



Experiment title: Structural investigation on inorganic-organic materials embedding transition metal oxoclusters

Experiment number:
08-01-790

Beamline:

Date of experiment:

from: 2.11.2007 to: 9.11.2007

Date of report:

12.3.2008

Shifts:

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Report:

The present experiment was the continuation of the previous Experiment n. 08-01-768, devoted to the investigation of inorganic-organic hybrid materials embedding two different zirconium oxoclusters [see ESRF Report 36671_A]. The results of this previous experiment have been the topic of the mentioned ESRF report, of a communication at an international conference, of a submitted paper and of a forthcoming one. Our attention was now focused on two further different kind of hybrid materials, based on the incorporation into PMMA matrix of the methacrylate-functionalised Cr₇Ni (C₃H₇)₂NH₂Cr₇NiF₈[H₂C=C(CH₃)COO]₁₆ (**1**) wheel cluster and of the acrylate functionalised Fe₃O(OAc)₆ [OAc = CH₂=CH-COO] (**2**). Also in this case, the aim of the XAFS measurement was to determine whether the clusters retain their structures even after polymerization with the chosen monomers. This is a crucial point, since many properties of these hybrid materials are dependent on the presence of the structurally intact oxoclusters. Furthermore, in order to ascertain whether the presence of functional polymerisable groups, allowing a covalent embedding of the cluster in the matrix, have some effect on the cluster stability, the iron trimer Fe₃O(OAc)₆ [OAc = CH₃-COO], isostructural with **2** but without functional groups, was also incorporated in a PMMA backbone. In one hybrid, also the Zn₃Cu phosphor was embedded, with the aim of preparing an electroluminescent hybrid. The investigated hybrid polymers were prepared by UV-activated free radical polymerization of the two organically modified inorganic building blocks with methylmethacrylate. X-Ray absorption measurements at the Cr, Ni, Fe, Zn, Cu K-edge were performed during 18 shifts of beamtime at the European Synchrotron Radiation Facility on the Italian beamline BM08 GILDA. During the experiments, 15 different samples were analysed (20 measurements) whose preparation, main features and compositions are summarized in the table below (Table 1). Due to the low Ni concentration in the wheel cluster and in the corresponding hybrid materials, the analyses at this edge were performed by choosing the fluorescence detection mode at room temperature. The monochromator was equipped with (311) Si crystals with the second crystal bent in order to focus the beam in the horizontal plane on the sample at each point of the spectrum.

Sample labelling	Description	Analysed species	Edge
Fe3O(Acr)6	Fe ₃ O(OAc) ₆ crystalline cluster	Fe ₃ O(OAc) ₆	Fe K
Fe3O(Ace)6	Fe ₃ O(OAc) ₆ crystalline cluster	Fe ₃ O(OAc) ₆	Fe K
Fe3OAcrid_1	Fe ₃ O(OAc) ₆ + MMA 1:100	Fe ₃ O(OAc) ₆	Fe K
Fe3OAcrid_2	Fe ₃ O(OAc) ₆ + MMA 1:100	Fe ₃ O(OAc) ₆	Fe K
Fe3OAcrid_3	Fe ₃ O(OAc) ₆ + MMA 1:50	Fe ₃ O(OAc) ₆	Fe K
Fe3OAce_1	Fe ₃ O(OAc) ₆ + MMA 1:100	Fe ₃ O(OAc) ₆	Fe K
GT139-07	(C ₃ H ₇) ₂ NH ₂ Cr ₇ NiF ₈ [H ₂ C=C(CH ₃)COO] ₁₆	Cr ₇ Ni cluster	Cr K, Ni K
GT139-07 MMA2	GT139-07 + MMA 1:100	Cr ₇ Ni cluster	Cr K, Ni K
GT139-07 MMA3	GT139-07 + MMA 1:100 + ZnS:Cu	Cr ₇ Ni cluster	Cr K, NiK, Zn K, Cu K
GT 274-A	{[(n-C ₃ H ₇) ₂ NH ₂][Cr ₇ NiF ₈ (O ₂ C ₄ H ₅) ₁₆]}	Cr ₇ Ni cluster	Cr K
GT1	GT 274 + MMA 1:200	Cr ₇ Ni cluster	Cr K
GT 274 MMA1	GT 274 + MMA 1:270	Cr ₇ Ni cluster	Cr K
GT3	GT 274 + MMA 1:200	Cr ₇ Ni cluster	Cr K
ZnS reference	ZnS reference, Aldrich	ZnS	Zn
ZnS:Cu	Cu-doped ZnS phosphors	ZnS and Cu	Zn, Cu

Table 1- Samples labeling and description

In the shown figure 1, the experimental EXAFS spectra of the samples GT139-07, GT139-07 MMA2, GT139-07 MMA3, GT 274-A, GT 274 MMA1 and GT3 are shown. The exact analysis is currently under progress. Nevertheless, it is obvious from a qualitative inspection, that the structure of the clusters GT139-07 and GT 274-A remain roughly intact after the incorporation into the polymer matrix. Small changes to the structure will be analyzed in the forthcoming data evaluation.

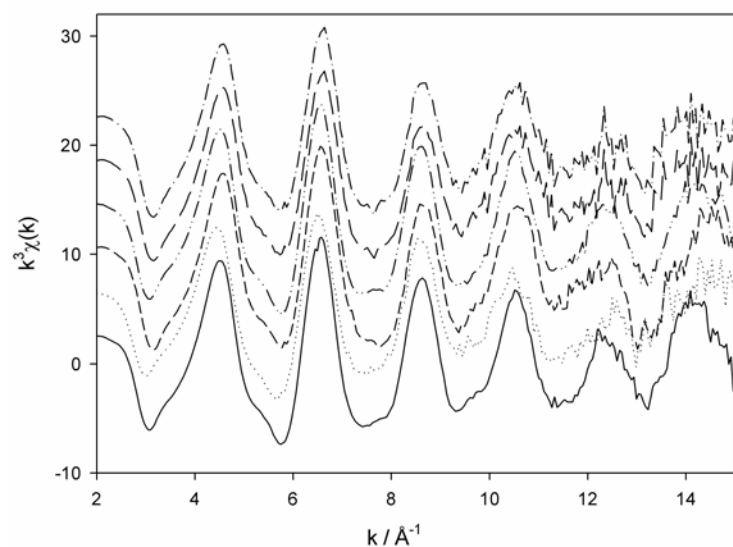


Figure 1: Experimental $k^3\chi(k)$ spectra of the Cr₇Ni clusters GT139-07 (solid line), GT139-MMA2 (dotted line), GT139-MMA3 (short dashed line), GT274-A (double dotted dashed line), GT274-MMA17 (long dashed line) and GT3 (dotted dashed line). The spectra were shifted for clarity.

The data quality was excellent and makes forthcoming measurements at GILDA desirable. In conclusions, the main results which have been obtained by this first preliminary experiment are the following:

- 1- the feasibility of EXAFS measurements in fluorescence mode on Zr-based inorganicorganic hybrid materials has been demonstrated
- 2- EXAFS is a powerful tool to investigate the structure of different Cr and Fe based oxoclusters also after their embedding in a polymer matrix
- 3- preliminary results show that the GT139-07 and GT1 oxoclusters retain their structural integrity once embedded in the polymer matrix.

References

1. Functional Hybrid Materials, Edited by P.G. Romero and C. Sanchez, Wiley, 2004
2. S. Gross, G. Trimmel, U. Schubert, V. Di Noto. Polym Adv Techn 2002; 13: 254
3. S. Gross, V. Di Noto, G. Kickelbick, U. Schubert, Mat Res Soc Symp Proc 2002, 726, Q4.1.1-Q4.1.9
4. F. Faccini, H. Fric, U. Schubert, K. Müller, E. Wendel, H. Bertagnolli, A. Venzo, S. Gross J. Mater. Chem. 2007.