	Experiment title: Quantum dots by size selected clusters	**Experiment number**: HS-796
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Aims of the experiment and scientific background

The realization of quantum dots deals with the growth of nanocrystals in a matrix, their size and size distribution, their stoichiometry, and their structure inside and at the interface of the quantum dot. Different procedures have been adopted in order to obtain size selected quantum dots; one of the most suitable is the three-dimensional clustering from a solid solution of semiconductor In_2O_3 and SnO_2 in a doped glass (SiO_2, B_2O_3). Of fundamental importance is the study of the growth mechanism of clusters with small size spread, i.e., the finding of an optimum growth regime with selected size and size distribution. Aim of this experiment is therefore the EXAFS study of the dynamical properties of In_2O_3 and SnO_2 nanoclusters forming quantum dots in a glass matrix.

Samples are prepared by controlled melting in very diluted regime. The glass matrices are insulating amorphous materials which undergo undercooled melt in a wide temperature range that can be modified by addition of convenient impurities; in this range the diffusion of a diluted solute can be controlled just modifying the viscosity of the matrix. The melting point of SiO_2 is $T(SiO_2)$=1996 K and $T(B_2O_3)$=723 K, but the corresponding glass transition range is respectively 1500-1900 K, and 470-530 K, where the viscosity changes as a function of the temperature; therefore the heat treatment can be set in a wide range depending on the composition. Because of the low melting point of both In and Sn we can use the entire glass transition range for the controlled precipitation of the quantum dots. Of course, a comparison with a semiconductor matrix (Si) in the crystalline or in the amorphous phase is particularly valuable. Another information of paramount interest can be obtained by the investigation about the compositional stoichiometry. Measurements done on metal nano inclusions seem to favor a model where the phonon spectrum in the precipitate is related to that of the matrix; in contrast the D-W factor of metal inclusions in oxides was reported as decreasing with decreasing size of the clusters.

Therefore, it is very important the knowledge of the local configuration, i.e., if the clusters are in crystalline phase, their n-n distance for few coordination shells in order to know if compression (or expansion) strain is induced in the clusters, their vibrational and thermodynamical behavior (Debye-Waller and Debye temperature), and the interface configuration related to the phonon coupling with the matrix.

Results

XAS experiments were performed at the beamline Gilda (ESRF, Grenoble) during the period 16-20 July 1999 on In_2O_3 and SnO_2 nanoclusters in borosilicate glasses at 77 K. In particular we observed SnO_2 in diluted concentration (0.5 %, 1%, 2 %) in the matrix (B_2O_3), and similarly for In_2O_3. The spectra were collected in the range 27700-28950 eV around the In K-edge (27940 eV) for the indium oxide samples and

in the range 28900-30200 eV around the Sn K-edge (29200) for the tin oxides. The measurements were done in fluorescence using an ultrapure Ge multidetector, but also the absorption detection was used for thick samples considering the very low absorbance of the matrix. For reference Sn and In foils were used together with the oxide highest concentration samples. In Fig. 1 we report the XANES region of the In oxide samples: its evident a modification of the shape for the sample at concentration 0.1 % with respect to the reference (2%); in fact, a feature, after the threshold, present for concentration 0.5% and 2% is missing at the lowest dilution and the also the EXAFS oscillations are strongly modified. Similar results are obtained for the tin oxide samples.

The analysis of the EXAFS spectra performed according to the standard procedure gave the following results:
--the diluted samples (0.1%) both of indium and tin oxide showed a molecular distribution in the matrix with a coordination limited to oxygen atoms as nearest neighbours; no evidence is found in second or higher shells of other metal atoms. The indium oxide samples shows a distorted first shell of 6 oxygen atoms with a contracted nn distance of 0.212 nm with respect to the standard cubic bixbyite distance In-O (0.217 nm). A distortion on the left side of the peak in the Fourier Transform is still under analysis, and a dramatic increase of the Debye-Waller factor is observed.

Similar conclusions can be drawn for the tin oxide 0.1% diluted sample.
--the 0.5% diluted samples show a different configuration very close to the 2% reference; here, a clustering is observed with a clear presence of In-In or Sn-Sn higher coordination shell. However the size of the clusters seems quite different and we are evaluating their morphology by comparison with a theoretical simulation which uses the FEFF code.

We point out the expected structural transition between 0.1% and 0.5% which should be better identified through an investigation in smaller dilution steps.

The present report constitutes a preliminary list of the results which will be completed and published in the near future.
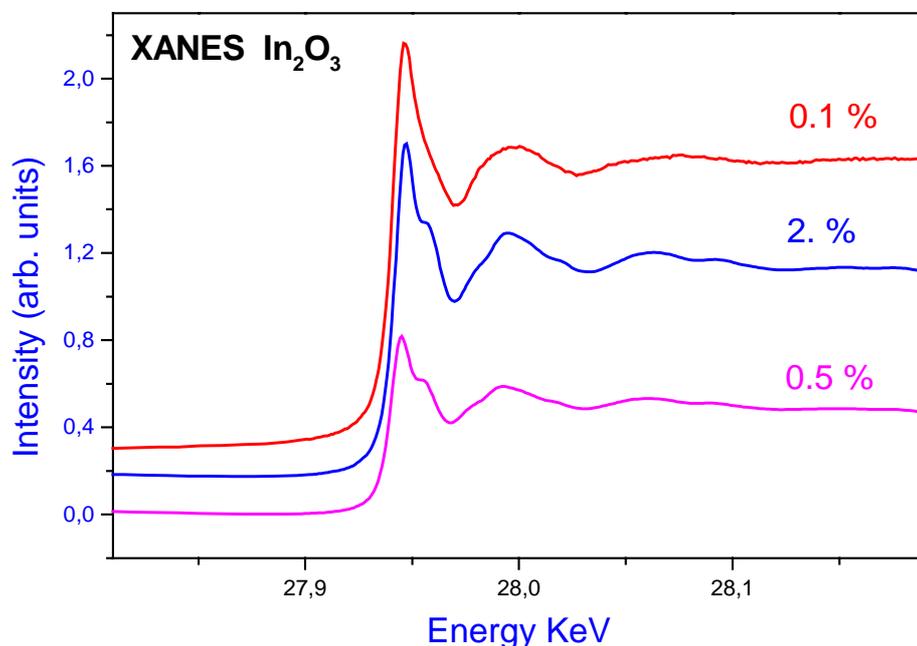
Fig. 1. Near edge structure for the indium oxide samples. Note that the curves are not normalized to the photon flux. A shift of about 1 eV is found between the peaks of 0.1% and 0.5% spectra.