

VIBRATIONAL SPECTRA OF SOLID SOLUTIONS OF BARIUM AND CALCIUM SULPHATES*

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The Raman and far infrared spectra of solid solutions of barium and calcium sulphates have been studied for various compositions of these solutions, prepared by a thermal treatment of their mixtures. It was confirmed that for certain concentration regions the isomorphism of the two sulphates is enforced.

Selective sorbents for the removal of radioactive strontium from waste solutions have been prepared in the Nuclear Research Institute, Prague - Řež, by a special thermal treatment of BaSO_4 and CaSO_4 mixtures^{1,2}. In connection with the studies of the sorption ability the structure of these sorbents has been studied using their infrared spectra³⁻⁵. It was found that for certain concentration regions these sulphates adopt alternatively the structure of its partner. Similar studies have been done also with the solid solutions SrSO_4 - CaSO_4 ⁶ and BaSO_4 - SrSO_4 ⁷ and at the present time the investigations of the systems MgSO_4 - SrSO_4 , MgSO_4 - CaSO_4 , and PbSO_4 - CaSO_4 are under progress (the last system was prepared by coprecipitation).

As these solid solutions have so far been spectroscopically studied only by their infrared spectra, in which only 2 from the 4 vibrational modes of the isolated SO_4^{2-} ion are active, an attempt has been made in this study to find out whether the structural changes in these systems can be unambiguously confirmed also by their Raman spectra, in which all the fundamental frequencies of SO_4^{2-} are active. Also the far infrared spectra of these samples have been measured.

EXPERIMENTAL

The solid-solution samples of BaSO_4 - CaSO_4 , containing 10, 40, and 70 mol per cents of BaSO_4 , respectively, have been prepared as previously described⁴. The BaSO_4 concentrations have been chosen so that the samples present a good representation of all structural types of these solid solutions. The preparation consists of a ten-fold heating of the pure compound mixtures to 1200°C and of their slow cooling down to the room temperature. During the eleventh repetition of this

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cycle the samples were rapidly cooled by immersion into liquid nitrogen. The samples of pure CaSO_4 and BaSO_4 were subjected to the same thermal treatment.

The Raman spectra of powdered samples were measured with a CODERG PHO spectrometer, Model 52, using the excitation by an Ar-Kr laser.

The infrared spectra in the $400\text{--}50\text{ cm}^{-1}$ region were measured by a RIIC FS-620 Fourier spectrometer and by a Perkin-Elmer (Hitachi) FIS-3 spectrometer, using the dispersion of homogenized powdered samples in polyethylene films.

RESULTS AND DISCUSSION

The SO_4^{2-} Raman-band wavenumbers and their assignments are given in Table I. It is evident from these spectra that in the studied samples the SO_4^{2-} symmetry is decreased due to the interaction of the anion with the crystal field so that the vibrations ν_2 , ν_3 , and ν_4 , degenerate for an isolated SO_4^{2-} , are split by lifting this degeneration. In the region of the ν_2 and ν_4 vibrations the expected number of bands, *i.e.* 2 for the doubly degenerate vibration ν_2 and 3 for the triply degenerate vibration ν_4 , has been found (except of the sample containing 40 mol % BaSO_4); from the total 5 bands observed in the region of the triply degenerate vibration ν_3 in the BaSO_4 sample one, evidently, could be attributed to the harmonic or combination frequency. The bands ν_3 and ν_4 , both active also in the infrared spectrum, have substantially lower intensities in the Raman spectra, and namely the ν_3 bands are ordinarily very weak. Practically identical spectra have been obtained for the thermally treated sample of BaSO_4 and for the untreated one supplied by Merck.

The spectra of the pure components BaSO_4 (the space group $Pnma = D_{2h}^{16}$) and CaSO_4 (the space group $Cmcm = D_{2h}^{17}$) differ substantially in practically all regions of the fundamental frequencies of SO_4^{2-} . The ν_1 bands differing by 30 cm^{-1} , the ν_4 bands with the highest frequencies (648 and 678 cm^{-1}) differing by the same difference, and finally the two separate ν_2 bands in CaSO_4 against the doublet in BaSO_4 are the most evident differences between these spectra. From Table I it can be shown that the spectrum of the sample with 40% BaSO_4 corresponds to a mixed structure of the two pure compounds (two bands of the ν_1 vibration, each of them having its frequency nearer to one of the components; one single broad band in the region of ν_3).

Spectrum of the sample with 10% BaSO_4 is — regardless of small frequency shifts of bands — practically identical with the spectrum of CaSO_4 . It might be assumed that the two spectra seem identical only because the solid solution contains such a small amount of BaSO_4 that this compound cannot cause any characteristic absorptions (*e.g.*, its second band in the ν_1 region or the corresponding changes in other spectral regions). However, the results of ref.⁹ contradict to this assumption as the comparison of the infrared spectra of solid solutions with those of mere $\text{BaSO}_4\text{--CaSO}_4$ mixture in the whole concentration region revealed that the characteristic bands of 10 mol % BaSO_4 or CaSO_4 admixtures appear quite clearly and unambiguously. Similarly,

the Raman spectra of the sample with 70% BaSO₄ and of the sample of pure BaSO₄ can be assumed as nearly identical in spite of the frequency shifts of several bands that are higher than those observed for the previous sample. The direction of the frequency shifts of the bands in the spectra of this sample and of the previous sample if compared with the spectra of pure BaSO₄ and CaSO₄, respectively, correspond to the differences in the structure of these solid solutions and of their pure components. In spite of the evident adaptation of the sample with 70% BaSO₄ to the structure of the barite group (*Pnma*) and of the sample with 10% BaSO₄ to the CaSO₄ structure (*Cmcm*) the sulphate groups in solid solutions appear in different force fields if compared with the pure components due to the partial substitution of the smaller Ca atom by a larger Ba atom and *vice versa*.

The far infrared spectra obtained using the interference spectrometer differed slightly from those measured by the absorption spectrometer, namely in the wavenumbers of several bands. In the region from 100 to 400 cm⁻¹ the metal-sulphate group bond and the lattice vibrations of the compounds under study are observed. The spectra of pure CaSO₄ and BaSO₄ differed quite substantially. In the spectrum of CaSO₄ we have found a broad band with the maximum at ~270 cm⁻¹, the bands at 191 and 175 cm⁻¹ and shoulders at 168 and 108 cm⁻¹, while in the BaSO₄ spectrum we have observed bands at 200 (with a shoulder at 215), 168, 144, 119, 94 (with

TABLE I

Wavenumbers (in cm⁻¹) of the SO₄²⁻ Bands in Raman Spectra and their Assignments

The vibrations were assigned following the approach usual for the isolated SO₄²⁻ (point group *T_d*)⁸; the abbreviations used mean: very strong (vs), strong (s), weak (w), shoulder (sh), broad (b).

Sample	ν_2	ν_4	ν_1	ν_3
CaSO ₄ , thermally treated	419	612	630	1 019 (vs) 1 114 (w) 1 132
	502	678		1 163 (w)
Solid solution (10 mol % BaSO ₄)	419	611	629	1 017 (vs) 1 113 (sh) 1 127
	499	676		1 160 (w)
Solid solution (40 mol % BaSO ₄)	435 (w) 457	627 (b) 655 (w)	998 (vs)	1 130 (b)
	537 (w)	670 (sh)	1 015 (s)	
Solid solution (70 mol % BaSO ₄)	457	622	637 (w)	995 (vs) 1 086 (w) 1 107 (w)
	462 (sh)	652		1 146 (w) 1 176 (w)
BaSO ₄ , thermally treated	454	619	632 (w)	990 (vs) 1 085 (w) 1 105 (w)
	463	649		1 142 1 168 (w)
BaSO ₄ (Merck) untreated	453	618	631 (w)	989 (vs) 1 084 (w) 1 105 (w)
	462	648		1 140 1 167 (w)

a shoulder at 100), and 82 cm^{-1} (with a shoulder at 70 cm^{-1}). The solid solution spectrum of the sample with 10% BaSO_4 was practically identical with that of pure CaSO_4 and no bands in the region $80\text{--}120\text{ cm}^{-1}$, that are characteristic of BaSO_4 , have been observed. In the spectrum of the sample with 40% BaSO_4 only a very broad band appeared with a weakly outlined doublet at 195 and 250 cm^{-1} that indicates a rather high degree of a chaotic arrangement of the crystal lattice of the sample. The spectrum of the sample with 70% BaSO_4 is composed of two broad bands that are shifted towards the long-wave region (if compared with the previous spectra) and they practically form an envelope of the two groups of bands of the pure BaSO_4 spectrum.

The comparison of the observed Raman spectra confirms the results of the infrared studies, namely that during the thermal treatment of the $\text{BaSO}_4\text{--CaSO}_4$ mixtures the isomorphism of these sulphates is enforced in spite of the fact that the natural samples of these two sulphates are not isomorphous. At low concentrations of CaSO_4 the solid solutions under study have the structure of the barite group and *vice versa*. This conclusion is borne out also by the far infrared spectra, regardless of the more inhomogeneous force fields and of the more perturbed microstructure (if compared with the SO_4 group in the medium infrared region) that are revealed by these spectra and that cause much broader, diffuse bands so that these spectra are not so characteristic.

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