

## X-RAY ABSORPTION SPECTROSCOPY AT 3d-METAL $L_{2,3}$ AND O K-EDGES IN COLUMBITES

Mirão, J.<sup>1</sup> & Figueiredo, M.O.<sup>2</sup>

<sup>1</sup> Geophysics Center, University of Évora, Apdo. 92, 7001-019 Évora, Portugal

<sup>2</sup> Cryst. Miner. C., ICT, Al. Afonso Henriques, 41-4º, 1000-123 Lisboa & CENIMAT, UNL, Caparica, Portugal  
e-mail: jmirao@uevora.pt

Columbites are economically important Nb and Ta ores typical of pegmatites. Structurally identical synthetic compounds are intensively studied due to magnetic and electronic properties that make them technologically important materials. The crystal structure of these oxide minerals is a derivative from  $\alpha$ -PbO<sub>2</sub> structure, based on a hexagonal closest packing of oxygen anions with cations half-filling the octahedral interstices in a chain-pattern. Cation octahedra share edges along each zigzag chain and vertices with adjacent chains in neighbouring layers. A triple unit cell comes out from the ordering of two consecutive layer levels of pentavalent cations interleaved by one layer of transition metals (Fe,Mn). Oxygen anions display a triangular coordination by coplanar cations from which at least one is pentavalent. Cation disordering induces the mixing of three possible configurations – three (Nb,Ta), two (Nb,Ta) plus one (Fe,Mn), one (Nb,Ta) plus two (Fe,Mn) – , a quite common feature in natural compounds that is apparently precluded in synthetics.

Ordering may be attained by heating mineral fragments in air and rapidly cooling from about 1000 °C (ERCIT et al., 1995), but some discussion still prevails on the oxidation of 3d transition metals upon heating (ZAWISLAK et al., 1997). To ascertain the valence state of Fe and Mn, soft X-ray absorption at metal  $L_{2,3}$  and O 1s edges was performed at BESSY\* using beam line D11.1A-PM3 (SX700 monochromator with an energy resolution better than 0.2 eV). Studied columbites (from Zambezia mineralurgical province in Mozambique) cover a wide range of compositions checked by electron microprobe. The ordering state of as-collected and heated samples was monitored by X-ray diffraction.

To model O 1s XANES spectra, *ab-initio* simulations were carried out based on the multiple scattering approximation implemented in the FEFF code (ANKUNDINOV et al., 1998). Comparison of experimental and calculated spectra with data collected from simple oxide minerals (FIGUEIREDO & MIRÃO, 2002) allows for identifying features of O 1s XAS spectra explained by hybridisation of oxygen 2p with metal 3d states disturbed by chemical bonding.

Conversely, intensity variations of particular features in metal  $L_{2,3}$  spectra indicates oxidation by heat treatment progressing from the surface inwards the mineral fragments.

\*Financing from EU is acknowledged. Thanks are due to Drs. R. Mittthank and T. Kachel for their support.

### References

- ANKUNDINOV, A.L., RAVEL, B., REHR, J.J. & CONRADSON, S.D. (1998): Phys. Rev. B, **58**: 7565-7576.  
ERCIT, T.S., WISE, P. & ČERNÝ, P. (1995): Am. Mineral., **80**: 613-619.  
FIGUEIREDO, M.O. & MIRÃO, J. (2002): Eur. J. Mineral., **14**: 1061-1067.  
ZAWISLAK, L., ANTONIETTI, V., CUNHA, J. & SANTOS, C.A. (1997): Sol. State Comm., **101**: 767-770