Correlation between the band-gap energy and the electrical conductivity in $MPr_2W_2O_{10}$ tungstates (where M = Cd, Co, Mn)

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Large number of rare-earth metal molybdates and tungstates are intensively studied because of their very interesting optical, electrical and magnetic properties. Diode pumped solid-state lasers based on these compounds demonstrate very high stability of emission of nano- or femtosecond pulses with high peak power. Rare-earth (RE) metal tungstates with the general formula of $MRE_2W_2O_{10}$ (where M = Cd, Co, Mn and RE = Y, Pr, Nd, Sm-Er) were synthesized by a high-temperature solid-state reaction of MWO_4 with corresponding RE_2WO_6 [1,2]. Optical properties of $CdNd_2W_2O_{10}$ and $CdY_{1-x}Nd_xW_2O_{10}$ solid solutions are appropriate for their potential applications as solid-state lasers [3]. Our earlier studies have shown that $MRE_2W_2O_{10}$ tungstates are paramagnetic insulators [4,5] with the exception of $MnPr_2W_2O_{10}$, which reveals both the ferrimagnetic order below 45 K and an anomalously large relative permittivity value $\varepsilon_r = 884$ [4].

The values of band gap energy E_g for $MPr_2W_2O_{10}$ were determined by analysis and the Kubelka-Munk transformation [6] of UV-Vis-NIR diffuse reflectance spectra (JASCO-V670 spectrophotometer equipped with an integrating sphere) recorded at room temperature and in the wavelength range of 200-900 nm. The electrical conductivity of tungstates under study was measured with the aid of the DC method using a KEITHLEY 6517B Electrometer/High Resistance Meter. For the electrical measurements, the powder samples were compacted in a disc form (10 mm in diameter and 1–2 mm thick) using a pressure of 1.5 GPa and then they were sintered for 2 h at 873 K. The temperature measurements of the electrical resistivity did not reveal any hysteresis in the temperature range 280–520 K. The electrical measurements revealed that all compounds under study are insulators with a giant electrical resistivity (ρ) of the order of $2.4 \cdot 10^8$ Ωm at 300 K showing a weak thermal activation of the Arrhenius type for $MPr_2W_2O_{10}$ (M = Co or Cd) and a stronger one for $MnPr_2W_2O_{10}$ above 350 K. From the experimental results the band gap energy has been determined to be 3.41 eV ($CdPr_2W_2O_{10}$), 2.66 eV ($CoPr_2W_2O_{10}$), and 2.45 eV ($MnPr_2W_2O_{10}$). The results are discussed in terms of the lowering the potential barrier of the studied tungstates. It has been found that those compounds containing the metal atoms with the unscreened electrons on the filled shells show low electrical conductivity and larger band gap energies (*e.g.*, $CdPr_2W_2O_{10}$) than those containing the metal atoms with the unscreened electrons on the unfilled shells contribute to the top of the valence band and the bottom of the conduction band (*e.g.*, $MnPr_2W_2O_{10}$). In conclusion, in a case of low carrier concentration the thermionic emission processes may occur and the carrier transport can take place over the potential barrier.

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