CHAPTER 9

CONCLUSIONS AND FUTURE DIRECTIONS

This thesis has focused on two aspects: (i) XAFS analysis of disordered nanoclusters and (ii) XAFS beamline development program.

9.1 XAFS analysis: In this work, we have characterized the structure of disordered nano-clusters in three unique configurations: (a) Ni/Pt nano-clusters embedded in multilayer film, (b) Ag/Pt and Au/Ag nanorods synthesized via Swift Heavy Ion Irradiation, (c) HgS-based Ayurvedic nano-medicine.

(a) Employing XAFS in grazing-angle X-ray Standing Wave mode, we have characterized Ni/Pt clusters generated by ion irradiation of Pt/Ni/C multilayer. The analysis strategy is challenging since it required decoupling of information from matrix layer, interface and embedded clusters. To the best of our knowledge, this is the first XAFS attempt of decoding the structure of embedded clusters in multi-layers. The clusters are formed by the migration of atoms from interface following ion-irradiation. Our XANES analysis directly establishes the correlation between chemical nature of the interface and the composition of bimetallic clusters. Pre-existing charge transfer at the pristine Ni/C and Ni/Pt interfaces keeps them integrated during irradiation. On the other hand, physically adsorbed Pt/C interface gets disrupted and Pt atoms migrate to C layer. They combine with pre-existing Ni atoms in the C layer to form Ni centered Ni-Pt nano-clusters. These clusters have ferromagnetic composition (Ni:Pt= 60:40) and are highly disordered beyond first neighbor, resembling metallic glasses.

This work is significant for the “dry” synthesis method of amorphous magnetic devices. We demonstrate that the cluster formation / configuration process is not random but can be controlled by manipulating layer (atomic migration length) and interfacial thickness / chemical state.

(b) Amorphous (Ag/Pt, Au/Ag) nano-rods, synthesized via Swift Heavy Ion Irradiation (SHII), were characterized for short-range-order "cluster" configuration. One of the primary interests was to determine whether the extreme conditions of SHII could induce alloying in bulk immiscible Ag/Pt. We realize that segregated seeds of disordered Pt and Ag clusters were pre-formed in the pristine co-sputtered system and SHII only improves the ordering (growth of Pt). The most likely reason for this is that SHII does not completely melt Ag and Pt for mixing. Further, the time-scale of SHII (ps) is unable to compete with much faster crystallization kinetics. [We have compared this case with bulk-miscible Au/Ag system synthesized via the same route. Au/Ag retained its alloyed state and no change in composition / ordering was observed with SHII.]

The implications of the amorphous structure on the applications of these SHII-synthesized nano-rods are: (i) Ag/Pt cannot be used for optical sensing, since it does not give rise to absorption band. However, the high aspect ratio is likely to enhance catalysis due to larger surface area for reactions. Currently, its catalytic activity (methanol oxidation) is under investigation. (ii) Au/Ag exhibits intense absorption band and can continue to be optical sensor despite amorphous character.

(c) We have used XAFS in conjunction with other complementary techniques viz. XRD, Raman, SERS, XRF, to investigate the structure of Hg based ayurvedic drug, "*Rasasindura*". Our XANES results clearly establish the absence of metallic Hg^0 in *Rasasindura*; instead, Hg is present in stable α-HgS nano-crystal form. Non existence of Hg^0 ensures absence of mercury based toxicity; in parallel, stable α-HgS form and robust (<3% defect) nano-particle structure ensure integrity of the drug within human body. Elimination of Hg^0 being the most crucial step in the synthesis, we emphasize strongly on the perfect execution of synthesis process. This is the first report of scientific evidence (and guidance) towards non-toxicity of heavy metal-based Ayurvedic drug. In the backdrop of global interest in Ayurveda vis-à-vis prejudice against heavy metal composition, our results provide significant lead that the chemical form of heavy metal, rather than its content, is the correct parameter to evaluate toxicity of Ayurvedic drugs. This should strengthen credibility of Ayurveda as holistic and cheaper solution. Future of this XAFS work involves binding of *Rasasindura* with human protein in order to understand its actual reaction mechanism within the body.

All of the systems investigated in this thesis are highly disordered clusters beyond first nearest neighbor. In continuation, we are investigating the correlation between glass forming ability and short-range-order in $Zr_{52}Ti_6Al_{10}Cu_{18}Ni_{14}$ glass (in conjunction with ab- initio Molecular Dynamics simulations). Further, we would extend our knowledge of XAFS disorder analysis to decipher the correlation between disorder and Metal-to-Insulator transition in $SrRu_{1-x}Ti_xO_3$.

9.2. Indus-2 XAFS beamline development program: Under XI Plan Project (35.10), we have augmented the XAFS facilities at Indus-2 to accommodate (i) high pressure and (ii) low temperature XAFS experiments. For high pressure XAFS experiments using DAC (sample size=50-80μm), we have installed bendable elliptical mirror to improve vertical focusing of the beam. This new setup has been tested for the worst experimental condition (space limit) and ~ 60% improvement in spot size was attained. Presently, automation of this setup is in progress that will encourage finer optimization of the beam size and efficient data collection.

For low temperature XAFS experiments, we have installed displex closed cycle cryostat, which we have tested down to 5K. We have demonstrated the feasibility of performing low temperature experiments using this cryostat in the temperature range 50-300K by measuring temperature dependent XAFS of Au foil. We have obtained data of reasonable quality, which matches international standard data and is reproducible inside and outside the cryostat. We have calibrated the temperature of the cryostat and observed that the temperature accuracy is $\Delta T \leq \pm 5K$. We now plan to pursue lower (<50 K) temperature-XAFS of non-standard samples.