Preparation and Characterization of Novel Solids in As-O-Mo, As(P)-O-Mo(W) and As(P)-O-Nb(W) systems.

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Mixed valence solids such as oxides based on molybdenum blues and tungsten bronzes recently found useful applications as semiconductors and catalysts. Despite some considerable efforts in the past, many of these interesting systems were not sufficiently investigated. We attempted systematic studies in this area of solid state chemistry and prepared several new systems for their subsequent investigations and evaluation of practical applications in the outlined above fields. Thus, interactions between fine powders of As_2O_3, P_2O_5, MoO_3, WO3 and Nb_2O_5 at different stoichiometry in quartz ampoules under vacuum at ~1000°C in the presence of metallic molybdenum within several weeks lead to shiny dichroic crystalline material that formed in cooler parts of the vessel. Sublimed crystals as well as main mass of powdery material were investigated using a variety of techniques including XRD methods (powder, single crystals), spectroscopy (visible diffusion reflectance, IR, Raman and EPR) and electrical conductivity studies.

Results evidenced the formation of new, complex solids of previously unknown compositions with one example of $P_4O_{44.78}Mo_{11.35}W_{0.65}$ shown in Figure 1. There were Mo(V) and Nb(IV) species, as well as trapped in the lattice O-radicals detected by the EPR spectroscopy (Figure 2).

Structures of new solids and aspects of their practical usefulness are discussed.

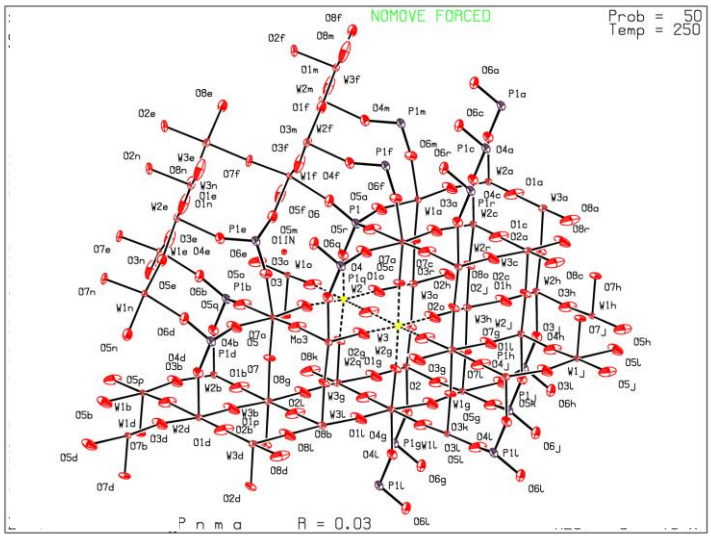

Figure 1. Fragment of structure of one of the obtained solids.

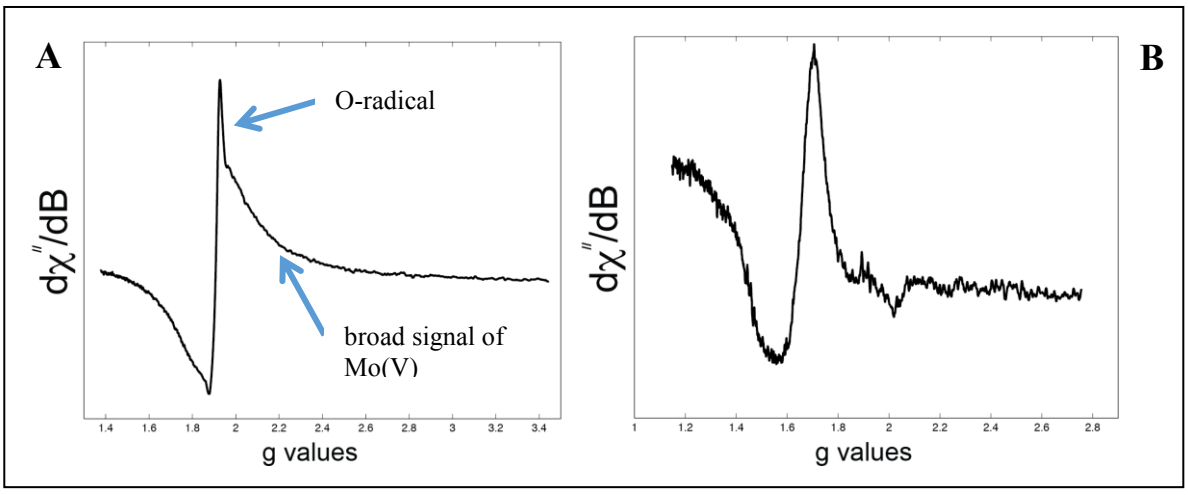

Figure 2. The EPR spectra of $P_4O_{44.78}Mo_{11.35}W_{0.65}$ powder at 80K showing both Mo(V) and oxygen radical (**A**), and Nb(IV) species in $P_3Nb_5O_{18}$ at 80K (**B**).