MULTIFUNCTIONAL TRANSITION-METAL CLUSTER BASED MATERIALS OF INTEREST IN THE FIELD OF THERMOELECTRICITY AND NANOTECHNOLOGIES

M. Guilloux-Viry, M. Potel, S. Cordier, V. Bouquet, P. Gall, P. Gougeon, F. Grasset, Y. Molard

Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS/University of Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, Frances

maryline.guilloux-viry@univ-rennes1.fr

Transition-metal cluster based solid-state family present a large variety of properties in relation with their specific electronic and structural characteristics. The properties depend strongly on the nature and on the condensation of the cluster. In the case of Mo clusters, different steps of condensation can be achieved which offer new potentialities which are nowadays of great interest in the field of energy and environmental applications.

Tetrahedral Mo_4 cluster constitutes building blocks for the design of clathrate-related giant frameworks [1]. Octahedral Mo_6 cluster is the origin of the well-known Chevrel phases series with the general formula $M_xMo_6X_8$ (where M is a cation and X=S, Se or Te). This series offers various properties like superconductivity [2] and unique insertion capabilities [3] in relation with the channels built up from the Mo_6X_8 units constituting a host network for a large variety of cations.

This opened structure has attracted considerable interest during the last decade in view of thermoelectric applications. Several compositions were investigated. In the $M_xMo_6X_8$ series $(Cu,Fe)_xMo_6Se_8$ was identified to be one of the best thermoelectric material with a ZT of 0.6 [4] Recently, a higher nuclearity molybdenum (Mo_9) cluster-based compound, $Ag_xMo_9Se_{11}$ (x=3.6-3.9) was evidenced to exhibit promising thermoelectric properties [5], notably with a low thermal conductivity resulting from its structural arrangement.

Moreover, the reversible insertion of cation in cluster-based compounds was early reported to be of great interest in the field of energy storage [6]. The high ionic mobility is still of great interest in this field [7] and also for electrochemical extraction and cation transfer [3]. Progress in elaboration of transition-metal clusters compounds open now the way to new applications and enhancement of performances. A new route of synthesis using a chemical solution precursor deposition gives access to $M_xMo_6S_8$ thin films. They were investigated for enhancement of electrochemical transfer junction for cation extraction [8], and are under study for development of metallic cation electrochemical sensor.

Finally, new trends appear recently with new achievements in the field of nanomaterials. Indeed, combining solid-state chemistry with solution chemistry and functionalization approach, transition-metal cluster based functionalized nanomaterials were synthesized. The resulting liquid crystals [9], co-polymers [10], multifunctional nanoparticles [11] open the way to new fields of applications.

After a brief presentation of transition-metal cluster based compounds, this talk will be divided in three parts: (i) transition-metal cluster materials of potentialities for thermoelectricity (ii) molybdenum cluster sulfides thin films for electrochemical devices (iii) new development in nanomaterials.

1- M. A Shestopalov,.A.Y. Ledneva, S. Cordier, O. Hernandez, M. Potel, T. Roisnel, N.G. Naumov, C. Perrin, Angew. Chem.-Int. Edit. **2011,** 50 (32), 7300-7303
2- A.P. Petrovic, R. Lortz, G. Santi, C. Berthod, C. Dubois, M. Decroux, A. Demuer, A.B. Antunes, A. Pare, D. Salloum, P. Gougeon, M. Potel, O. Fischer, Phys. Rev. Lett. **2011,** 106
3- S. Seghir, C. Boulanger, S. Diliberto, J.-M. Lecuire, M. Potel, O. Merdrignac-Conanec, Electrochemistry Communications 10 (2008) 1505–1508
4- T. Caillat, J. P. Fleurial, G. J. Snyder, Solid State Sci., **1999,** 1, 535

5- T. Zhou, B. Lenoir, M. Colin, A. Dauscher, R.A. Al Orabi, P. Gougeon, M. Potel, E. Guilmeau, Appl. Phys. Lett. **2011,** 98
6- J.M. Tarascon, T.P. Orlando, J.M. Neal, Journal of the Electrochemical Society, 1988, 135, 804-808
7- E. Levi, G. Gershinsky, D. Aurbach,bO. Isnard, G. Ceder| Chem. Mater. **2009,** 21, 1390–1399
8- S. Seghir, C. Boulanger, S. Diliberto, J.M. Lecuire, V. Bouquet, M. Potel, M. Guilloux-Viry, Electrochem. Commun. **2010,** 12 (12), 1734-1737.
9- Y. Molard, F. Dorson, V. Circu, T. Roisnel, F. Artzner, S. Cordier, Angew. Chem. Int. Ed. **2010,** 49, 3351 –3355
10- Y. Molard, F. Dorson, K.A. Brylev, M. A. Shestopalov, Y. Le Gal, S. Cordier, Y. V. Mironov, N. Kitamura, C. Perrin, Chem. Eur. J. **2010**, 16, 5613 – 5619
11- V. Roullier, V. Marchi-Artzner, O. Cador, F. Dorson, T. Aubert, S. Cordier, Y. Molard, F. Grasset, S. Mornet, H. Haneda, Int. J. Nanotechnol. **2010,** 7 (1), 46-57