

# New electronic conductor scheelite oxynitrides in Sr(Ca)-Ln-W-O-N systems

Maria-Luisa Martinez-Sarrin

*Universidat de Barcelona - ESPAA*

## Abstract

New oxynitrides were prepared in Sr(Ca)-Ln-W-O-N systems (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Y) by thermal ammonolysis of corresponding oxides at 575C. These oxides  $\text{Sr}(\text{Ca})_{1-3x/2}\text{LnIII}_{xx/2}\text{WO}_4$  ( $0 \leq x \leq 0.4$ ) were obtained by solid state reaction among  $\text{Sr}(\text{Ca})\text{CO}_3$ ,  $\text{Ln}_2\text{O}_3$  and  $\text{H}_2\text{WO}_4$  at 1000C. In contrast with the pale-coloured oxide precursors, the resulting oxynitride powders are black, indicating partial reduction of tungsten. Oxides and oxynitrides showed a cation-defect tetragonal scheelite structure-type. In addition, oxynitrides presented anionic vacancies created through the N/O substitution and tungsten reduction.

EPR measurements were consistent[1] with the presence of some W(V) in nitrated samples while oxides only showed W(VI). In addition, Eu-containing oxynitrides reveal anomalous unit cell parameters and nitrogen content within the Ln series, due to the formation of EuII during nitridation, as confirmed by XPS.

Impedance Spectroscopy (IS) measurements were carried out on well-sintered samples of oxynitrides showing electronic conductivity in contrast to the corresponding oxides that behaved as dielectrics at the same temperature. The presence of tungsten in two oxidation states may be responsible of electronic conductivity via a hopping mechanism.

[1] V.V.Laguta, J.Rosa, M.I.Zaritskii, M.Nikl and Y.Usuki, *J.Phys.:Condens. Matter.*, 1998, 10, 7293-7302.