The electrical *n-p* phase transition in the $Sb_{0.92}V_{0.92}O_4$ and $Sb_2V_2O_9$ compounds

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Modern chemical processes and petroleum refining are strongly dependent on the use of the active and selective solid catalysts. Pure $Sb_{0.92}V_{0.92}O_4$ and its various preparations with excess of either vanadia or antimony oxide, including mechanical mixtures, are promising as a new class of catalysts that are active and selective in ammoxidation of propane to acrylonitrile [1] and in reduction of NO with ammonia [2]. The $Sb_{0.92}V_{0.92}O_4$ ($SbVO_{4.35}$) compound is well known in the literature. It crystallises in a tetragonal system and belongs to a space group $P4_2/mnm$ [3]. Mössbauer spectroscopy studies [4] showed that a compound obtained at 800 °C in air from Sb_2O_3/V_2O_5 mixture has a chemical formula $V^{3+}_{0.28}$ $V^{4+}_{0.64}Sb^{5+}_{0.92}$ $\Box_{0.16}O_4$ and, in agreement with the previous statements [5–7], it is a non-stoichiometric [8, 9] rutile-type phase [4]. Antimony in this phase is in +5 oxidation state and vanadium – in +4 and +3. The concentration of vanadium (III) in this phase is insignificant and the oxidised vanadium antimonite formed by calcination Sb_2O_3/V_2O_5 mixture in air may be best formulated as $Sb^{+5}_{0.92}$ $V^{+4}{}_{0.92}O_4$.

Information on the reactions between V_2O_5 and α-Sb_2O_4 (giving the $Sb_2V_2O_9$ ($SbVO_{4.5}$) product) is fragmentary. The relevant phase diagram was constructed by Renaud [5]. The eutectic formed by V_2O_5 and $Sb_2V_2O_9$ melts at 657 °C and its composition corresponds to that of an oxide mixture containing 91% V_2O_5 and 9% α-Sb_2O_4. Indexing of the $Sb_2V_2O_9$ ($SbVO_{4.5}$) powder diffraction pattern confirmed that this phase crystallises in a tetragonal system ($a = b = 461.476$ pm, $c = 305{,}113$ pm) and has a rutile-type structure [10]. Recently the $Sb_{0.92}V_{0.92}O_4$ and $Sb_2V_2O_9$ compounds have been also obtained by a decomposition of $SbVO_5$ in air and in argon, respectively [11]. $SbVO_5$ is a compound known for not long. It can be obtained both from an equimolar mixture of Sb_2O_3/V_2O_5 and of Sb_2O_4/V_2O_5 by heating them in air at temperatures not exceeding 650 °C [11, 12]. $SbVO_5$ decomposes in the air atmosphere at ∼710 °C and in the atmosphere of argon at ∼660 °C.

The $Sb_{0.92}V_{0.92}O_4$ and $Sb_2V_2O_9$ compounds of the V-Sb-O system have been obtained from an equimolar mixture of Sb_2O_3/V_2O_5 and from a mixture of α-Sb_2O_4/V_2O_5, respectively [3, 11]. The above oxide mixtures were homogenised by grinding in an agate mortar, shaped into pastilles and heated in a silted furnace in air. The temperature was raised from ambient to 800 °C at 10 °C/min. The samples were kept at 800 °C for 17 h. After this period the heating was stopped and the samples were allowed to cool slowly to room temperature in the closed furnace. The phase analysis for the compounds under study was done by the X-ray HZG-4/A-2 diffractometer using CoK_α radiation. The X-ray studies showed that the diffraction patterns of the $Sb_{0.92}V_{0.92}O_4$ and $Sb_2V_2O_9$ compounds are almost identical [11].

The electrical conductivity σ of the compounds under study have been measured in the temperature range from 300 to 600 K by the standard four-point method using a HP 34401A digital multimeter. The maximal error of $\delta\sigma/\sigma$ is less than ±0.6%. The activation energy E_A and the temperature coefficient of resistivity α_{TCR} were determined from the formulae $\sigma = \sigma_0 \exp(-E_A/kT)$ and $\rho = \rho_0(1 + \alpha_{TCR}\Delta T)$, respectively. For electrical measurements the polycrystalline powder samples were compacted in disc form (10 mm in diameter and 2 mm thick), using a pressure of 1.0 GPa.

The thermoelectric power was measured with the aid of a differential method. The sample holder for the thermopower measurements on powder pastille contained two copper rods which served as heat source and heat sink. The mean temperature T and the temperature gradient ΔT (of about 7 K) were measured with the aid of two copper-constantan thermocouples which were inserted in the rods close to the sample. The temperature gradient was maintained by a smaller heater in one of the rods using a PID regulating technique. The sample holder as a whole was kept in a temperature controlled cryostat which permitted measurements between 300 and 600 K. The thermoelectric voltages were measured with the aid of a HP 34401 A digital multimeter. The accuracy of the value of thermopower was estimated to be better than 0.3 V/K.

The results of the electrical conductivity (σ) and thermoelectric power (S) measurements are presented in Table I and Figs 1 and 2. All compounds under study are semiconductors which have the comparable values of the temperature coefficient of resistivity α_{TCR} and the high temperature activation energy E_A (see Table I). The change of values of the electrical resistivity is about

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TABLE I The electrical parameters of the $Sb_{0.92}V_{0.92}O_4$ and $Sb_2V_2O_9$ compounds: ρ is the electrical resistivity at room temperature, α_{TCR} is the temperature coefficient of resistivity, and E_A is the activation energy

			E_A (eV)	
Compound	$\rho(10^6\ \Omega m)$	$\alpha_{TCR}(10^{-3}\ K^{-1})$	300 K	500 K
$Sb_{0.92}V_{0.92}O_4$	0.75	−20.8	0.33	0.47
$Sb_2V_2O_9$	1.91	−23.8	0.26	0.47

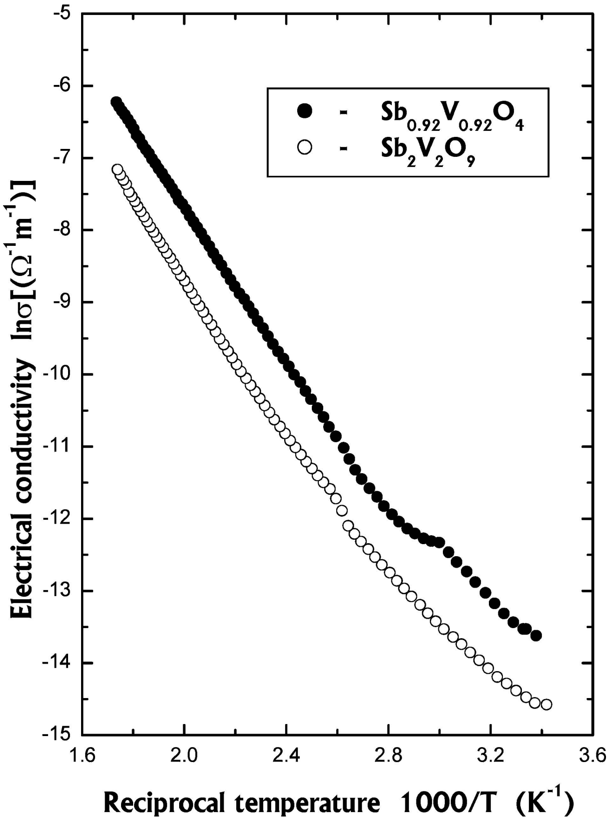

Figure 1 The electrical conductivity (lnσ) versus reciprocal temperature ($10^3/T$) for the $Sb_{0.92}V_{0.92}O_4$ and $Sb_2V_2O_9$ compounds.

three orders of magnitude in the temperature range of 300–600 K. Above 360 K: (1) the $Sb_{0.92}V_{0.92}O_4$ and $Sb_2V_2O_9$ compounds have a hole (*p*-type) and an electron (*n*-type) electrical conductivity, respectively, and (2) the thermoelectric power S is practically temperature independent in $Sb_{0.92}V_{0.92}O_4$ compound and it slowly increases with temperature in $Sb_2V_2O_9$ compound. Below 360 K the electrical *n*-*p* phase transition in both compounds is observed (see Fig. 2).

The $Sb_{0.92}V_{0.92}O_4$ and $Sb_2V_2O_9$ compounds are almost insulators at room temperature as the electrical resistivity is close to 1.0 MΩm (see Table I). The temperature dependences of the electrical conductivity reveal a typical Arrhenius behaviour. These dependences show extrinsic and intrinsic regions of the electrical conductivity. However, the difference between the activation energies of the extrinsic and intrinsic regions is small (see Table I). It means that the impurity levels and/or vacancy levels lie deeply in the forbidden gap.

From the above considerations and the thermopower studies we conclude that at high temperatures an electronic (or hole) thermal conductivity is added. In particular, the holes in $Sb_{0.92}V_{0.92}O_4$ apparently do not interact with phonons. Therefore we observe that the thermopower is really temperature independent above 360 K. In $Sb_2V_2O_9$ electrons are scattered by phonons and we observe a lowering of modulus of thermopower with the increase of temperature. We suggest that electrical and thermal conductivities are activated in the opposite way in $Sb_2V_2O_9$ and independent from each other in $Sb_{0.92}V_{0.92}O_4$. The nature of the *n*-*p* phase transition in the compounds under study could be explained by an existence of the vanadium mixed valence band (V^{3+}, V^{4+}) from one side and the ion vacancies, suggested by Canovas *et al.* [13], from the other.

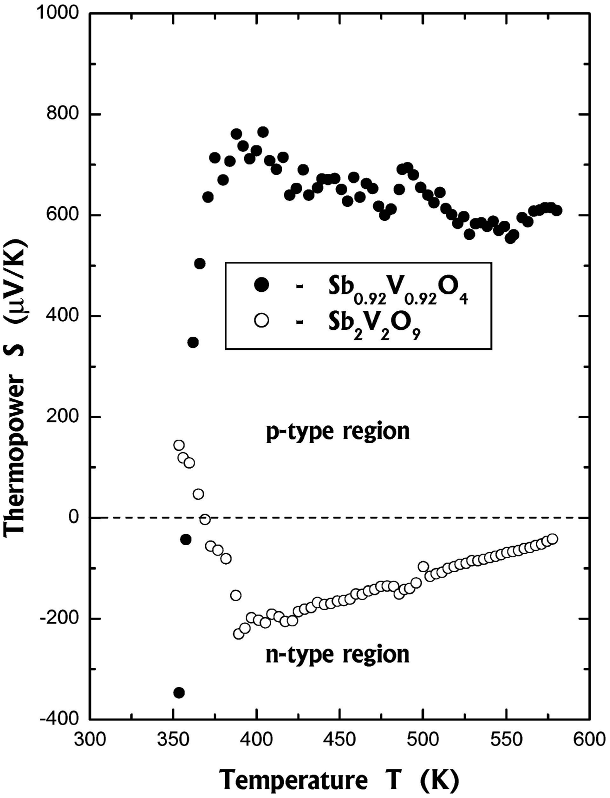

Figure 2 Thermoelectric power *S* versus temperature *T* for the $Sb_{0.92}V_{0.92}O_4$ and $Sb_2V_2O_9$ compounds.

One can conclude that: (1) the *p*-type conductivity in the non-stoichiometric $Sb_{0.92}V_{0.92}O_4$ compound is connected with an excess of cation vacancies by contrast to the *n*-type $Sb_2V_2O_9$ compound, (2) the vanadium mixed valence band is mainly responsible for an electronic transport.

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