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Dielectric properties and electrical conductivity of the hybrid organic–inorganic polyvanadates $(H_3N(CH_2)_4NH_3)[V_6O_{14}]$

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ABSTRACT

Plate-like crystals of the polyvanadate $(H_3N(CH_2)_4NH_3)[V_6O_{14}]$ have been synthesized via an hydrothermal treatment. X-ray powder diffraction, scanning electron microscope, Fourier transform infrared spectroscopy, electron spin resonance and complex impedance spectroscopy were used to analyze the hybrid material. The frequency dependence of AC conductivity at different temperatures indicates that the CBH model is the probable mechanism for the AC conduction behavior. The conductivity was measured by complex impedance spectroscopy which is equal to $31.10^{-3}\ \Omega^{-1}\ m^{-1}$ at 443 K. The Arrhenius diagram is not linear, it presents a rupture situated at 357 K and the activation energies' average values are 0.22 eV and 0.14 eV, deduced from the Arrhenius relation.

1. Introduction

Vanadium pentoxide with tunable oxidation states (V^{5+}, V^{4+}) has been extensively used as a well-known transition metal oxide. The lithium vanadate $Li_xV_2O_5$ has attracted a great interest because of high conductivity of lithium ion to gain a high cathode utility of a cell and mixed conduction to increase the charge–discharge efficiency [1,2].

We are especially interested in hybrid organic–inorganic material because they combine a layered structure suitable for the insertion reaction with electrochemical properties and a mixed ionic–electronic conductivity [3–5]. In particular, there has been much interest in the vanadium oxides because of the incorporation of protons or alkali ions into their lattices to form electronically conducting compound [6,7]. Incorporation of the two counterparts into a single structure may generate organic–inorganic hybrid vanadium oxides and combine their properties in various fields such as catalysis, medicine, molecular electronics, magnetism and photochemistry [8–10].

The crystalline V_2O_5 is currently used as a precursor and several vanadium oxides have been recently synthesized using amines, ammonium cations ($N(CH_3)_4^+$, CH_3NH_2) or diamines $H_2N{-}(CH_2)_n{-}NH_2$ ($n=2$; 3, 4) as organic templates [11–20]. They all exhibit a layered structure in which protonated amines are inserted between negatively charged vanadium oxide planes. It has been shown that the structure of the layers and particularly the coordination of vanadium centers are strongly dependent on the pH of the aqueous solution.

This paper deals with the hydrothermal synthesis, dielectric properties and electrical conductivity of the mixed valence polyvanadates $(H_3N(CH_2)_4NH_3)[V_6O_{14}]$ plate-like crystals. To our knowledge, no report on the dielectric properties and electrical conductivity of the material has been conducted so far. Indeed, an effort is made to discuss the electrical/dielectric properties in the mixed valence polyvanadates $(H_3N(CH_2)_4NH_3)[V_6O_{14}]$ in order to propose a model process, therefore, explaining the origin of their electric properties.

2. Experimental

2.1. Synthesis

The synthesis of $(H_3N(CH_2)_4NH_3)[V_6O_{14}]$ was performed according to an earlier publication [19]. This synthesis involves on the dissolution of crystalline V_2O_5 (0.207 g, Aldrich 99%), 1,4-diaminobutane (0.1 g, Aldrich 99.6%) in H_2O (5 mL) with a molar ratio 1:1:245. The mixture was heated under hydrothermal conditions (48 h, 453 K) in a Parr Teflon-lined digestion bomb. Black plate-like crystals are precipitated from the solution (Fig. 1). The scanning electron micrographs shows that the as-obtained material is made of a homogenous phase with particles uniformly sized about $2 \times 0.4 \times 0.05\ mm^3$ which presents a lamellar morphology.

2.2. Measurements

The X-ray powder diffraction (XRD) patterns of all samples were recorded on an X'Pert Pro Panalytical diffractometer using

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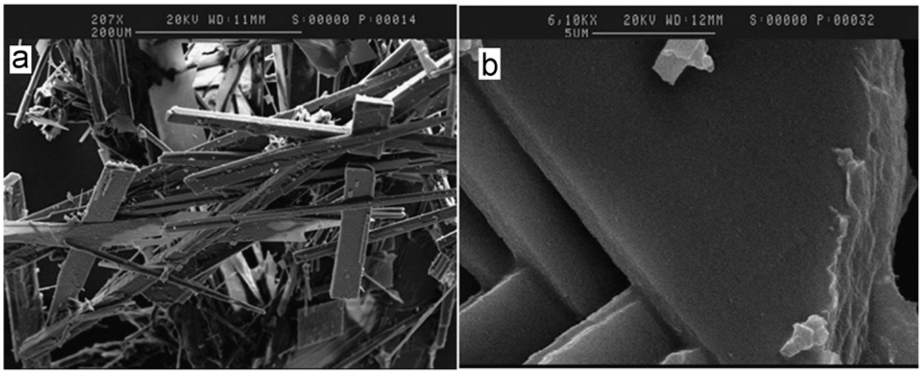

Fig. 1. Plate-like crystals SEM micrograph of $(NH_3(CH_2)_4NH_3)[V_6O_{14}]$.

Cu K_α radiation ($\lambda = 1.54186$ Å) and graphite monochromator. The XRD measurements were carried out by a step scanning method (2θ range from 2° to 50°), the scanning rate is 0.03 °/s and the step time is 3 s.

Solid samples were coated with gold in a Balzers Union SCD 40 sputter-coater and studied by Scanning Electron Microscopy (SEM) with a Cambridge Stereoscan 120 instrument at an accelerating voltage of 10 kV.

Infrared spectra were recorded on a Nicolet 360 spectrometer using KBr pellets in the region of 4000–400 cm^{-1}.

ESR spectra were recorded on a X-band Brucker spectrometer ($v = 9.47$ GHz) equipped with a heating device.

The electrical conductivity measurements were performed using a two-electrode configuration. The finely grain samples were pressed into pellets of 13 mm diameter and 0.7 mm thickness using a hydraulic press at a pressure. The measurements were performed as a function of both temperature (290 K to 428 K) and frequency (5 Hz to 13 MHz) with 3 °C steps, employing a Hewlett-Packard 4192 A LF automatic bridge monitored by a HP Vectra microcomputer. To ensure good electrical contact between the sample and the electrical junctions a layer of silver paint was deposited on the surfaces of the pellet. The DC conductivity (σ_{dc}) is obtained by using the iterative non linear-least-squares fitting. The value of R^2 (regression coefficient indicating goodness of fit) for all the fittings, is in excess of 0, 98,905. The fitting was done using Microcal Origin 6.0.

3. Results and discussion

3.1. X-ray diffraction

The X-ray diffraction pattern of a powder exhibits the peaks typical of a layered structure (Fig. 2). The compound is the layered hybrid vanadates $(H_3N(CH_2)_4NH_3)[V_6O_{14}]$ which crystallizes in the monoclinic system with the following unit cell parameters $a = 9.74(2)$ Å, $b = 6.776(5)$ Å, $c = 12.60(2)$ Å, $\beta = 96.1(1)$, $V = 827(2)$ $Å^3$ and $Z = 2$ [19]. This compound contains mixed-valence V^{5+}/V^{4+} vanadium oxide layers built from $[V^{V}O_4]$ tetrahedra and pairs of edge-sharing $[V^{IV}O_5]$ square pyramids with protonated organic amines occupying the interlayer space. No peaks of any other phases or impurities were detected from XRD patterns, indicating the high purity of the products.

3.2. Infrared spectroscopy

The FTIR spectrum of the as-synthesized $[NH_3(CH_2)_4NH_3][V_6O_{14}]$ plate-like crystals is shown in Fig. 3. The bands centered between 500 cm^{-1} and 1000 cm^{-1} can be attributed to various vibration of V–O type. Indeed, the band located at 989 cm^{-1} corresponds to $V{=}O$ stretching mode [20–22]. The bands in the range of 1390–1467 cm^{-1} are assigned to characteristic peaks of C–N and C–C [23]. The band at about 1660 cm^{-1} is ascribed to the stretching mode of N–H and O–H vibration. The band situated at around 3428 cm^{-1} is related to the bending mode of N–H and O–H vibration [24–27]. The band located at 3083 cm^{-1} is due to protonated $[-NH_3]^+$ vibrations in $(H_3N(CH_2)_4NH_3)^{2+}$. While, the band located at 2844 cm^{-1} is related to the axial stretching of aliphatic C–H groups [27].

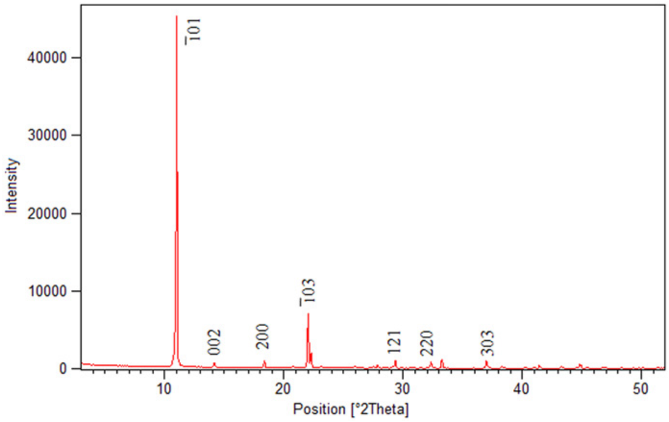

Fig. 2. X-ray diffractogram of $(NH_3(CH_2)_4NH_3)[V_6O_{14}]$.

3.3. Electron spin resonance

The low temperature electron spin resonance spectrum of the title compound $[NH_3(CH_2)_4NH_3][V_6O_{14}]$ recorded at 77 K exhibits a broad signal with a poorly resolved hyperfine structure (Fig. 4(a)). It can be represented by the axial spin Hamiltonian:

$$H = g_{//}\beta H_z Sz + 2g\,\beta(H_x Sx + H_y Sy) + A_{//} Sz I_z + A(S_x Ix + S_y Iy)$$

where the parallel direction "z" corresponds to the short $V{=}O$ bond. The parallel features measured on the spectrum give: $g_{//} = 1936$ and $A_{//} = 182$ Gauss. These values are typical of V^{4+} ions ($S = 1/2$, $I = 7/2$) in a $[VO_5]$ environment [28–30]. The overall shape of the ESR signal does not change at room temperature (Fig. 4(b)) but the line width broadens suggesting some electron delocalization between V^{4+} and V^{5+} ions.

3.4. Impedance analysis

Cole–Cole plots for $[NH_3(CH_2)_4NH_3][V_6O_{14}]$ in the temperature range 290–393 K are displayed in Fig. 5. The impedance diagrams show a typical semicircle response which became smaller with increasing temperature. At lower frequencies a spike is observed