Report on the experiment HD-160
Local order and chemical state of Co and Au in field-assisted ion-exchanged glass

EXAFS analyses were performed at either the Co K-edge (7709 eV) or the Au LIII-edge (11919 eV) on 18 field-assisted ion exchanged soda-lime glass samples prepared at different conditions (electric field, temperature), in order to determine the local order around the dopant metals within the glass matrix, aiming at relating the local chemistry to the preparation parameters with the final purpose to define suitable mthodologies for the control in nancomposite glasses preparation. Several informations were collected in this experimental run for both the sample types. As concerns the cobalt-doped samples, temperature was demonstrated to play the main role in promoting the aggregation, while the applied electric field mainly affects the diffusion properties.

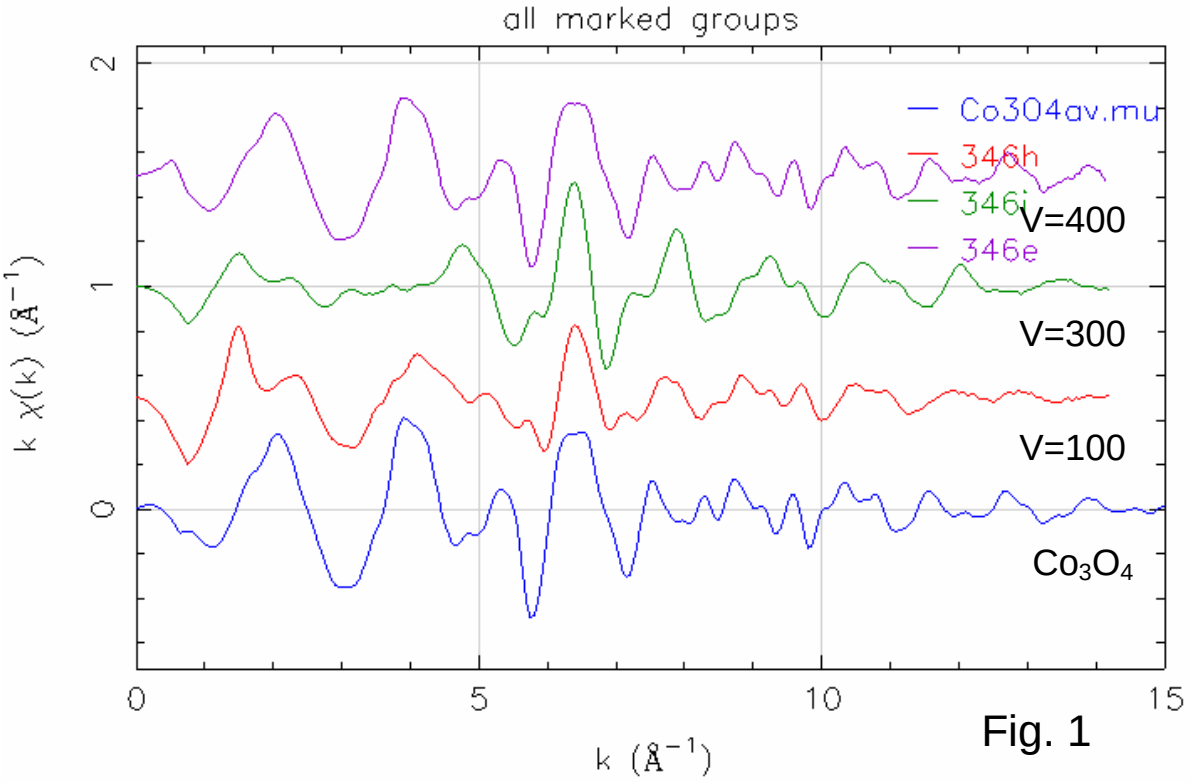

Fig. 1

Figure 1 shows the EXAFS spectra at Co edge for the samples treated at T=400 ºC. They indicate that in the sample doped at V=400 V a Co_3O_4 phase is mainly present, while in the sample doped at V=300 V mainly a metallic Co phase is evident. In the sample doped at V=100 V, the Co site is somehow intermediate between the two, indicating that both Co-oxide and Co metallic clusters are likely present. In the case of gold-doped samples, preparation parameters seemd to affect the metal state in a more complex way. Gold atoms, less mobile than any other species in all these exchange experiments, tend to form sub-nano aggregates depending on both temperature and local concentration, which is affectd by the diffusion regime depending on the external applied electric field.

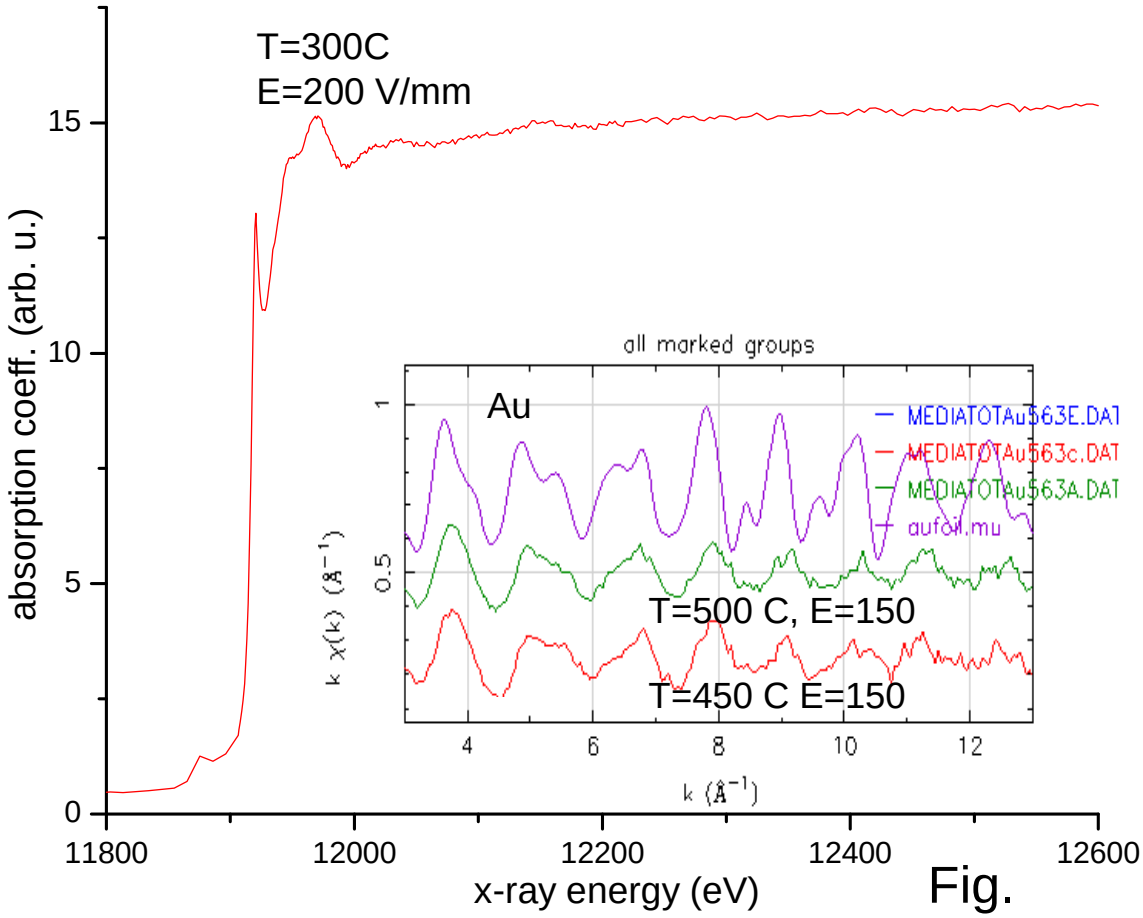

Fig.

Figure 2 shows some representative results for Au-doped samples: the EXAFS signal from the samples processed at T=450-500 ºC is very similar to that one of Au foil, so indicating that Au metallic precipitates are present in the exchanged layer. On the other hand, the XANES spectrum of the sample processed at lower temperature (T=300 ºC) exhibits a strong white line, indicating that part of the Au dopant is oxidized. Samples annealed in different atmospheres after the ion exchange process were also examined. The first tests confirm the effectiveness of annealing atmosphere selection in modifying the metal state following different routes. In particular, cluster formation and growth was shown to depend on both temperature and atmosphere. A grazing incidence XAFS configuration was also tested to select the probed depth by varying the incidence angle, but the relatively limited number of samples that could be actually examined allowed to have only some suggestion for further experiments: in particular, differences in the collected spectra were pointed out only for thick (several microns) exchanged layers, especially in the samples where the diffusion profile was less step-like (i.e., in the case of low electric field values).

To summarize, the aggregation in nanocluster structures resulted to depend on the state of metal after the exchange, which in turn came out to depend on the penetration depth as well as on the annealing atmosphere. By relating the observed behaviors to the treatment parameters, this experimental study allowed a further refinement of the protocols for controlled glass nanocomposites preparation.