

Intercalation of lanthanide ions into vanadyl phosphate dihydrate

J.P.L. Ferreira* and H.P. Oliveira

Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo.
Avenida Bandeirantes-3900, Departamento de Química, CEP: 14040-901.

* billbrujah@usp.br

Abstract – Lanthanide ions containing intercalates, of the general formula $M_xVOPO_4 \cdot 2H_2O$, where $M=La, Nd, Eu$ and Tb , have been prepared by reflux method. The results of both structural and morphological studies carried out upon these intercalation compounds are reported.

The vanadyl phosphate dihydrate, $VOPO_4 \cdot 2H_2O$, and its intercalation compounds are the subject of considerable interest for their applications as catalysts or cathode materials. The catalytic behavior observed in this family of compounds is particularly interesting since they can be used in the mild oxidation of hydrocarbons to molecules of economic interest. Numerous arrangements with varied M/V/P ratios, with different M cations, different environments for vanadium (octahedral, square pyramidal, trigonal bipyramidal, tetrahedral), and different oxidation states of the vanadium element (III, IV, V) are observed in this family. We report here on synthesis and characterization of a new series of lanthanide-metal-intercalated vanadyl phosphate dihydrates whose general formula is $M_xVOPO_4 \cdot 2H_2O$ with $M= La, Nd, Eu$ and Tb .

For all intercalation compounds, the diffraction patterns present broad and low intensities peaks, suggesting a decrease in crystallinity and the maintenance of the interlayer long-range order. In addition, neither contraction in the interlamellar space owing to an electrostatic attraction between the vanadyl phosphate layers and the intercalation cation was observed nor an expansion due to the presence of lanthanide ions into lamellar structure was observed. Probably, the cations are arranged in a regular manner, in such way that their placements do not distort original structure.

The infrared spectra of the matrix and of the intercalated compounds exhibit vibrational bands around $1085cm^{-1}$, and $948cm^{-1}$, $670cm^{-1}$, $570cm^{-1}$ assigned to the P–O stretching vibration of the PO_4 tetrahedral group, V–O stretching of the vanadyl group (V=O), V–O–P, and O–P–O bending vibrations, respectively. Accordingly, the lanthanide ions do not affect significantly the overall matrix structure, corroborating the diffraction data. EPR technique shows characteristic lines from the unpaired 3d electron (V^{IV} , $S=1/2$, $I=7/2$) localized around vanadium centres with a clear hyperfine structure of an axially distorted crystal field. After the intercalation, the signal broadens. This effect can be explained by the reduction of V^V to V^{IV} which enhances the spin-spin exchange interaction, *i.e.*, as the content of V^{IV} increases the hyperfine EPR interactions tend to disappear.

The morphology of these investigated compounds were analyzed by the SEM technique, the micrograph for $VOPO_4 \cdot 2H_2O$ exhibited a typical square-like morphology with some grains forming a 90° angle with the surface, as shown in Fig. 2. This characteristic is drastically changed after reaction with the guest rare earth ions, as shown in Fig. 3.

Intercalation of lanthanide ions leads to lamellar solids with low crystallinity in relation to the matrix due to octahedric distortion caused by reduction of vanadium ions (V^V to V^{IV}). Besides, it was observed a decrease of the interlamellar distance in function of the electroneutrality balance between the lamellar sheets.

Acknowledgements: FAPESP and CAPES.

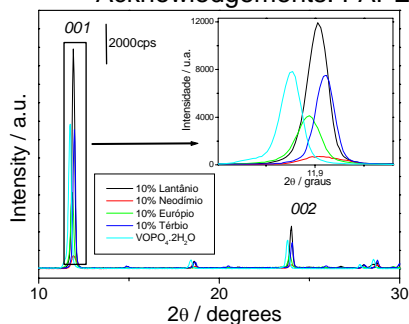


Figure 1. X-ray diffraction (DRX)

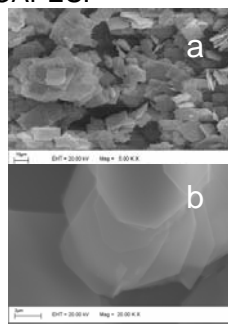


Figure 2. SEM images of $VOPO_4 \cdot 2H_2O$: (a)5.00kX e (b)20.00kX.

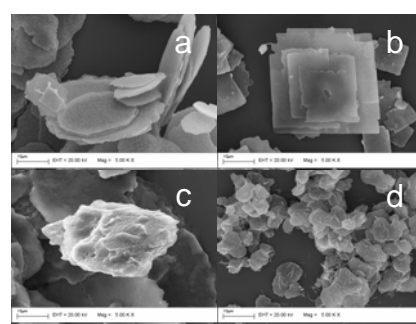


Figure 3. SEM images: (a)10%Lanthanum, (b)10%Neodymium, (c)10%Europium e (d)10%Terbium.

References

[1] Johnson, J.W., A.J. Jacobson, J.F. Brody, and S.M. Rich, *Inorganic Chemistry*, 1982. **21**(10): p. 3820-3825.