

Novel non-linear-optical 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 well mixed fine powders of As_2O_3 , P_2O_5 , MoO_3 , WO_3 and Nb_2O_5 at different stoichiometry in quartz ampoules under vacuum at $\sim 1000^\circ\text{C}$ in the presence of metallic molybdenum (or niobium) within several weeks lead to shiny dichroic crystalline materials formed in cooler parts of the reaction vessel. An addition of small quantities of metals – Mo or Nb – was done with the aim of partial reduction of their highly oxidized Mo(VI), W(VI) or Nb(V) species to corresponding Mo(V), W(V) and Nb(IV) centers in order to form mixed valence solids. Sublimed crystals were investigated using a variety of techniques with prime emphasis on the X-ray analysis followed by spectroscopy (visible diffusion reflectance, IR, Raman and EPR), second harmonic generation (SHG), thermal analysis under N_2 and air atmosphere, and single crystals electrical conductivity studies.

Results evidenced the formation of new complex solids of previously unknown compositions and structures. All crystallized in non-centrosymmetric, polar space groups. Thermogravimetric data and careful ICP analyses studies allowed accurate determination of content of solids and % of reduced metal ions. All new solids exhibit strong *second-harmonic-generation* (SHG effect; based on YAG 1064 nm tests with detection of 532 nm photons) and rare *photosalient* effect when crystals physically move in the laser beam.

Four new cool structures of these solids and aspects of their practical usefulness are discussed.

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