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Vibrational spectrum of Pb_2CrO_5

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The phase of Pb_2CrO_5 composition is a ceramic material with dielectric [1] properties and probably with interesting optical characteristics [2]. It can also be formulated as $PbCrO_4 \cdot PbO$, which reveals a structural analogy with lanarkite, $PbSO_4 \cdot PbO$, and $PbMoO_4 \cdot PbO$ [3].

In order to achieve an advance in the spectroscopic characterization of materials of this type, we have investigated the infrared and Raman spectra of this phase.

Very pure samples of $PbCrO_4 \cdot PbO$ have been obtained by solid-state reaction of stoichiometric PbO/Cr_2O_3 mixtures which were sintered in air at 650° C for 2 h, after a previous calcination at 500° C [2]. Their purity was checked by chemical analysis and X-ray diffractometry.

The infrared spectra were recorded with a Perkin Elmer 580 B spectrophotometer, using the KBr-pellet technique. The Raman spectra were registered with a Spex-Ramalog 1403 double-monochromator spectrometer, using the 647.1-nm line of a krypton laser as the excitation source.

The spectra obtained are shown in Fig. 1:

The material is monoclinic, space group $C2/m$ and $Z = 4$ [2]; the ideally tetrahedral CrO_4^{2-} anions are located on C_s positions in the crystal lattice. Therefore, and according to a site symmetry analysis [4, 5], a total activation and a complete removal of degeneracies of the vibrational modes of the tetrahedral ions are expected. These predictions are in good agreement with the observed spectral data.

In the stretching region, the main infrared band, centred at 850 cm^{-1}, is very broad and poorly defined. Nevertheless, some other details can be observed, as weak shoulders at 885 and 835 cm^{-1}. These three absorptions correspond to the expected components of the antisymmetric-stretching mode ν_3 and their Raman counterparts are located at 849 (which probably involves the two higher energy phonons) and 838 cm^{-1}. The strongest Raman line, placed at 826 cm^{-1} can be unambiguously assigned to the symmetric-stretching mode ν_1. This mode is not observed in the infrared spectrum, in which it is usually very weak and may therefore be obscured by the ν_3-band broadening.

As expected, in the bending region the spectra are not so easy to interpret because the internal deformation modes of the CrO_4^{2-} ions are partially overlapped by PbO motions. Nevertheless, the Raman spectrum is still clearly understandable. The strongest line in this region, located at 343 cm^{-1} can be confidently assigned to one of the two expected symmetric-bending ν_2 components (cf. [5]) whereas those located at 382 and 356 cm^{-1} are probably two of the antisymmetric-bending components (ν_4). The remaining lines, 333 (very weak) and 324 cm^{-1}, are assignable to PbO modes.

The infrared spectrum in this region is not so well defined, although the band with components at 428, 415 and 402 cm^{-1} is probably the ν_4 vibration whereas the doublet at 365 to 350 cm^{-1} could be related to the ν_2 mode. But, as pure PbO also has infrared bands in the region below 480 cm^{-1} [6], some of the bands in this region are certainly of a complex nature involving not only chromate bendings. The strong infrared band at 312 cm^{-1} can be unambiguously assigned to a PbO mode.

In this context it is also interesting to comment on some related materials previously investigated, such as $V_2O_5 \cdot 4PbO$ or $V_2O_5 \cdot 8PbO$ [7] and $PbSO_4 \cdot 4PbO$ [8], that show a similar behaviour in the bending region in which a superposition between internal XO_4 modes and PbO motions can be observed. The fact that significant frequency differences between corresponding infrared and Raman bands can sometimes be observed is attributed to the

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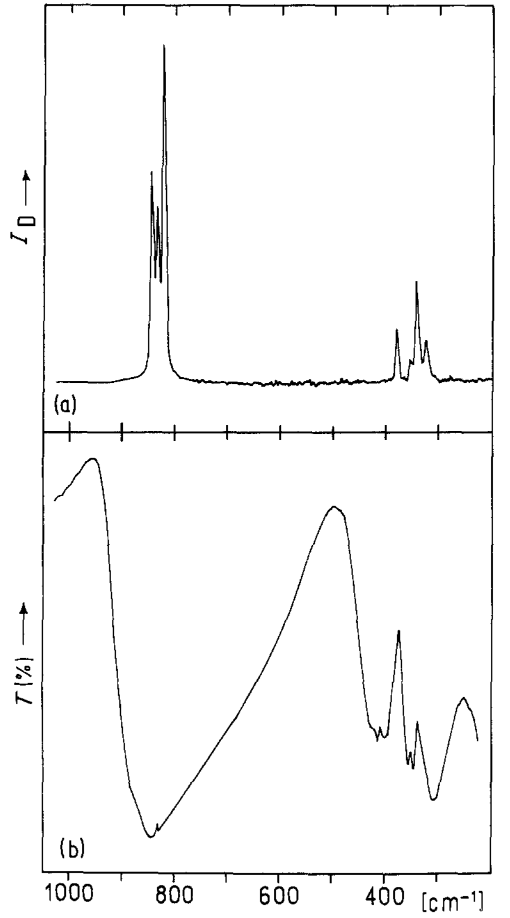

Figure 1 (a) Raman and (b) infrared spectra of Pb_2CrO_5.

presence of important coupling effects in the unit cell. Some differences can also be observed if the spectra of $PbCrO_4 \cdot PbO$ and pure $PbCrO_4$ are compared. In general, a slight displacement to higher wavenumbers can be observed in the case of the pure chromate.

The spectroscopic results presented here show that Pb_2CrO_5 possesses very characteristic and well defined infrared and Raman spectra which can be clearly interpreted on the basis of the simple site-symmetry rules and may lead to a rapid and straightforward characterization of this interesting ceramic material.

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