Correlation between the Band-Gap Energy and the Electrical Conductivity in $MPr_2W_2O_{10}$ Tungstates (Where M = Cd, Co, Mn)

B. Sawicki[a], E. Tomaszewicz[b], M. Piątkowska[b], T. Groń[a,*], H. Duda[a] and K. Górny[a]

[a]University of Silesia, Institute of Physics, Uniwersytecka 4, 40-007 Katowice, Poland

[b]West Pomeranian University of Technology, Department of Inorganic and Analytical Chemistry,

al. Piastów 42, 71-065 Szczecin, Poland

The values of the direct allowed energy gap determined from the UV-vis-NIR measurements and Kubelka–Munk transformation decrease from 3.38 via 2.70 to 2.42 eV for $MPr_2W_2O_{10}$ in the sequence M = Cd, Co, Mn, while the values of the activation energy increase from 0.11 via 0.44 to 0.47 eV in the same sequence. In other words, the higher the activation energy, the smaller the energy gap. Because the energy gap is typical for insulators, so electron transport phenomena are considered under the Poole–Frenkel effect and small-polaron mechanism.

1. Introduction

Metal molybdates and tungstates form important class of materials widely used in several technical applications. Activated by rare earth (RE) ions molybdate and tungstate phosphors have an efficient absorption band covering the wide ultraviolet range and extending to visible light range [1, 2]. Light emitting diodes (LED) employing RE-doped molybdates and tungstates have many advantages over conventional light sources, such as being energy-saving, environmentally friendly, compact and portable. Molybdates and tungstates have been also used as solid state scintillators, laser-host materials, and Raman lasers. Diode pumped solid-state lasers based on RE-doped molybdates and tungstates demonstrate very high stability of emission of nano- or femtosecond pulses with high peak power.

RE metal tungstates with the general formula of $MRE_2W_2O_{10}$ (where M = Cd, Co, Mn and RE = Y, Pr, Nd, Sm–Er) have been synthesized for the first time by us by a high-temperature solid-state reaction method of MWO_4 with corresponding RE_2WO_6 [3, 4]. 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 ceramic lasers [5]. Our earlier studies have shown that isostructural $MRE_2W_2O_{10}$ tungstates crystallize in the orthorhombic system [3, 4] and they are paramagnetic insulators [6, 7] with the exception of $MnPr_2W_2O_{10}$, which reveals both the ferrimagnetic order below 45 K and an anomalously large relative permittivity value $\varepsilon_r = 884$ as well as the semiconducting properties [6].

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*corresponding author; e-mail: Tadeusz.Gron@us.edu.pl

This paper presents the optical and electrical properties of $MPr_2W_2O_{10}$ tungstates (M = Cd, Co, Mn). The main motivation is to find a correlation between these properties in order to clarify the mechanism of electron transport in the compounds under study.

2. Experimental details

The values of band gap energy E_g for $MPr_2W_2O_{10}$ were determined by analysis and the Kubelka–Munk transformation [8] 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 the 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.

3. Results and discussion

The diffuse reflectance spectra of $MPr_2W_2O_{10}$ are shown in Fig. 1. They were converted to the absorption coefficient $F(R)$ values according to the Kubelka–Munk function [8]: $F(R) = (1 - R)^2/2R = \alpha/S$, where α is the absorption coefficient (in cm^{-1}) and S is the dispersion factor. α [9] is related to the incident photon energy and given by: $\alpha = A(E - E_g)^n$, where A is a constant characteristic for material, E is the photon energy, E_g is the band gap energy and n is a constant of different values, $1/2$, $3/2$, 2 or 3, depending on the type of electronic transition. After the extrapolation of linear part of the plot $\alpha h\nu^2$ vs. $h\nu$ graph to the abscissa (Fig. 2) the energy gap values are as follows: 3.38 eV ($CdPr_2W_2O_{10}$), 2.70 eV ($CoPr_2W_2O_{10}$) and 2.42 eV ($MnPr_2W_2O_{10}$).
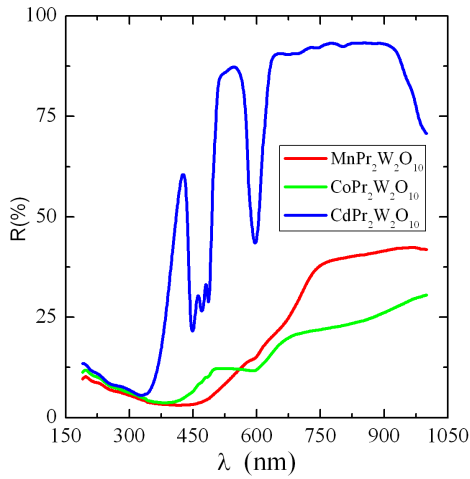
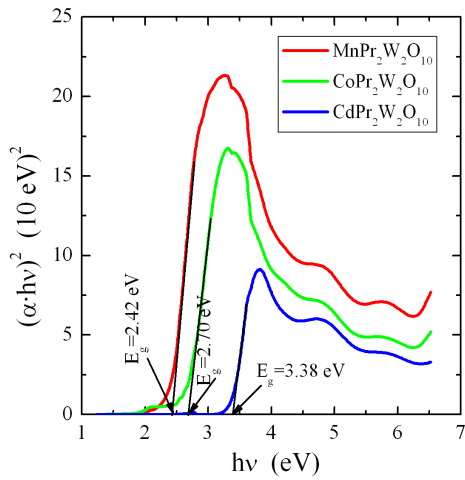Fig. 1. Solid state diffuse reflectance UV-vis-NIR spectra of $MPr_2W_2O_{10}$ (M = Cd, Co, Mn).

Fig. 2. Calculations of band gap of $MPr_2W_2O_{10}$ (M = Cd, Co, Mn). Linear fit is marked by solid black line.

The electrical measurements revealed that all compounds under study are insulators with a giant electrical resistivity (ρ) of the order of 2.4×10^8 Ωm at 300 K showing in Fig. 3 a weak thermal activation for $CdPr_2W_2O_{10}$ and a stronger one of the Arrhenius type for $MPr_2W_2O_{10}$ (M = Co and Mn). The results of thermoelectric power investigations in Fig. 4 show n-type conductivity for all tungstates under study, probably due to oxygen vacancies playing a role of the double donors.

The most spectacular finding is that the higher the activation energy, the smaller the energy gap. The question arises what mechanism is responsible for the electrical conductivity in the tungstates under study with the energy gap of more than 2.4 eV, especially for the compounds containing the transition metal (TM) ions, such as Co and Mn, with the unscreened electrons on the unfilled $3d$ shells. Therefore, it is unlikely that the thermal energy kT was able to activate the electrons in these compounds having such a large band gap. From this

point of view it is evident that for $CdPr_2W_2O_{10}$ a low electrical conductivity and large band gap energy is observed. It is well known that in a case of low carrier concentration the thermionic emission processes may occur and the carrier transport can take place over the potential barrier, especially in those TM ions, which potential barrier is susceptible to the electric field. The above-mentioned mechanism describes well the Poole–Frenkel model [10, 11].
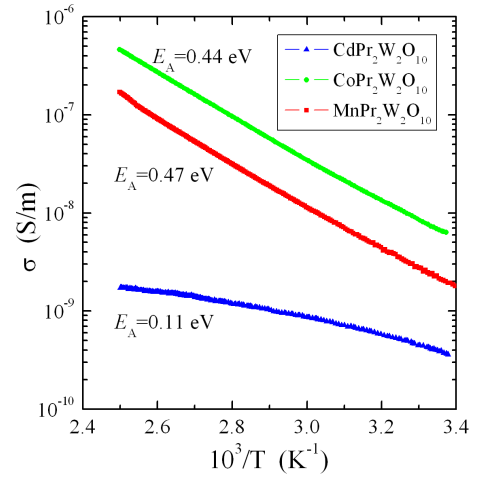

Fig. 3. Electrical conductivity σ vs. reciprocal temperature $10^3/T$ of $MPr_2W_2O_{10}$ (M = Cd, Co, Mn).
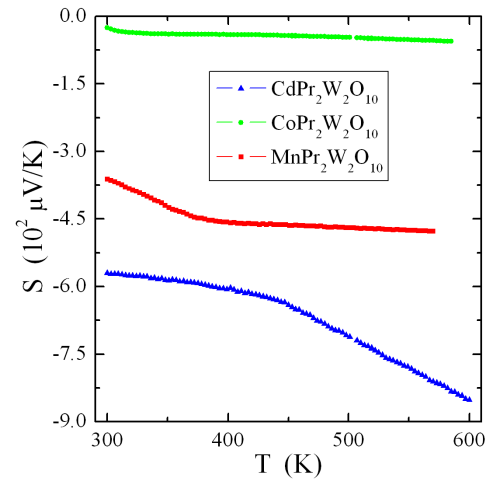

Fig. 4. Thermoelectric power S vs. temperature T of $MPr_2W_2O_{10}$ (M = Cd, Co, Mn).

Alternatively, one can attempt to interpret these effects as eventually due to conduction of small polarons, generated here as electrons together with their associated defective oxygen lattice, playing a role of the double donors in the n-type conductivity of $MPr_2W_2O_{10}$ tungstates under study (Fig. 4). Generally, the interactions of phonon and electronic subsystems lead to the formation of spin or structural polarons [12, 13], which in turn have characteristic temperature dependences of the carrier mobility [14] like

$$v = v_0 T^{-3/2} \mathrm{e}^{-E_\mathrm{h}/kT}, \qquad (1)$$

where v_0 is the infinite temperature mobility and E_h is the hopping energy of polarons. As one can see from Fig. 3 activation energies are comparable for $MPr_2W_2O_{10}$ (M = Co and Mn) and they are four times higher than for $CdPr_2W_2O_{10}$, thus one should expect a similar dependence for the hopping energy of polarons. The estimated value of this energy for the $SbVO_{4.96}$ insulator with the sharp resistivity dip is $E_\mathrm{h} = 34.5$ meV [12]. Therefore, for $MPr_2W_2O_{10}$ (M = Co and Mn) $E_\mathrm{h} = 138$ meV is expected.

4. Conclusions

We have observed unusual large electrical conductivity in the $MPr_2W_2O_{10}$ tungstates (M = Co and Mn) having lower values of the band gap in comparison with $CdPr_2W_2O_{10}$. This anomaly was interpreted in a framework of the Poole–Frenkel effect and the small-polaron mechanism. The most spectacular correlation is that the higher the activation energy and the electrical conductivity, the smaller the energy gap.

Acknowledgments

References

[1] M. Guzik, E. Tomaszewicz, S.M. Kaczmarek, J. Cybińska, H. Fuks, *J. Non-Cryst. Solids* **356**, 1902 (2010).

[2] E. Tomaszewicz, M. Guzik, J. Cybińska, J. Legendziewicz, *Helv. Chim. Acta* **92**, 2274 (2009).

[3] E. Tomaszewicz, *J. Therm. Anal. Cal.* **93**, 711 (2008).

[4] E. Tomaszewicz, S.M. Kaczmarek, *Rev. Adv. Mater. Sci.* **23**, 88 (2010).

[5] M. Guzik, E. Tomaszewicz, Y. Guyot, J. Legendziewicz, G. Goulon, *J. Mater. Chem.* **22**, 14896 (2012).

[6] Z. Kukuła, E. Tomaszewicz, S. Mazur, T. Groń, H. Duda, S. Pawlus, S.M. Kaczmarek, H. Fuks, T. Mydlarz, *Philos. Mag.* **92**, 4167 (2012).

[7] Z. Kukuła, E. Tomaszewicz, S. Mazur, T. Groń, S. Pawlus, H. Duda, T. Mydlarz, *J. Phys. Chem. Solids* **74**, 86 (2013).

[8] P. Kubelka, F. Munk, *Z. Tech. Phys. (Leipzig)* **12**, 593 (1931).

[9] J. Tauc, R. Grigorovici, A. Vancu, *Phys. Status Solidi (b)* **15**, 627 (1966).

[10] H.H. Poole, *Philos. Mag. S6* **32**, 112 (1916).

[11] J. Frenkel, *Phys. Rev.* **54**, 647 (1938).

[12] T. Groń, E. Filipek, S. Mazur, H. Duda, A.W. Pacyna, T. Mydlarz, K. Bärner, *Philos. Mag. Lett.* **90**, 519 (2010).

[13] T. Groń, E. Filipek, H. Duda, S. Mazur, K. Bärner, *Solid State Phenom.* **170**, 5 (2011).

[14] J. Appel, *Solid State Phys.* **21**, 193 (1968).