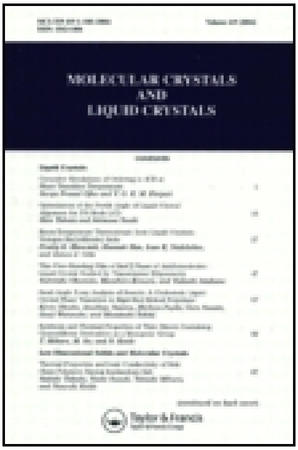

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Pressure Induced Anisotropic Electrical Conductivity in Vanadium (V) Oxide-Based Tubular Structures

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PRESSURE INDUCED ANISOTROPIC ELECTRICAL CONDUCTIVITY IN VANADIUM (V) OXIDE-BASED TUBULAR STRUCTURES

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The hydrothermal treatment of vanadium pentoxide xerogel previously intercalated with long-chain primary amines leads to micro and nano-tubular products whose walls are conformed by amine bilayers sandwiched between V_2O_5 lamellae. The microcrystalline powder product may be partially ordered at a macroscopic scale by pressure. Effects of the pressure are observed in the morphology, the intensity of the reflections in the X-ray diffractograms as well as in the electrical conductivity. The anisotropy degree estimated as the ratio of the electrical conductivities perpendicular and parallel to the direction of the applied pressure is about 10^2 at room temperature.

INTRODUCTION

During the last years an increasing interest in the synthesis and properties of nanostructured materials like layered nanocomposites and nanotubes

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has been observed [1,2]. Potential nanotechnological applications of these products in fields like the electrochemistry [3], the electronic [4], or the optic [5] have encouraged the development of new knowledge in this area [6]. Moreover, the formation of such kind of structures implying interesting phenomena like molecular recognition, self-assembling and/or template assisted synthesis of new supramolecular structures [7] as well as the size effects on the properties of chemical species observable at the nanometer scale make these studies being relevant contributions to fundamental knowledge.

Beyond the chemistry of carbon nanotubes, which has reached a relatively high development, much attention has been focused now in the transition metal oxide and sulfide nanotubes [8,9,10]. Indeed, the synthesis and characterization of many tubular species derived of compounds like ZrS_2, $NbSe_2$, have been described [11,12]. Although in most of the cases the goal of the studies have been the obtaining of pure oxide or sulphide nanotubes, the preparation of some functionalized products, like the single wall MoS_2 nanotubes doped with iodine or the multiwall V_2O_5 nanotubes intercalated with amines, have been reported [13,14]. Specially interesting is the procedure discovered by Nesper *et al.* for synthesising vanadium oxide nanotubes (VO_x–NTs) with very good yields by hydrothermal reactions using different amines as templates [15,16].

Considering intrinsic anisotropy of nanostructured layered and tubular products, we are focussing our attention on the preparation of macroscopic relatively ordered microcrystalline samples with anisotropic properties. In this work, we describe the synthesis of layered V_2O_5-amine nanocomposites which are then used as precursor for the preparation of VO_x–NTs as well as the use of pressure for manufacturing specimens of the nanotube samples in which an appreciable anisotropy degree is induced.

EXPERIMENTAL DETAILS

The (VO_x–NTs) nanotubes were produced from a V_2O_5 xerogel by a hydrothermal treatment.

A mixture of t-butyl alcohol and orthorhombic V_2O_5 was refluxed for 6 h to form the xerogel. Water was added to the resulting dark yellow solid and the remaining *t*-butyl alcohol was removed together with water excess under vacuum. Water was added to obtain a suspension. The material was aged at room temperature yielding a red-brown colloidal V_2O_5.

The xerogel and a primary amine hexadecylamine (**HDA**) molar ratio 1:2 were stirred in ethanol for 2 h and left aging for 2 days. The composite was transferred into a Teflon-lined autoclave and held at 180°C for 3 days under auto generated pressure. The product was washed with deionised water an alcohol several times and then dried under vacuum.

Compositions were determined by elemental chemical analysis (SISONS model EA-1108) and atomic absorption spectrometry (UNICAM 929). Further characterization was performed by X-ray diffraction analysis (SIEMENS D-500, Cu-Kα, $\lambda = 1.5418\,\text{Å}$, operation voltage 40 kV, and current 30 mA); scanning electron microscopy (Phillips M300, XL-30); and transmission electron microscopy (JEOL 100-SX). Elemental analysis calculated for V_2O_5 $(HDA)_{0.69}$: N: 2.44 (2.63); C: 35.18 (36.12); H: 7.20 (7.00).

The samples for electrical measurements were prepared by pressing the polycrystalline powder at 2.29 Mpa, in a specially designed die, to obtain parallelepiped pellets of about $5 \times 5 \times 2\,\text{mm}^3$. The density was determined from the weight and volume of the samples. Microscopic ordering was investigated observing the faces parallel and perpendicular to the direction of the applied pressure by SEM.

The electrical conductivity were measured by electrochemical impedance spectroscopy with an AUTOLAB potentiostat/galvanostat PG-STAT12 and frequency response analyzer, FRA module, using ion blocking electrodes built by sputtering a film of about 300 Å gold on opposite faces of the pellets.

RESULTS AND DISCUSSION

Synthesis of Precursors

The precursors used for the synthesis of V_2O_5 based nanostructured materials were obtained by the intercalation of long-chain primary alkyl amine into the vanadium pentoxide xerogel. The products have layered structures with interlaminar spaces in the range 37–43A; this distance, which may be univocally determined by powder X-ray diffraction analysis of the samples, increases with increasing length of the amines. Observed features may be well described by a model considering the products as an intercalation compound in which a bilayer of the amine has been inserted in the 2-D space of the inorganic host. Such a process may be considered as an exchange reaction where water molecules existing between the VO_x layers are replaced by the amine.

$$\begin{aligned} &V_2O_5 * 1.5H_2O + C_nH_{2n+1}NH_2(n = 12,\ 16,\ 18) \\ &\quad \rightarrow\ V_2O_5(C_nH_{2n+1}NH_2)_{x(x\approx 0.30)} \end{aligned}$$

The self assembling of the host as a bilayer in the interlaminar spaces is certainly expected because of the amphiphilic properties of these amines which may be considered as neutral surfactants [17,18].

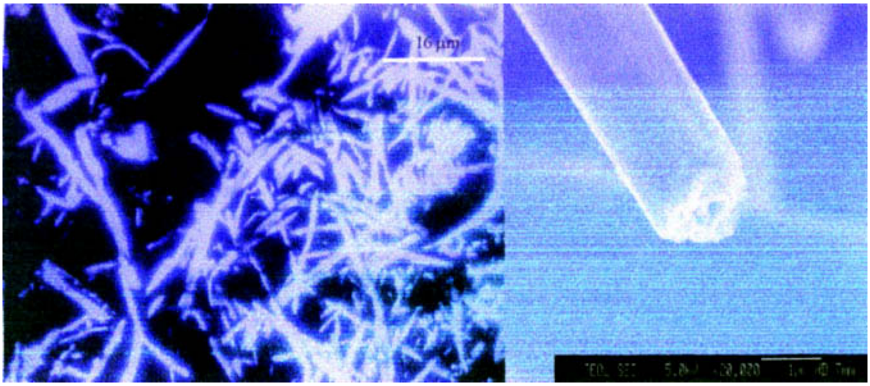

FIGURE 1 SEM image of hydrothermal product of vanadium pentoxide compounds (right), SEM image the microtube of vanadium pentoxide (left).

Synthesis of Nanostructured Products

The treatment of these laminar organic-inorganic nacomposites under hydrothermal conditions leads to nanostructured products, that agreeing with results first described by Nesper *et al.* [15]. The SEM and TEM microgra-

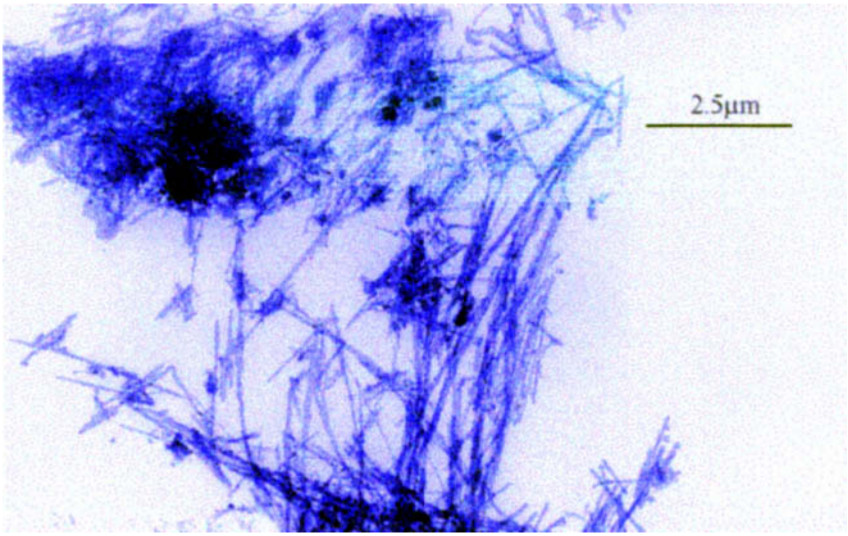

FIGURE 2 TEM image of hydrothermal product of vanadium pentoxide compounds.

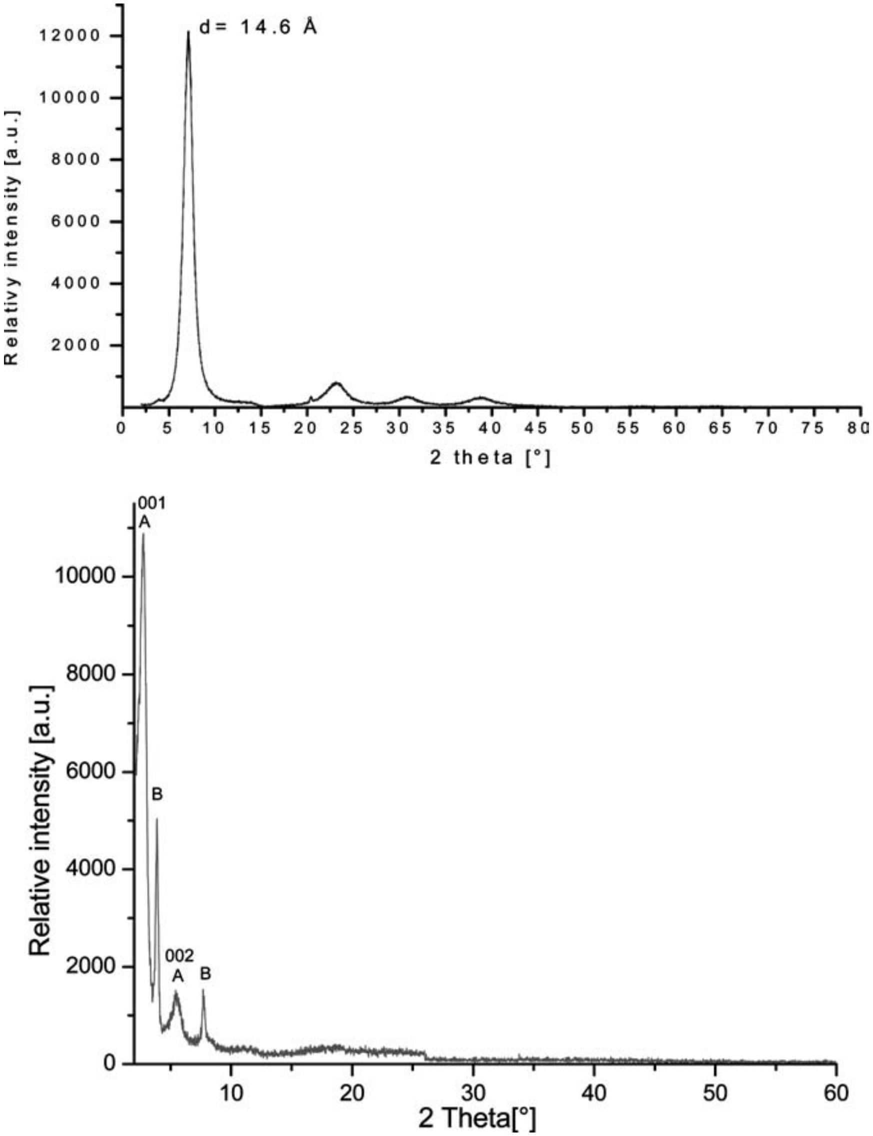

FIGURE 3 Powder X-ray diffraction pattern of Xerogel vanadium pentoxide (top) and a XRD pattern of V_2O_5 $(HDA)_{0.69}$ (bottom), we observed in this difractogram two sets of reflections (A and B) representing two kind of layers distances. The peak (A) with highest intensity at $2\theta = 2.73$ and the peak (B) with the highest intensity at $2\theta = 3.87$.

phies of the black powder obtained directly from the hydrothermal reaction are shown in Figures 1 and 2 respectively. A mixture of micro and nanotubes is observed; best results are obtained using the hexadecylamine. In Figure 3 is illustrated the powder X-ray diffraction pattern of the same rough product where the presence of at least two phases may be identified; that agrees with the observation of Y. Li [19], who also established that the products is a mixture of nano and micro tubular structures However, well formed nanotubes, like those shown in Figure 4, are an important part of the sample $V_2O_5\text{-}(HDA)_{0.69^*}1.03\ H_2O$. In the diffractogram of this product are clearly identified the 001 Brag plane diffractions indicating a high ordered laminar system. Observed interlaminar distance for the case of the HDA is 3.42 nm, a feature which agrees well with the length of the amine alkyl chain. Similarly to laminar compounds commented above, the walls of the tubes would be constituted by amine bilayers sandwiched

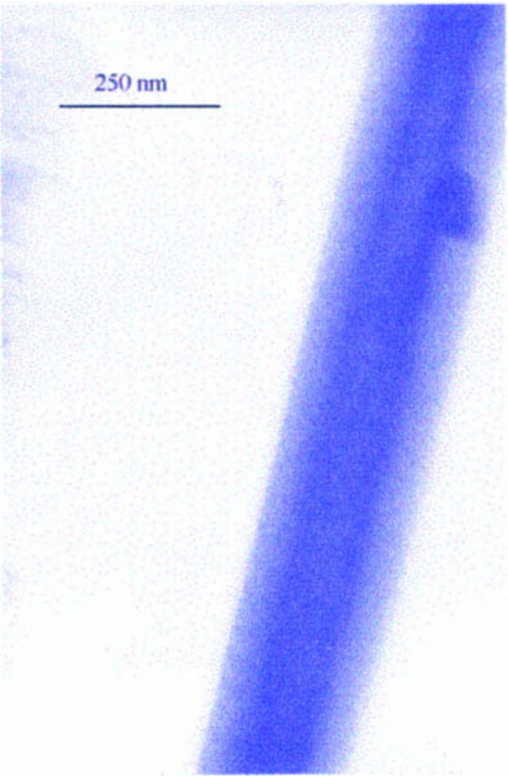

FIGURE 4 TEM image a nanotube of vanadium pentoxide compounds.

between V_2O_5 lamellae. Molecular dynamic calculations [20] confirm such a description.

Macroscopic Ordering

Considering the high anisotropy of the tubular structures contained in the samples discussed above, experiments directed to reach a macroscopic ordering were performed by pressing the powders in a special die (see scheme in Fig. 5). Resulting parallelepipedal pellets clearly show morphological, structural, as well as electrical anisotropic properties.

In Figure 5 are shown SEM micrographies of the sample before and after pressing the powder. Especially interesting are the fissures which appear to be not randomly distributed but following some preferential directions.

The comparison of the X-ray diffraction patterns of the powder sample before and after pressing shows that the intensity of the observed 00l reflections increases significantly (see Figs. 3 and 6). This phenomena,

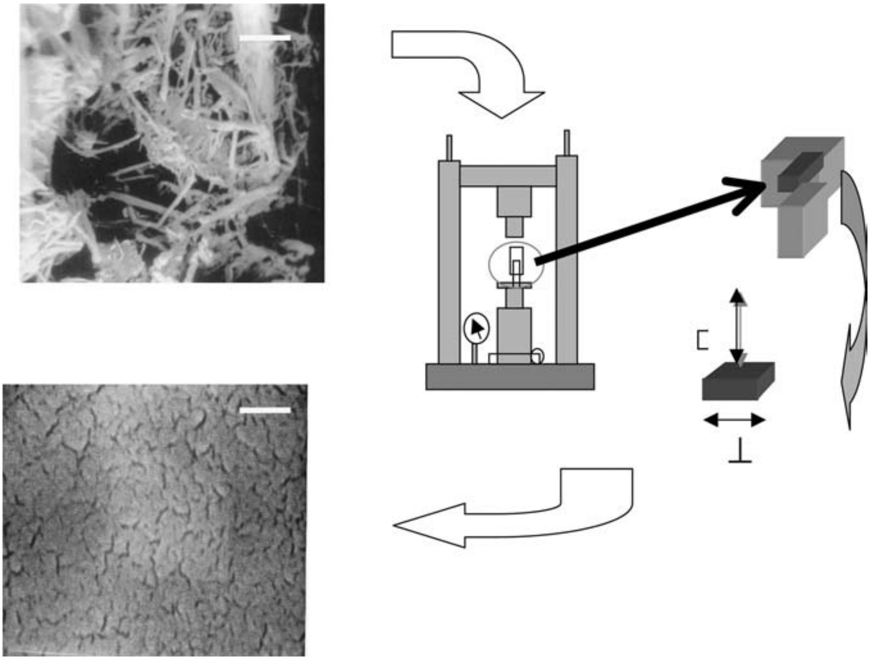

FIGURE 5 Diagram to how come the samples are prepared by pressing un ordered V_2O_5 nanotubes into a paralepiped, in the SEM micrographics the bar is equal a 4 µm.

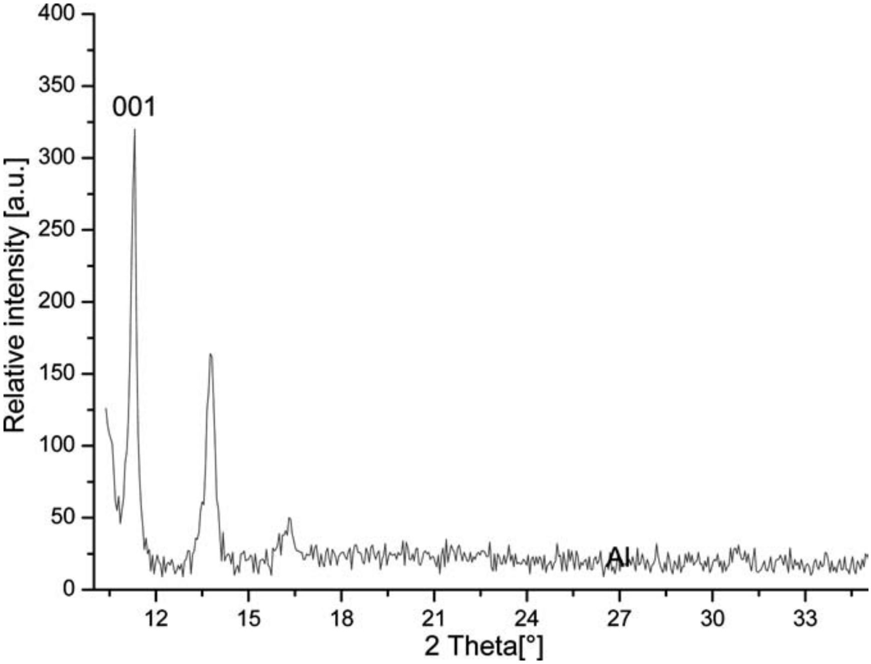

FIGURE 6 Wide–angle X-ray (XRD) patterns of pellets of vanadium pentoxide compounds V_2O_5 $(HDA)_{0.69}$.

which has also been observed in layered intercalates [20], may be ascribed to the existence of preferential orientations of the intrinsically anisotropic powder grains or micro crystals in the pellets.

The more notorious effect of the pressure in the studied samples was observed in the measurements of the electrical conductivity of the pressed samples. As observed in Figure 7, the conductivity is about two orders of magnitude larger in the direction perpendicular to the applied pressure ($\sigma_\perp$) than in the parallel one ($\sigma_{||}$). As expected, the conductivity increases with increasing temperature and the Arrhenius plots always show, in the measured temperature range, a nearly linear behavior. From these slopes apparent activation energy for the process may be calculated (see Table 1).

Such a behavior should arise principally from two components, the intrinsic difference between the conductivity along and through the walls of the tubes and the difference between the intergrains resistance in both directions. Thus, starting from an statistical orientation of the tubes which changes when pressure is applied, the resistance of the system could be thought of as a parallel circuit of two resistors $R_{//}$ and $R_\perp$, which are proportional to the product of both, the specific resistance in each direction

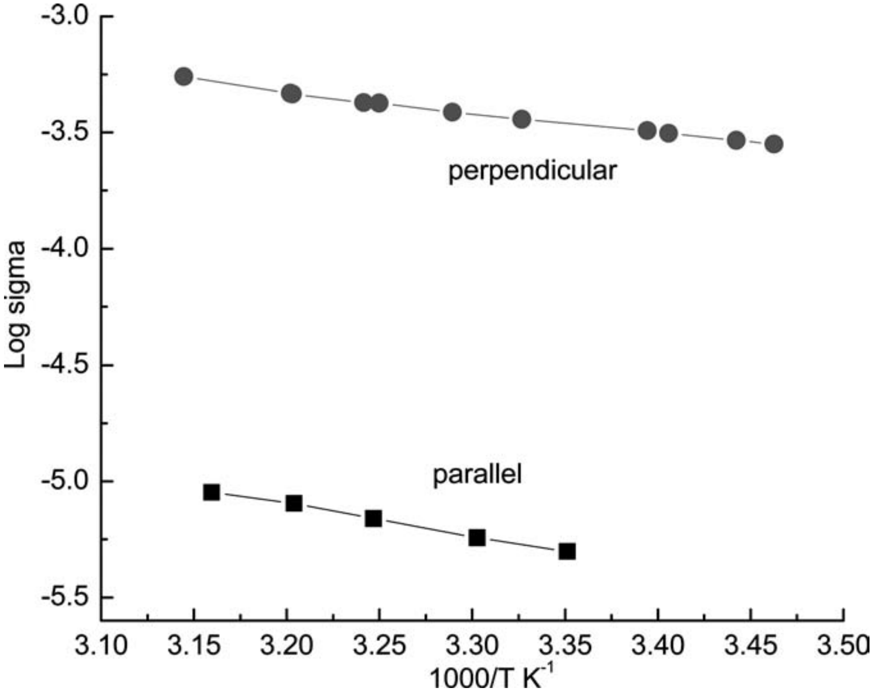

FIGURE 7 Arrhenius Plots of the conductivity measured parallel and perpendicular to applied pressure show an anisotropic ratio of about 10^2 for the conductivity.

and a number equivalent to the ratio of parallel to perpendicular tubes with respect to the direction of applied pressure. Since the electrical conductivity of vanadium pentoxide derivatives in the direction parallel to the tube long axe, like that of molybdenum disulfide amine intercalate lamellae, it may be assumed that the electrical conductivity observed in both directions, at least at relatively low and medium pressures, corresponds almost entirely to the contribution of the tubes oriented in the same direction, that perpendicular to the direction of the applied pressure. Although the

TABLE 1 Electrical Conductivity of V_2O_5 $(HDA)_{0.69}$

	σ (S cm.$^{-1}$) a 25°C	E_a (kJ mol^{-1})	E_a (eV)	Regretion coefficient
Perpendicular ($\sigma_\perp$)	$3.45 \cdot 10^{-4}$	33.14	0.34	0.9964
Parallel ($\sigma||$)	$4.90 \cdot 10^{-6}$	52.12	0.54	0.9966

resistance associated to inter-grain distances should be different for particles oriented parallel or perpendicularly to each other, considering the discussion above, the contribution of inter-grain resistance to the observed conductivity in the pressed pellets could be considered, in a first approach, to be the same in both directions. The similarity of the activation energies ($E_{a||}/E_{a\perp} = 1.58$) in both directions, estimated from the dependence of the conductivity on the temperature commented above, agrees with such an interpretation [21,22,23].

CONCLUSIONS

The tubular products obtained from the hydrothermal treatment of lamellar V_2O_5 xerogel with long chain primary amines may be ordered in some extend by pressure. Induced anisotropy may be detected by structural changes in X-ray diffractograms, by the morphology of the surfaces and, specially, by the electrical conductivity. Thus, the anisotropy degree obtained from the ratio of the conductivity along the directions perpendicular and parallel to the applied pressure reach a value of ca 10^2.

REFERENCES

[1] Ajayan, P. M., Sthepane, O., Redclich, Ph., & Colliex, C. (1995). *Nature*, *117*, 265.

[2] Rao, C. N. R. & Nath, M. (2003). *Dalton Trans.*, 1–24.

[3] Dobley, A., Ngala, K., Yang, S., Zayalji, P. Y., & Whittingham, M. S. (2001). *Chem. Mater.*, *13*, 4382.

[4] Saito, S., Sawada, S. I., Hawada, M., & Oshima, A. (1993). *Mater. Sci. Eng*, *B19*, 105.

[5] (a) Tenne, R., Margulis, L., Genut, M., & Hodes, G. (1992). *Nature*, *360*, 444.
(b) Feldman, Y., Wasserman, E., Srolovich, D. J., & Tenne, R. (1995). *Science*, *267*, 222.

[6] A special issue on nanoscale materials, (1999). *Acc. Chem. Res.*, *32*.

[7] Lehn, J. M. (1995). "Supramolecular Chemistry", VCH Verlagsgesellschaft.

[8] Zelesky, C. M. & Dorhout, P. K. (1998). *J. Am. Chem. Soc.*, *120*, 734.

[9] Zhu, Y. Q., Hsu, W. K., Grobert, N., Chang, B. H., Terrones, M., Terrones, H., Kroto, H. W., & Walton, D. R. M. (2000). *Chem. Mater.*, *12*, 1190.

[10] Jun, C., Suo-Long, L., Zhan-Liang, T., & Feng, G. (2003). *Chem. Commun.*, 980–981.

[11] Nath, M. & Rao, C. N. R. (2002). *Ang. Chem., Int. Ed.*, *41*, 3451.

[12] Gálvan, D. H., Kim, J.-H., Maple, M. B., Avalos-Berja, M., & Adem, E. (2000). *Fullerene Sci. Technol.*, *8*, 143.

[13] Krumeich, F., Muhr, H. J., Nierderberger, M., Bieri, F., Schnyder, B., & Nesper, R. (1999). *J. Am. Chem. Soc.*, *121*, 8324.

[14] Dobley, A., Ngala, K., Yang, S., Zavalji, P. Y., & Whittingham, M. S. (2001). *Chem. Mater.*, *13*, 4382.

[15] Spahr, M. E., Bierly, P. S., Nesper, R., Haas, O., & Novak, P. (1999). *J. Electrochem. Soc.*, *146*, 2780.

[16] Rao, C. N., Govindaraj, A. G., Deepak, F. L., Gunary, N. A., & Nath, M. (2001). *Appl. Phys. Lett.*, *78*, 1853.

[17] Yang, P., Deng, T., Zhao, D., Feng, P., Pine, D., Chmelka, B. F., Whitesides, G. W., & Stucky, G. (1998). *Science*, *282*, 2244.
[18] Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli, J. C., & Beck, J. C. (1992). *Nature*, *359*, 710.
[19] Xiang, C., Xiaoming, S., & Li, Y. (2002). *Inorganic Chemistry*, *41*, 4524.
[20] Benavente, E., Santa Ana, M. A., Mendizábal, F., & González, G. (2002). *Coord. Chem. Rev.*, *224*, 87.
[21] González, G, Santa Ana, M. A., Sanchez, V., & Benavente, E. (2000). *Mol. Cryst. Liq. Cryst., 353*, 301.
[22] Sánchez, V. (2000). Doctoral Theses, Universidad de Chile.
[23] Sánchez, V., Benavente, E., Santa Ana, M. A., & González, G. (1999). *Chem. Mater.*, *11*(9), 2296.