water, were designated as "equilibrium" ones.

The infrared absorption spectra ( $1300-200$   $\text{cm}^{-1}$ ) were measured, after grinding  $\approx 10$  mg sample in Nujol ( $\approx 50$  mg), in a cell provided with CsI windows, the path-length being  $0.02$  mm. A Perkin-Elmer double-beam grating spectrometer, model 225, was used.

The samples for X-ray study were ground in an agate mortar and sealed in Lindemann-glass capillaries (inside diameter  $0.3$  mm). Powder patterns were made at  $25 \pm 1^\circ\text{C}$  in a  $114.6$  mm Debye-Scherrer camera, adapted for an asymmetric film loading, by using filtered  $\text{CoK}\alpha$  radiation ( $\lambda = 1.79021$  Å). No internal standard was used for defining  $2\theta$  scale. All the exposures were taken at strictly constant geometrical conditions so that a direct comparison of diffraction line widths could be made. Positions of the diffraction lines were measured with an overall accuracy of  $0.05$  to  $0.1^\circ 2\theta$  and corrected for film shrinkage wherever possible. For calculation of the unit cell parameters and their standard deviations, the Cohen least squares method<sup>6</sup> with the Nelson-Riley extrapolation function<sup>7</sup> and unit statistical weights of the individual reflections were applied. All the calculations involved were performed with an IBM 7040/7044 digital computer.

## RESULTS AND DISCUSSION

In the infrared spectra, essentially seven absorption bands of different intensities, excluding faint outlines of very weak bands in the region of  $\nu_2(\text{SO}_4)$  vibration and a mostly poorly resolved shoulder at  $1220-1245$   $\text{cm}^{-1}$ , were observed, corresponding to  $\nu_1$ ,  $\nu_3$  and  $\nu_4$  vibrations\* of the  $\text{SO}_4^{2-}$  anion in the barite-type compounds and, probably, to metal-oxygen vibration around  $\approx 200$   $\text{cm}^{-1}$  (Fig. 1). Regarding structure-similarity of the pure sulphates, no qualitative changes could be expected manifesting themselves through a variation in number of absorption bands as observed recently in the spectra of the metastable  $\text{BaSO}_4$ - $\text{CaSO}_4$  mixed crystals<sup>2,3</sup>. Only frequency shifts proportional to changes in the cation-induced crystal field should be found.

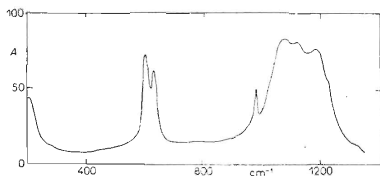


FIG. 1

The IR Absorption Spectrum of the  $\text{BaSO}_4$ - $\text{SrSO}_4$  Mixed Crystals, in Nujol Mull (Schematic)

\* Conventional designation of vibrations for the  $T_d$  point group is accepted.

For the samples of all series, the frequency of a sharp band of the totally symmetric stretching vibration  $\nu_1$  (forbidden in the infrared for the  $T_d$  point group) was found to evenly decrease over range  $993-981\text{ cm}^{-1}$  on going from the pure  $\text{SrSO}_4$  to the pure  $\text{BaSO}_4$  crystals. As compared with the behaviour of other vibrations, the  $\nu_1$  vibration is evidently the least sensitive to the homogeneity level of the crystals studied.

A similar trend was also observed for other absorption bands, the frequencies of which decreased with rising  $\text{BaSO}_4$  content as follows:  $\nu_3$ ,  $1085 \rightarrow 1065$ ,  $1128 \rightarrow 1113$ ,  $1192 \rightarrow 1169$ , shoulder,  $1243 \rightarrow 1223$ ;  $\nu_4$ ,  $609 \rightarrow 606$ ,  $640 \rightarrow 632\text{ cm}^{-1}$ . The behaviour of  $640 \rightarrow 632\text{ cm}^{-1}$  band of  $\nu_4$  showed a disagreement with the data of Steger and Danzer<sup>4</sup>, who found no shift of the band in their IR spectra. The shift determined experimentally in this work agrees well with theoretical predictions<sup>8</sup>. Concerning  $\nu_3$  and  $\nu_4$ , the concentration dependence of their band maxima appeared to be rather ambiguous unlike the  $\nu_1$  band. Relatively large differences were obtained between the spectra of the samples prepared by thermal cycling and

TABLE I  
Unit Cell Parameters  $a$ ,  $b$ ,  $c$  of the  $\text{BaSO}_4$ - $\text{SrSO}_4$  Mixed Crystals ( $\text{\AA}$ )<sup>a</sup>

BaSO <sub>4</sub> mole %	Coprecipitated Samples			Heat Treated Samples		
	$a$	$b$	$c$	$a$	$b$	$c$
Before water treatment						
0	$8.37 \pm 1$	$5.35 \pm 1$	$6.87 \pm 1$	$8.351 \pm 9$	$5.340 \pm 7$	$6.857 \pm 8$
20	$8.41 \pm 2$	$5.36 \pm 2$	$6.90 \pm 2$	$8.46 \pm 1$	$5.364 \pm 9$	$6.92 \pm 1$
40	$8.51 \pm 3$	$5.38 \pm 2$	$6.95 \pm 2$	$8.57 \pm 1$	$5.390 \pm 6$	$6.984 \pm 6$
60	$8.68 \pm 3$	$5.42 \pm 2$	$7.06 \pm 3$	$8.67 \pm 1$	$5.412 \pm 9$	$7.042 \pm 9$
80	$8.81 \pm 2$	$5.43 \pm 1$	$7.08 \pm 2$	$8.78 \pm 1$	$5.434 \pm 6$	$7.100 \pm 7$
100	$8.87 \pm 2$	$5.45 \pm 1$	$7.14 \pm 1$	$8.853 \pm 9$	$5.448 \pm 8$	$7.134 \pm 9$
After water treatment <sup>b</sup>						
0	$8.34 \pm 1$	$5.34 \pm 1$	$6.86 \pm 1$	$8.349 \pm 7$	$5.340 \pm 5$	$6.855 \pm 7$
20	$8.39 \pm 3$	$5.37 \pm 2$	$6.89 \pm 2$	$8.47 \pm 2$	$5.36 \pm 1$	$6.93 \pm 1$
40	$8.54 \pm 4$	$5.38 \pm 2$	$6.95 \pm 2$	$8.55 \pm 2$	$5.39 \pm 1$	$6.98 \pm 1$
60	$8.64 \pm 5$	$5.39 \pm 3$	$6.99 \pm 3$	$8.65 \pm 2$	$5.41 \pm 1$	$7.03 \pm 1$
80	$8.79 \pm 4$	$5.41 \pm 1$	$7.06 \pm 2$	$8.77 \pm 2$	$5.42 \pm 1$	$7.08 \pm 2$
100	$8.85 \pm 2$	$5.43 \pm 1$	$7.14 \pm 1$	$8.89 \pm 1$	$5.44 \pm 1$	$7.16 \pm 1$

<sup>a</sup> Short abbreviations for errors are used, e.g.  $8.37 \pm 1$  instead of  $8.37 \pm 0.01$ . <sup>b</sup> The so-called "equilibrium forms".

those of the remaining three series, the latter exhibiting a considerably irregular decrease in the  $\nu_3$  and  $\nu_4$  frequencies with increasing  $\text{BaSO}_4$  content in the mixed crystals. The maximum of the band assigned ordinarily to the metal-oxygen vibration (for  $\text{SrSO}_4$  around  $215 \text{ cm}^{-1}$ ), displayed only a small shift (by a few  $\text{cm}^{-1}$  units) to lower frequencies when moving from the pure  $\text{SrSO}_4$  to the mixed crystals containing up to 40–60 mol %  $\text{BaSO}_4$ . For higher  $\text{BaSO}_4$  contents, however, the band maximum appeared outside the instrument range.

Aging of samples in aqueous suspension made the frequency shifts of absorption bands of the coprecipitates more even whereas for the samples prepared by thermal treatment the effect was of an opposite character.

X-ray diffraction data revealed the presence of a single phase with the barite-type structure in all the samples studied. The calculated unit cell parameters together with their standard deviations are summarized in Table I. The parameters of the mixed crystals of all the four series increased with rising  $\text{BaSO}_4$  content according to the Végard's rule. Small deviations from the rule, observed largely for the samples prepared by coprecipitation, proved to be insignificant from the statistical point of view.

Starting from a visual estimate of diffraction line widths, the following relations could be established: 1) The widths of a given line decrease in the sequence: coprecipitate, equilibrated coprecipitate, heat-treated sample, and its equilibrium form over the whole concentration range investigated, the differences in the widths between the coprecipitated samples and their equilibrium forms being within an experimental error. 2) For all the sample series, except the samples synthesized by thermal cycling, the widths of powder lines of the mixed crystals considerably exceeded those of the pure sulphates. The validity of the relation 1) is first related to differences in crystallite size of the samples under consideration. A marked broadening observed for the samples prepared by precipitation as well as for the equilibrium forms of both types, including the pure sulphates, indicates that mean crystallite size of the samples lies somewhere below  $10^{-5} \text{ cm}$ . On the other hand, the powder patterns of the samples synthesized by thermal cycling, exhibiting extremely sharp diffraction lines with small discontinuities, show the presence of a significant portion of crystallites with a mean size  $\geq 10^{-4} \text{ cm}$ . As seen from the relation 2), the line broadening observed in the case of the mixed crystals, in contrast to the pure components, is at least partially due to lattice distortions induced owing to an inhomogeneous distribution of  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  cations.

A direct comparison of diffraction profiles using a Zeiss microphotometer, model G III, revealed that the line widths of the mixed crystals prepared by thermal cycling coincide within the experimental error with those of the thermally treated pure sulphates. In the special case, the widths can be regarded as being essentially determined by instrumental aberrations themselves and, therefore, the heat treatment

applied leads not only to a crystallite growth but also to removing a substantial part of lattice distortions (internal stress).

Starting from the results of both IR spectroscopy and X-ray diffraction, the conclusion was made that the distribution of alkali earth cations in the heat-treated samples is much more homogeneous as compared with that for the coprecipitated samples and, moreover, very close to a perfectly random distribution. The presence of lattice distortions in the mixed crystals prepared by coprecipitation becomes evident from irregular frequency shifts in the IR spectra and from a significant internal-stress contribution to the total broadening of powder lines in the X-ray patterns.

Aging processes taking place during a long-time contact of the mixed crystals (prepared by coprecipitation) with redistilled water aid an elimination of the lattice distortions and, consequently, a homogenizing the samples but the effect of the processes is apparently less significant than that of the thermal treatment. However, when "equilibrating" the samples synthesized by thermal cycling, a simultaneous reduction of both the crystallite size and the homogeneity level probably occurs.

Sorption studies performed using the samples of all the four types<sup>9</sup> confirmed the important role of homogeneity of the mixed crystals with respect to  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  distributions in separating  $^{90}\text{Sr}$  from liquid radioactive wastes.

#### REFERENCES

1. Vojtěch O., Moravec J., Volf F., Dlouhá M.: *J. Inorg. Nucl. Chem.* **32**, 3725 (1970).
2. Moravec J., Vojtěch O.: Report ÚJV 2596-Ch, Inst. Nucl. Res., Prague-Řež 1971.
3. Vojtěch O., Moravec J., Křivý I.: *J. Inorg. Nucl. Chem.* **34**, 3345 (1972).
4. Steger E., Danzer K.: *Ber. Bunsenges. Phys. Chem.* **88**, 635 (1964).
5. Strassman F., Walling E.: *Ber.* **71**, 4 (1938).
6. Cohen M. U.: *Rev. Sci. Instr.* **6**, 321 (1935).
7. Nelson J. B., Riley D. P.: *Proc. Phys. Soc. (London)* **57**, 160 (1945).
8. Britzinger H., Hester R. E.: *Inorg. Chem.* **5**, 980 (1966).
9. Vojtěch O., Selecká H.: Report ÚJV 2820-Ch, Inst. Nucl. Res., Prague-Řež 1972.