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Electrical Transport Properties of $Yb_{8-x}Y_xV_2O_{17}$ ($x = 0, 2, 8$)

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The UV-vis-NIR and electrical properties of $Yb_{8-x}Y_xV_2O_{17}$ for $x = 0$, 2, and 8 were investigated. The band energy gap of 2.6 eV determined for $Yb_6Y_2V_2O_{17}$ ($x = 2$) and comparable for the remaining compounds with $x = 0$ and 8 is characteristic for insulators. Low electrical conductivity with a characteristic minimum shifting to higher temperatures from 322, via 360 to 370 K in the sequence $x = 0$, 2 and 8, which decreases with increasing content of ytterbium was observed. Temperature dependence of thermoelectric power showed n–p transition at 410 and 467 K for $x = 0$ and 2, respectively, and n-type conductivity for $x = 8$, indicating mainly n-type electrical conductivity. A breakdown voltage of 26 V/mm is mainly observed for the I–V characteristics at 400 K and showing a varistor-like behavior.

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1. Introduction

Complex oxide systems based on rare earth metal oxides are of great interest for creation of new materials for production e.g. of plasma displays, electroluminescent diodes, or fluorescence lamps [1–5].

Preliminary studies of the ternary oxides V_2O_5–Yb_2O_3–Y_2O_3 system have shown that, in one of its sections, i.e. in the system $Yb_8V_2O_{17}$–$Y_8V_2O_{17}$, a previously unknown phase of the formula $Yb_6Y_2V_2O_{17}$ is formed [6]. The new phase $Yb_6Y_2V_2O_{17}$ was obtained by heating a mixture of the three oxides, i.e. Yb_2O_3, V_2O_5 and Y_2O_3 in a molar ratio (3:1:1) in air, between temperatures 873 and 1823 K [6]. The X-ray powder diffractogram showed that $Yb_6Y_2V_2O_{17}$ is isostructural with $Yb_8V_2O_{17}$ which crystallizes in the triclinic systems [7]. This result is contrary to the literature data [8]. According to the results of our research the elementary cell parameters of new phase $Yb_6Y_2V_2O_{17}$ which were refined with the use of the program REFINEMENT are as follows: $a = 0.8972$ nm, $b = 0.9292$ nm, $c = 0.9824$ nm, $\alpha = 77.668°$, $\beta = 106.301°$, $\gamma = 116.291°$ [7].

In the present study the electrical and optical properties of $Yb_{8-x}Y_xV_2O_{17}$ for $x = 0$ and 8 [7–9] as well as for a new phase ($x = 2$) were carried out.

2. Experimental details

The powder diffraction patterns of the samples obtained were recorded with the aid of the diffractometer EMPYREAN II (PANalytical, Netherlands) using Cu K_α with graphite monochromator. Ultraviolet–visible and near-infrared (UV–vis–NIR) diffuse reflectance spectra were recorded at room temperature and in the wavelength range of 200–900 nm using a JASCO-V670 spectrophotometer equipped with an integrating sphere. In order to determine the energy gap, E_g, these spectra were transformed using the Kubelka–Munk function: $F(R) = (1 - R)^2/2R$, where R is reflectancy [%] [10, 11]. The sample morphology was observed on SEM images. Scanning electron microscopy study was performed on JSM-1600, JEOL, Japan with an X-ray energy dispersive analysis — EDX (ISIS-300, Oxford).

The electrical conductivity $\sigma(T)$ and the I–V characteristics have been measured with the aid of the DC method in the temperature range 300–400 K using a KEITHLEY 6517B Electrometer/High Resistance Meter. The thermoelectric power $S(T)$ was measured in the temperature range 300–600 K with the aid of a Seebeck Effect Measurement System (MMR Technologies, Inc., USA). For the electrical measurements, the powder samples were compacted in a disc form (10 mm in diameter and 2 mm thick) using a pressure of 1.5 GPa and then they were sintered during 2 h at 1073 K. The electrical and thermal contacts were made by a silver lacquer mixture (Degussa Leitsilber 200).

3. Results and discussion

Figure 1 shows a fragments of diffraction pattern (XRD) of $Yb_8V_2O_{17}$ (Fig. 1a), $Yb_6Y_2V_2O_{17}$ (Fig. 1b) and $Y_8V_2O_{17}$ (Fig. 1c) obtained in the context of this paper, which are almost identical to that shown in [7].

The SEM image of new polycrystalline phase is presented in Fig. 2.

The morphology of $Yb_{8-x}Y_xV_2O_{17}$ for $x = 2$ ($Yb_6Y_2V_2O_{17}$) crystallites is very similar to those of the matrix *i.e.* $Yb_8V_2O_{17}$ [7]. They look like polygons of irregular shapes and different sizes, varying from 0.5 to 9 μm (Fig. 2).

The UV-vis-NIR measurements and the Kubelka–Munk transformation [10,11] (Fig. 3) have shown that all phases of $Yb_{8-x}Y_xV_2O_{17}$ are insulators for the energy gap of 2.6 eV for $Yb_6Y_2V_2O_{17}$ ($x = 2$), whose value is comparable to that of other samples ($x = 0$ and 8).

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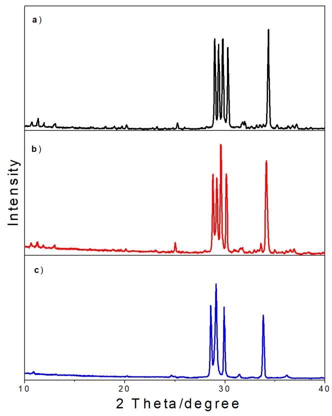

Fig. 1. Fragments of XRD powder patterns of the: a) $Yb_8V_2O_{17}$, b) $Yb_6Y_2V_2O_{17}$, c) $Y_8V_2O_{17}$.

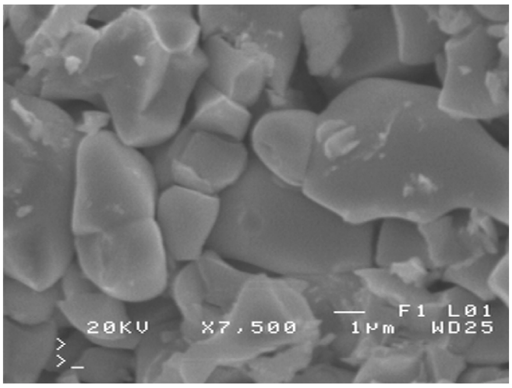

Fig. 2. SEM image of $Yb_6Y_2V_2O_{17}$.

The compounds under study showed low electrical conductivity, $\sigma(T)$, with a characteristic minimum shifting to higher temperatures from 322, via 360 to 370 K in the sequence $x = 0$, 2 and 8 (Fig.4). It is noteworthy that the electrical conductivity decreases with increasing content of ytterbium. The temperature dependence of thermo-

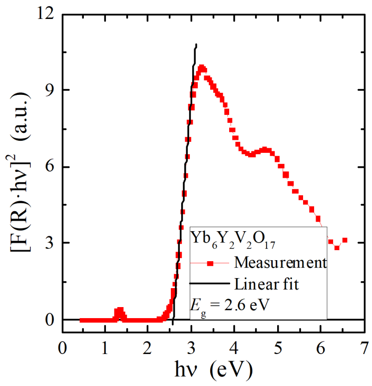

Fig. 3. Plots of $(F(R)h\nu)^2$ vs. the energy of the incident photon $h\nu$ for $Yb_6Y_2V_2O_{17}$. E_g is the band gap energy.

power, $S(T)$, showed n–p transition at 410 and 467 K for $x = 0$ and 2, respectively, and n-type conductivity for $x = 8$, indicating mainly n-type electrical conductivity (Fig. 5) probably due to predominant contribution of oxygen vacancies. In this case, the thermoelectric power increases as the content of ytterbium increases.

TABLE I

The voltage at the point of breakthrough V [V] and breakdown voltage V_b [V/mm] of $Yb_{8-x}Y_xV_2O_{17}$ for the specimen thickness of 2 mm at 300 K and 400 K.

x	Compound	V (300 K)	V_b (300 K)	V (400 K)	V_b (400 K)
0	$Yb_8V_2O_{17}$	–	–	60	30
2	$Yb_6Y_2V_2O_{17}$	92	46	44	22
8	$Y_8V_2O_{17}$	–	–	54	27

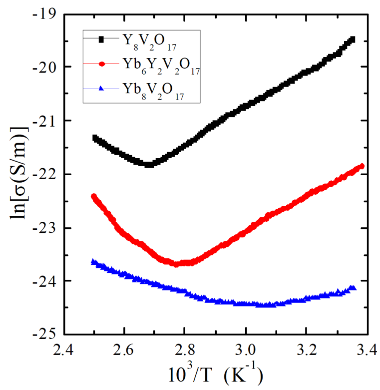

Fig. 4. The electrical conductivity ($\ln\sigma$) vs. reciprocal temperature T^{-1} for $Yb_{8-x}Y_xV_2O_{17}$ ($x = 0$, 2 and 8).

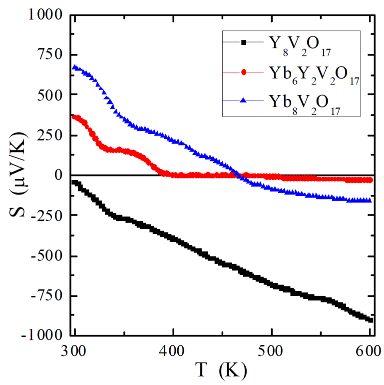

Fig. 5. The thermoelectric power S vs. temperature T for $Yb_{8-x}Y_xV_2O_{17}$ ($x = 0$, 2 and 8).

The most interesting observation concerns the nonlinear $I - V$ characteristics (Figs. 6–8) for all the phases under study, similar to back-to-back Zener diodes but with much greater current and energy handling capabilities [12]. A breakdown voltage V_b ~26 V/mm (Table I) is mainly observed for the I–V characteristics at 400 K and it is almost twice lower than the value of V_b at 280 and 300 K, showing a varistor-like behavior. From the physics research of varistors follows that the non-linearity $I-V$ characteristics in this case may be due to the phenomenon of grain-boundary where a barrier to majority charge carriers exists in the depletion layers of the adjacent grains [12].

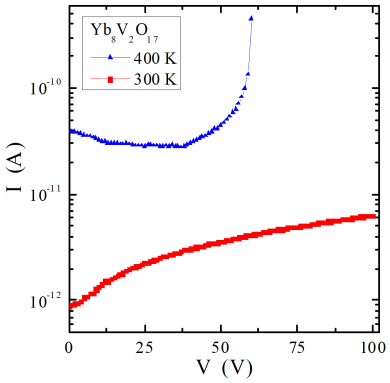

Fig. 6. The $I-V$ characteristics at 300 and 400 K for $Yb_8V_2O_{17}$.

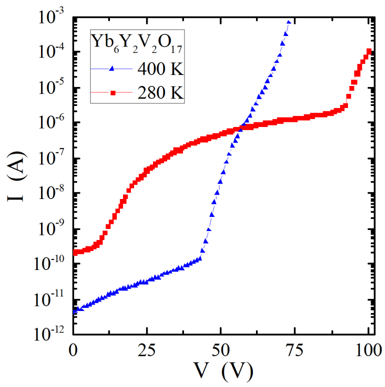

Fig. 7. The $I-V$ characteristics at 280 and 400 K for $Yb_6Y_2V_2O_{17}$.

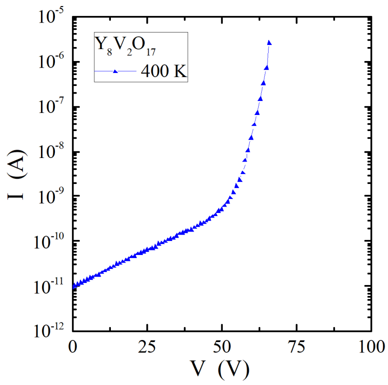

Fig. 8. The $I-V$ characteristics and 400 K for $Y_8V_2O_{17}$.

The studied materials can be used as the voltage stabilizers, the electronic power systems and the transient surge suppression in electronic circuits.

4. Conclusions

We have investigated the UV-vis-NIR spectroscopy and electrical properties of $Yb_{8-x}Y_xV_2O_{17}$ phases for $x = 0$, 2 and 8. All samples turned out to be insulators with the band energy gap of 2.6 eV, low electrical conductivity mainly of n-type with a characteristic minimum shifting to higher temperatures in the sequence $x = 0$, 2 and 8 which decreases with increasing content of ytterbium and the breakdown voltage of 26 V/mm which is mainly observed for the $I-V$ characteristics at 400 K and showing a varistor-like behavior. The solid solutions under study can be considered as varistors and for applications as the electronic power systems

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