

IR spectroscopic characterization of tetrabasic lead sulphate

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The knowledge of the physicochemical properties of the basic lead sulphates is of great interest from the point of view of the technology of lead-acid batteries.

Crystallographic data for the tetrabasic lead sulphate, $\text{PbSO}_4 \cdot 4\text{PbO}$, have recently been reported [1] and as it is also possible to obtain this phase in a very pure form [1, 2], we have investigated its infrared (IR) spectrum in order to obtain an insight into the spectroscopic behaviour of such materials and also to facilitate their identification by this method.

Pure samples of $\text{PbSO}_4 \cdot 4\text{PbO}$ have been obtained in the form of microcrystalline powders, by the reaction of PbO with diluted H_2SO_4 (specific gravity = 1.4 g cm^{-3}) at 80°C during 4 to 6 h and subsequent heating of the product at 550°C [2]. The samples were characterized by their powder diagram [1].

The IR spectra were recorded with a Perkin Elmer 580 B-spectrophotometer using the KBr pellet technique. The spectrum of one of the prepared $\text{PbSO}_4 \cdot 4\text{PbO}$ samples is shown in Fig. 1.

As $\text{PbSO}_4 \cdot 4\text{PbO}$ belongs to the monoclinic system, space group $P2_1/c$ and $Z = 4$, the ideally tetrahedral SO_4^{2-} ions are located in the crystal on the general C_1 positions. Therefore, according to a site symmetry analysis [3, 4], a total activation and a complete removal of degeneracies of the vibrational modes of the tetrahedral ion are expected. These predictions are fully confirmed both in the stretching and bending regions of the sulphate vibrations.

The antisymmetric stretching vibration ν_3 appears to be split into four components, located at 1051, 1077, 1105 and 1135 cm^{-1} . The fact that there is one band more than those predicted by the site symmetry analysis can be explained by the activation of a combination mode or by the contribution of dynamic crystal field effects, which originate in the interaction between the anions in the unit cell.

The symmetric stretching vibration ν_1 , which is also activated in the crystal, is clearly seen as a sharp band at 965 cm^{-1} .

In the bending region, the antisymmetric deformation mode ν_4 appears as a well defined doublet at 609 to 600 cm^{-1} , whereas the third expected component can be seen as a weak shoulder at 614 cm^{-1} . The symmetric bending vibration ν_2 , which usually lies around 450 cm^{-1} [3] is overlapped by the strong band multiplet lying below 500 cm^{-1} (peaks at 483, 445 (sh), 430 (sh), 372, 341 (sh), 290 and 278 (sh) cm^{-1}). This last multiplet is surely associated with PbO modes, as has been shown in our former study of the phases $\text{V}_2\text{O}_5 \cdot 4\text{PbO}$ and $\text{V}_2\text{O}_5 \cdot 8\text{PbO}$, which present strong absorptions in the same spectral range [5]. Pure PbO also possesses strong bands in this region [6].

Comparison of the $\text{PbSO}_4 \cdot 4\text{PbO}$ spectrum and that of pure PbSO_4 [7] shows a slight displacement of all bands to lower wave numbers in the case of the basic sulphate.

As it has been shown by Dapo [2], basic lead sulphates always retain some amount of carbon dioxide and water. He postulates that, in general, the composition of tetrabasic lead sulphate may be formulated as $(\text{PbSO}_4)_{1-x}(\text{PbCO}_3 \cdot \text{H}_2\text{O})_x \cdot 4\text{PbO}$. The CO_2 and H_2O can be eliminated by the heating process at 550°C [2].

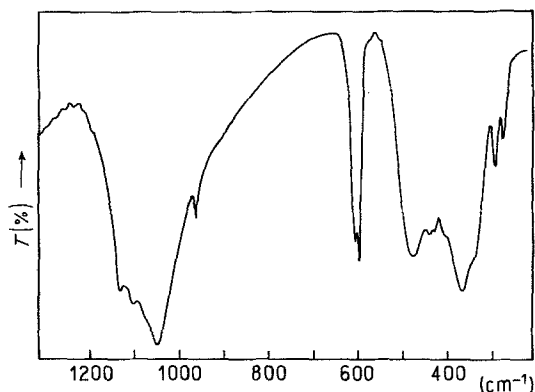


Figure 1 Infrared spectrum of $\text{PbSO}_4 \cdot 4\text{PbO}$.

IR spectra of samples not subjected to the heat treatment are slightly more diffuse than those of pure $\text{PbSO}_4 \cdot 4\text{PbO}$. The sulphate bands appear at 1132, 1095, 1040, 962 and $610/601\text{ cm}^{-1}$, i.e. slightly displaced in relation to those of the pure material. The disappearance of one of the ν_3 components in the carbonated samples, strongly supports the idea that the origin of the fourth band in this region, in the case of pure $\text{PbSO}_4 \cdot 4\text{PbO}$, must be a dynamic coupling effect. As the CO_3^{2-} ions occupy a part of the SO_4^{2-} positions in the lattice, they cause a diminution of the SO_4/SO_4 interactions and partially suppress this coupling effect. The spectrum also shows two of the carbonate bands (1400 cm^{-1} , strong and broad; 685 cm^{-1} , medium and well defined), whereas the water bands are very weak and not clearly defined.

Finally, it is very interesting to comment that when pure $\text{PbSO}_4 \cdot 4\text{PbO}$ samples are maintained for some weeks in direct contact with air, they absorb newly atmospheric CO_2 , which is easily detected by the appearance of the two characteristic carbonate absorption bands. But the incorporated CO_2 can be eliminated by a short reheating of the sample at 550°C .

This study has also shown that the spectroscopic behaviour of tetrabasic lead sulphate is in good agreement with the theoretical expectations based on a site symmetry analysis. The IR spectrum, which is very characteristic and repro-

ducible, shows two typical regions, one dominated by the internal SO_4^{2-} vibrations (1200 to 600 cm^{-1}) and the other by PbO modes (550 to 250 cm^{-1}). Also, carbonate impurities, which can usually be present in these materials, are easily detected by their strong IR absorptions at 1400 and 685 cm^{-1} .

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