ON THE PRESENCE OF HYDROUS DEFECTS IN DIFFERENTLY COLOURED WULFENITES ($PbMoO_4$): AN INFRARED AND OPTICAL SPECTROSCOPIC STUDY

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Several samples of wulfenite, $PbMoO_4$, varying in colour from colourless to yellow, orange and red, have been characterised by means of IR and optical absorption spectroscopy and by microprobe analyses. A distinct pleochroic band group with absorption maxima centred at 3380 and 3150 cm^{-1} can be seen in the IR spectra of wulfenite single-crystals, indicating the presence of hydroxyl groups. The pleochroic and thermal behaviour of the OH stretching bands along with deuteration experiments, as well as results obtained from synthetic flux-grown samples, exclude the presence of submicroscopic hydrous mineral inclusions (mainly considered were phases belonging to the alunite-crandallite mineral group) as their primary origin. Whereas jarosite and plumbogummite, in which the OH absorption bands coincide in shape and position with the IR absorption phenomena visible in wulfenite, decompose already at 250 °C, the OH bands of wulfenite persist up to 500 °C. A significant CO_2 absorption pattern which evolves upon heating the samples to 500 °C is attributed to the decomposition of included carbonates (siderite and smithsonite), which were found by means of a scanning electron microscope and EDX analyses.

The pleochroic scheme and the band positions were used to postulate a model for the OH incorporation mode, based on the assumption of vacancies on Mo and Pb sites in the structure of this 'nominally anhydrous mineral', where the latter case presumes an interstitial OH group occupying the vacant Pb position.

Optical absorption spectra of coloured natural samples show a broad and polarised band around 23000-24000 cm^{-1}, preceding the fundamental UV absorption edge, which has been identified as the reason for the colour of the mineral. The comparison with synthetic $PbMoO_4$ single-crystals, doped with variable amounts of Cr^{6+}, yielded conclusive evidence that trace amounts of the CrO_4^{2-} anion group, substituting for MoO_4^{2-}, determine the variable colour. Besides, in one sample, trace amounts of Nd^{3+} have been spectroscopically identified.

To confirm the assignment of the observed absorption patterns to Nd, a $PbMoO_4$ sample doped with Nd^{3+} has been synthesised using the coupled substitution $Nd^{3+}As^{5+}$ $Pb^{2+}Mo^{6+}$. In natural samples, V^{5+} is believed to provide the necessary charge balance, as samples with observable REE bands have enhanced contents of V_2O_5.