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**ELECTRICAL PROPERTIES
OF LAYERED COMPOUNDS DERIVED
FROM VANADYL PHOSPHATE DIHYDRATE**

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A set of layered compounds derived from vanadyl phosphate dihydrate in which a part of vanadyl groups is replaced with a trivalent metal (Fe, Mn, Cr, Al, Ga) was prepared. Electrical properties of the modified vanadyl phosphates were studied by total and electronic conductivities investigation in a wide temperature range as well as by thermoelectric power (Seebeck coefficient) measurements.

Introduction

$\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, as a layered material, belongs among compounds which are able to uptake other chemical species (molecules or ions) into their interlayer space. Such compounds are a special type of inclusion compounds called intercalates. The original layered solid is usually denoted as a host, the species placed in the interlayer space is called a guest. The procedure of entering the guest species into layered structure of host is called intercalation. All intercalation reactions are accompanied by partial or total transfer of charge to the lattice and cause a change

of the interlayer distance (basal spacing). This can cause a change in electrical properties of the pristine host material. Due to the structural anisotropy of the layered compounds, unique electrical properties of these materials are expected. The conductivity in the intercalates can be associated with two basic types of charge transfer:

- a) by the intercalated ions present in the interlayer space
- b) by electrons moving along the layers

Most of the intercalates are classified as ionic conductors, very often as protonic conductors because of protons being prevailing charge carriers. Unless the electronic conductivity is negligible, the materials are considered to be mixed ionic-electronic conductors.

Vanadyl phosphate dihydrate, $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, is a compound with tetragonal structure consisting of sheets of $(\text{VOPO}_4)_\infty$ which are connected by molecules of water located in the interlayer space. The layers are formed by distorted VO_6 octahedra which share their equatorial oxygen atoms with PO_4 tetrahedra. One of two water molecules is coordinated to the vanadium atom in an axial position thus completing the VO_6 vanadium octahedron; the other is anchored more loosely through H-bonds to the oxygens of the tetrahedral phosphate groups [1]. This compound, together with other vanadium phosphates, is of interest due to its applications in catalysis especially as a catalytic precursor in an industrial oxidation of butane to maleic anhydride [2]. The activity or selectivity of these catalysts can be enhanced by an addition of other metals into their structures [3]. This addition can be accomplished for example by an intercalation of the desired metal ion. Recently, another method of preparation of VOPO_4 containing trivalent metals in the $(\text{VOPO}_4)_\infty$ layer has been published [4–7]. The layers of $(\text{VOPO}_4)_\infty$ can be modified by replacing a fraction of vanadyl groups (VO) in the parent vanadyl phosphate by trivalent metal ions M^{3+} to form compounds with a general formula $[\text{M}(\text{H}_2\text{O})]_x(\text{VO})_{1-x}\text{PO}_4 \cdot 2\text{H}_2\text{O}$. In this case, the $\text{M}(\text{H}_2\text{O})^{3+}$ ions partially replace the equivalent amount of the VO^{3+} oxocations which are randomly distributed in the host layer. Two moles of water per one mole of the compound are probably intercalated in the same fashion as in $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$.

Parent vanadyl phosphate dihydrate is a mixed protonic-electronic conductor in the range from 20 to 60 °C [8]. The strong acidic character of vanadyl phosphate layers leads to the formation of the H_3O^+ ions serving as charge carriers in the interlayer region. Proton mobility in this material can be described by a Grotthus-type mechanism [9]. The process of proton moving in an infinite network of hydrogen bonds consists of two steps: the translation of a proton from an oxonium ion to a water molecule along the hydrogen bond and subsequent reorientation (rotation) of the water molecule formed from the oxonium to be able to take up the next proton [10]. As a consequence of the loss of water in vanadyl phosphate dihydrate, the protonic component of the conductivity decreases with increasing

temperature so that monohydrated $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ turns out to be an electronic conductor at 70 °C. The electronic conductivity of anhydrous VOPO_4 is enhanced by water and more generally by Lewis bases chemisorbed on surface sites.

The aim of this paper is to determine a character of conductivity in the materials studied both in hydrated and anhydrous forms and compare it with that of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and anhydrous VOPO_4 .

Experimental

Five different compounds based on modified $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ were prepared [5]. The layers of $(\text{VOPO}_4)_\infty$ are modified by a partial substitution of the vanadyl group $(\text{VO})^{3+}$ by trivalent metal cations M^{3+} ($\text{M} = \text{Fe}, \text{Mn}, \text{Cr}, \text{Al}$ and Ga) forming compounds with the general formula $[\text{M}(\text{H}_2\text{O})]_x(\text{VO})_{1-x}\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (these compounds will be indicated shortly as MVOP further). All these compounds exist as hydrates at room temperature. Anhydrous forms of these materials were prepared by heating the hydrated forms at 300 °C for 3 hours.

The electrical properties of the compounds prepared were studied by AC conductivity measurements (total conductivity) using impedance spectroscopy method, DC conductivity measurements (electronic conductivity), and thermoelectric power (Seebeck coefficient) measurements. Pellets ($8 \times 3 \times 2$ mm) for the conductivity measurements were obtained by pressing an appropriate amount of the samples (0.15 g) in a rectangular matrix. The sheets of the crystals in the pellets are considered to be preferably oriented with the layers of vanadyl phosphate perpendicular to the direction of the pressure. Graphite paste was coated on two opposite sides of the pellets as a reversible interface to electrons but irreversible to ions for the conductivity measurements. For the thermoelectric power measurements, the opposite sides of the pellets of the hydrated forms of the intercalates were sputtered with carbon.

The AC conductivity was measured on a Tesla BM 653 IMPEDANCE METER in the frequency range 10 Hz – 500 kHz. The values of the impedance measured were recorded and evaluated by a method described recently [11]. The temperature dependence of the AC conductivity was measured in dry nitrogen atmosphere in the region from -20 to 130 °C for the hydrated forms of the samples and in the region from 80 to 180 °C for the anhydrous compounds. Linear courses of the conductivity in the temperature region from -20 to 20 °C were approximated by equation

$$\ln \sigma = \frac{A}{T} + B \quad (1)$$

where parameter $A = -E_A/R$. By using this equation, the values of the conductivity at 25 °C were extrapolated ($\ln\sigma_{25}$ and σ_{25} respectively) and then the values of the activation energy E_A were calculated.

The DC conductivity measurements were carried out in the same measuring cell as the AC conductivity using input voltage 0.5 V. The output magnitude of current was recorded in the dependence on time and converted to resistance. The temperature dependence of the Seebeck coefficient was measured with a temperature gradient of 14 °C in the region from 0 to 200 °C.

Results and Discussion

The AC conductivity of the hydrated modified vanadyl phosphates was plotted as a natural logarithm of the conductivity $\ln\sigma$ in dependence on reciprocal temperature $1/T$ (see Fig. 1). This is demonstrated in Fig. 1 for FeVOP as an example together with parent VOPO_4 for comparison; this dependence for all other compounds studied is similar to that of FeVOP. The conductivity increases with temperature up to about 70 °C and decreases at higher temperature. In agreement with thermal analysis [4] this temperature region is closely related to the first step of the dehydration. No change in the thermal dependence of the conductivity corresponding to the loss of the second molecule of hydration water was observed. The linear parts of the conductivity in the temperature region from -20 to 20 °C used for the calculations of the total conductivity at 25 °C and the activation energy are given in Fig. 2. Parent vanadyl phosphate dihydrate seems to be about one order of magnitude more conducting intercalate than the other samples (Table I). The values of the conductivity σ_{25} and also the activation energy E_A calculated are higher for modified vanadyl phosphates than for $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$.

The conductivity of the anhydrous forms of the samples increases linearly with temperature (Fig. 3). Using equation (1) and extrapolating to room temperature, the values of the activation energy E_A and the total conductivity σ_{25} at 25 °C were obtained (Table II). The conductivities of the anhydrous samples are about three orders of magnitude lower than those of the hydrates. The parent vanadyl phosphate shows about one order of magnitude higher conductivity compared with the modified vanadyl phosphates and its activation energy is consequently lower.

To obtain the ratio of the total conductivity to the electronic conductivity, the following process was performed. At first, the AC conductivity measurements of modified vanadyl phosphates were carried out at 25 °C and 58% of relative humidity (the measuring cell was purged with nitrogen humidified at 25 °C by bubbling through a saturated NaBr solution). Then the DC conductivity measurements were carried out at the same conditions. The values of σ_{AC} and σ_{DC} were obtained and the degree of electronic conductivity (σ_{DC}/σ_{AC}) and ionic conductivity ($(\sigma_{AC} - \sigma_{DC})/\sigma_{AC}$) were subsequently calculated. The results are given in Table III.

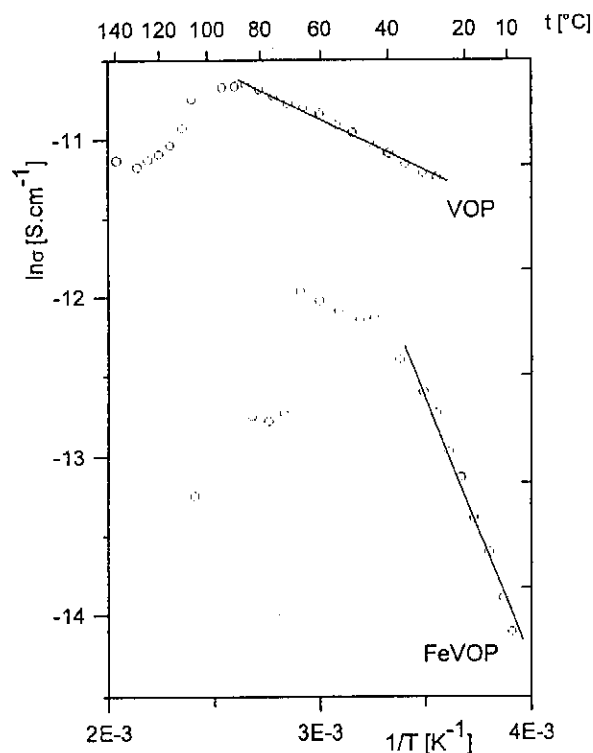


Fig.1 Temperature dependence of the total conductivity for parent $VOPO_4 \cdot 2H_2O$ and FeVOP as an example of modified vanadyl phosphate

Table I Activation energies of the total conductivity E_A and the total conductivities σ_{25} extrapolated to 25 °C of the hydrated forms of the samples

Sample	E_A , kJ mol ⁻¹	$\sigma_{25} \times 10^6$, S cm ⁻¹
$VOPO_4 \cdot 2H_2O$	17.34	85.20
FeVOP	33.72	2.43
MnVOP	26.11	0.84
CrVOP	27.09	22.32
AlVOP	25.95	4.94
GaVOP	30.70	7.49

The degree of the ionic conductivity is close to 100 per cent in all the samples studied. Parent $VOPO_4 \cdot 2H_2O$ has the values of the total and electronic conductivities about one order higher than those of modified vanadyl phosphates in wet nitro-

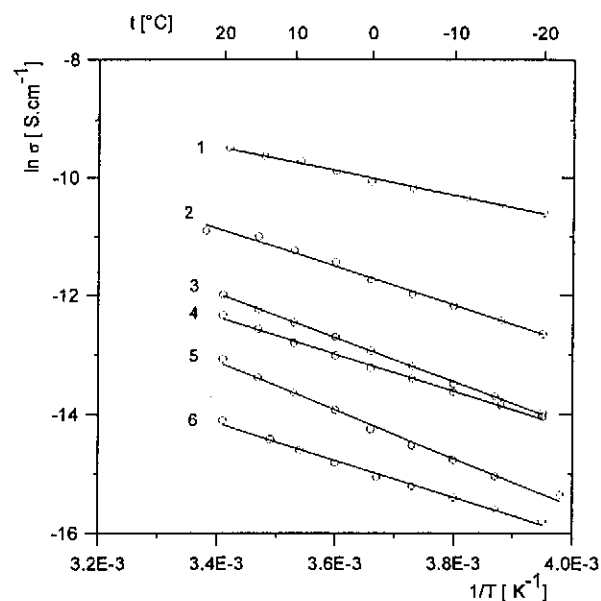


Fig.2 Temperature dependence of the total conductivity in low-temperature region for modified vanadyl phosphates and parent $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$: 1 – $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, 2 – CrVOP, 3 – GaVOP, 4 – AlVOP, 5 – FeVOP, 6 – MnVOP

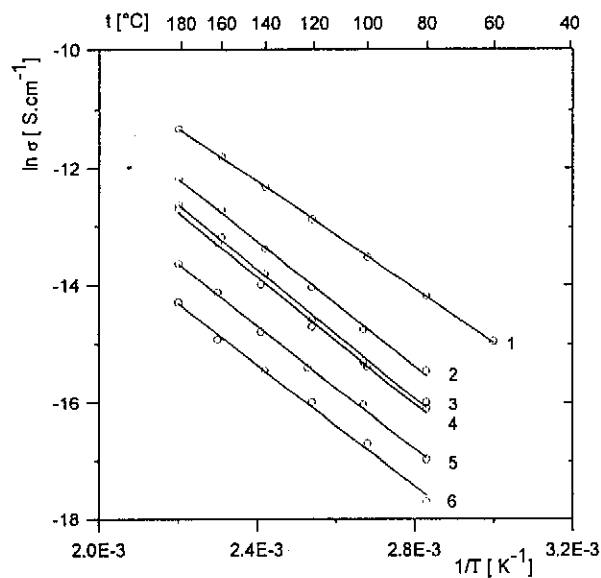


Fig.3 Temperature dependence of the total conductivity for anhydrous modified vanadyl phosphates and parent VOPO_4 : 1 – VOPO_4 , 2 – FeVOP, 3 – GaVOP, 4 – CrVOP, 5 – MnVOP, 6 – AlVOP

Table II Activation energies of the total conductivity E_A and the total conductivities σ_{25} extrapolated to 25 °C of the anhydrous forms of the samples

Sample	E_A , kJ mol ⁻¹	$\sigma_{25} \times 10^9$, S cm ⁻¹
VOPO ₄	37.88	63.1
anhydrous FeVOP	44.00	11.2
anhydrous MnVOP	43.75	2.8
anhydrous CrVOP	45.02	5.4
anhydrous AlVOP	43.30	1.5
anhydrous GaVOP	45.45	5.9

Table III Comparison of the AC and DC conductivities of the VOPO₄·2H₂O and modified vanadyl phosphates at 25 °C and 58% of relative humidity

Sample	$\sigma_{AC} \times 10^6$, S cm ⁻¹	$\sigma_{DC} \times 10^6$, S cm ⁻¹	σ_{DC}/σ_{AC}	Ionic conductivity, %
VOP	87.89	0.780	0.009	99.1
FeVOP	2.97	0.134	0.045	95.5
MnVOP	4.10	0.178	0.043	95.7
CrVOP	13.76	0.346	0.025	97.5
AlVOP	8.34	0.236	0.028	97.2
GaVOP	8.35	0.170	0.020	98.0

gen atmosphere. Based on an assumption that protons are the only possible mobile ions in these compounds, the ionic conductivity can be considered to be solely a protonic conductivity. Like the parent VOPO₄·2H₂O, modified vanadyl phosphates are, therefore, mixed protonic-electronic conductors with prevailing protonic conductivity. The statement agrees well with the results of the electromotive force measurements (EMF) [8,12].

The measurements of the AC and DC conductivities were carried out to investigate contribution of the electronic conductivity of the samples formed as dihydrate, monohydrate and anhydrous compounds. Two of the substituted vanadyl phosphates, those modified by Cr³⁺ and Al³⁺ ions, were selected for this measurement. The AC and DC conductivity measurements of the hydrated forms of the samples were carried out at 25 °C in dry nitrogen atmosphere. Then the samples were kept at 51 °C and 65 °C for two days. It is presumed that these conditions are sufficient for the formation of the monohydrates. After cooling to room temperature, the AC and DC conductivities of the monohydrates were measured immediately.

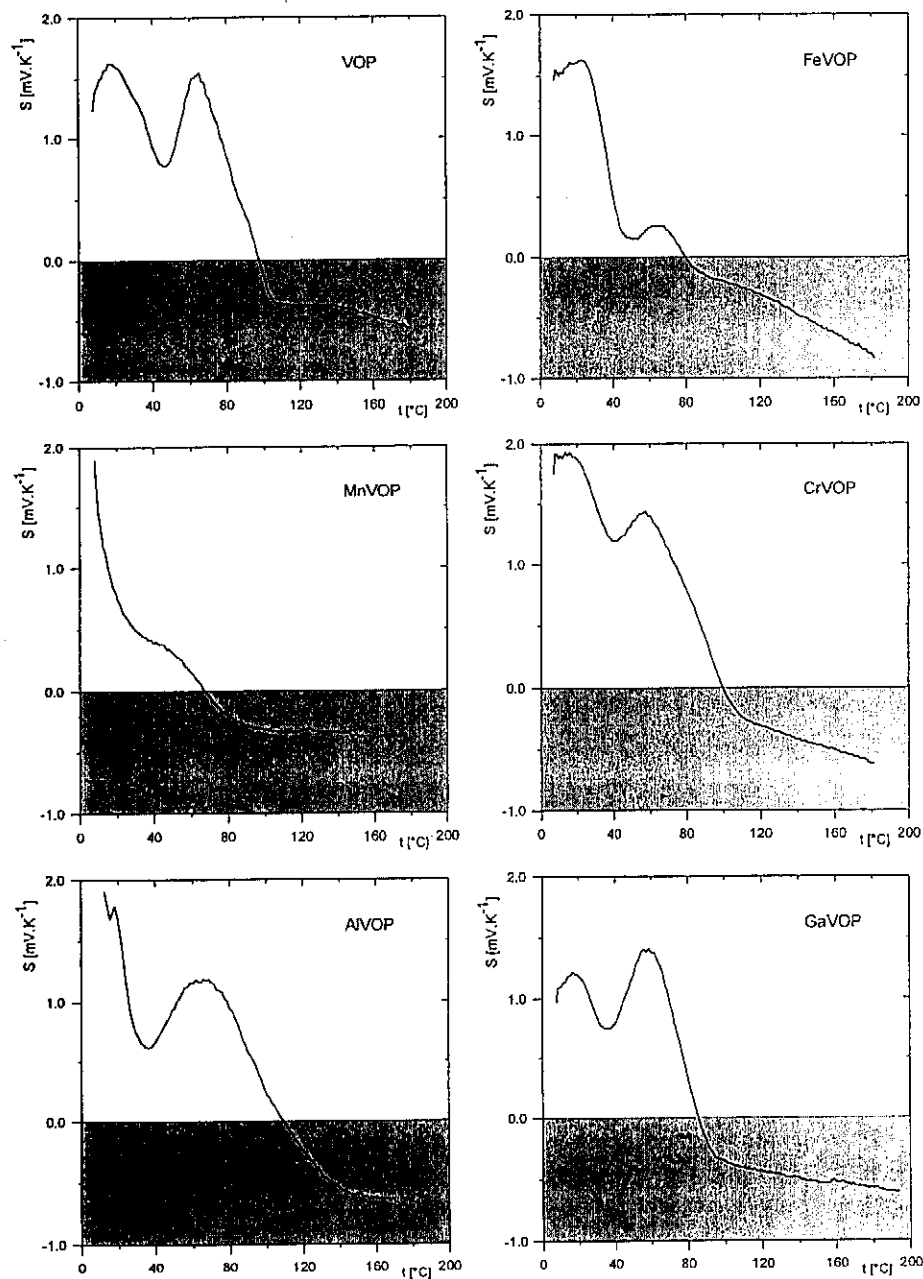


Fig.4 Temperature dependence of the Seebeck coefficient for $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ and modified vanadyl phosphates

Table IV AC and DC conductivities at 25 °C in dry nitrogen atmosphere for CrVOP and AIVOP samples as dihydrates, monohydrates and anhydrous

Sample	CrVOP			AIVOP		
	$\sigma_{AC} \times 10^6$, S cm ⁻¹	$\sigma_{DC} \times 10^6$, S cm ⁻¹	Ionic conductivity, %	$\sigma_{AC} \times 10^6$, S cm ⁻¹	$\sigma_{DC} \times 10^6$, S cm ⁻¹	Ionic conductivity, %
dihydrate	5.232	0.096	98.2	1.032	0.025	97.6
monohydrate	0.464	0.118	74.6	0.160	0.053	66.9
anhydrous	0.010	0.009	10.0	0.002	-	-

Subsequently, the CrVOP and AIVOP samples were heated up to 180 °C to form anhydrous compounds and the AC and DC conductivities were measured at 25 °C. The results of this conductivity investigation are given in Table IV (the anhydrous form of vanadyl phosphate modified by Al³⁺ was not measured because of its very low conductivity). The samples in the form of dihydrates show prevailing ionic (protonic) conductivity. The loss of one of two molecules of hydrate water decreases the ionic conductivity and the anhydrous CrVOP sample is an electronic conductor.

The thermoelectric power of modified vanadyl phosphates and VOPO₄·2H₂O was investigated as a temperature dependence of the Seebeck coefficient (*S*). The shape of this dependence is similar for all the samples and the value of *S* decreases in two steps (Fig. 4) with increasing temperature. After the first drop at 20 °C, the Seebeck coefficient retains its positive value. The second drop at 60 – 70 °C changes the sign of *S* to negative values. This indicates the change in the conductivity mechanism in the sample from protonic to electronic. It can be considered that both drops of the Seebeck coefficient are closely related to the dehydration steps of the samples [13]. A discrepancy between the temperatures of the dehydration of the intercalates observed by thermal analysis [4] and the thermoelectric power measurements can be given by a difference between temperature of the electrodes in the Seebeck coefficient measurements.

Conclusion

Modified vanadyl phosphates with the general formula [M(H₂O)]_x(VO)_{1-x}PO₄·2H₂O (M = Fe, Mn, Cr, Al a Ga, x = 0.15 – 0.25) possess similar electrical properties as the parent VOPO₄·2H₂O. The compounds are mixed protonic-electronic conductors. Protons generated by the dissociation of water molecules are prevailing charge carriers in the dihydrate forms of the samples, whereas anhydrous compounds appear to be electronic conductors. Lower conductivity of modified

vanadyl phosphates compared with parent $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ is probably caused by lower acidity of the $(\text{M}_x\text{VOPO}_4)_\infty$ layers, which leads to suppression of the dissociation of water molecules and consequently to lower concentration of H^+ ions. Moreover, rotation of the H_3O^+ ions through the Grotthus-type charge transfer of protons is hindered due to the smaller basal spacing [14]. Protons are also less mobile due to the stronger interactions between water molecules and $(\text{M}_x\text{VOPO}_4)_\infty$ layers. Trivalent metal cations reduce charge transfer by electrons along the layers, thus modified anhydrous vanadyl phosphates are less conducting compounds than VOPO_4 . The influence of the type of trivalent cation or its content in the layers on conductivity was not observed.

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