EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Proposal to the ISOLDE and Neutron Time-of-Flight Committee

Study of chemically synthesized ZnO nano particles under a bio template using radioactive ion beam

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Abstract

This is a project proposal to study nano sized semiconductor ZnO system, useful in biology and medicinal purposes, using radioactive ion beam from ISOLDE. Doping of the nano particles with Cu , Cd and Ga ions (in their variable valancy states) are expected to impart chages in the electrical structure and properties in the said system under study.

The morphological changes, chemical environnent, micro structure, electrical and optical properties of the nano size particles of ZnO system (developed under a bio template of folic acid) after the interaction with radioactive ion beam will be studied. The provision of perturbed angular correlation (PAC) study with respect to the changes in chemical environment, where ever possible will be attempted.

Requested shifts: 18 shifts, (split into 6 runs over 2-3 years)

I Introduction of the subject area under study :

Due to wide applications of next generation opto-electronic devices, Zinc Oxide (ZnO) nano particles have become a subject of diverse research interest over the years [1]. ZnO also constitutes to be one of the promising non-toxic and biocompatible wide band gap semiconductor particles, which has gained attention due to its exceptional electrical and optical characteristics [2,3]. Moreover, the synthesis and characterization of ZnO nanostructures have attracted great interest because of their biomedical applications as well [4,5]. Chemical growth and physical study of ZnO nano crystallites under a bio template under physiological condition is therefore relevant.

Uniform ZnO nano particles have been prepared by sol-gel method, in presence of folic acid, by only varying concentration of the latter at room temperature. Folic acid is a member of the Vitamin B family and necessary for the healthy function of a variety of bodily processes. All the prepared samples have been characterized by the X-ray powder diffraction (XRD) and we estimated the crystalline size and strain (calculated by Williamson-Hall plot method) from the broadening of the XRD peaks. Williamson-Hall plot has been employed to distinguish the grain size and strain with consideration of the instrumental broadening [1,6]. Transmission electron microscopy (TEM) has been used to study the external morphology and their size distribution, whereas preparation of ZnO was testified by Fourier-transform infrared spectra (FT-IR) for the characteristic stretching frequency in relation to the conjugative chemical environment. The UV–vis absorption spectroscopy of all the prepared ZnO samples has also been studied. It is pertinent to include here that the photo luminescence (PL) study conducted on the synthesized samples yeild important emission characteristics in visible region The possible formation mechanism of ZnO nanoparticles under the influence of folic acid and the detailed study of structural changes with concentration of folic acid constitute a detailed chemical study in ZnO nano structure formation [to be reported elsewhere 7].

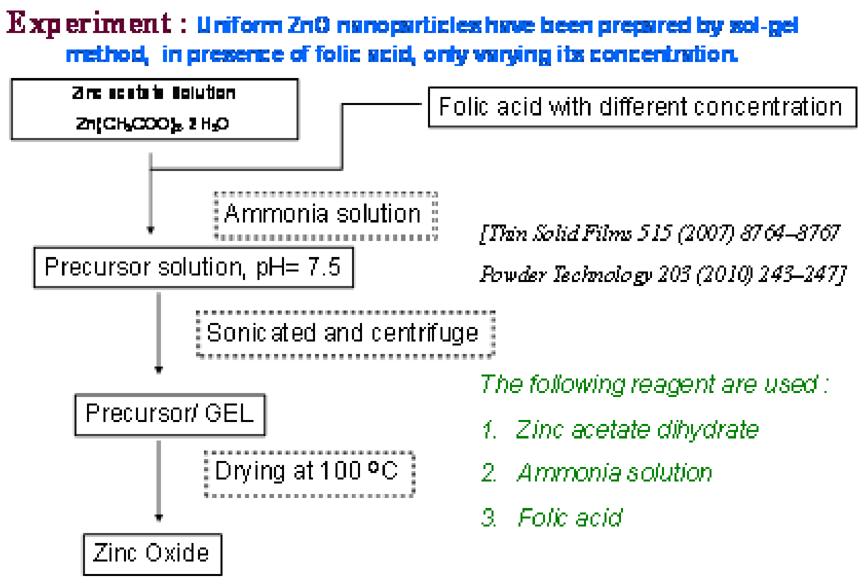
So far, a detailed description of results on the as grown chemical sample from our own investigation, comprising of profoundly interesting luminescent properties is thus readily available with us. However further study of its properties with doping of tracer ions that are biologically pertinent like Cu (Z=26) , Ga (Z=31) in their respective variable valence state would constitute an unique aspect of study. The uniqueness is expected to relate the chemical aspect in the nano domain by modifying the nano structure aspects and biologically it could be significant as both Cu and Ga are important in physiological activities of bio systems (even in humans) [8,9] such as their absorption in proteins and smaller units like peptides.

Some times toxic elements of the Zn group (IIB), such as Cd, if present as a contaminant can give rise to different properties of the semiconducting system / they are harmful for the living system which can be probed, by different experimental techniques as well. Such studies are also important from environmental pollution effects.

II Preparation method of the sample :

The ZnO nano particles were prepared under normal physiological condition , with respect to room temperature , 25C, near to neutral or slightly alkaline medium in the presence of folic acid varying in concentration in small percentage. All reagent used were of spectroscopic purity grade.

We give our preparation process as under in a flow chart :



III Experiments to be performed: *Sample preparation method (given in the form of flow chart)*

We shall bring the prepared sample for implantation.

a) Irradiation with radio active ion beam of $Cu^{(n+)}$ z=29, $Ga^{(n+)}$ z=31, $Cd^{(n)}$ z=48 with low energy (Energy range several 10 KV to about 60KV) and appreciable current and fluence will be needed on the prepared samples. Diffusion of the doped ions will be of interest, if machine is available such studies can be performed on line.

b) Depending up on doped ionic state and their concentration further studies on their spectroscopic properties, UV-Vis range and PL Studies will be required.

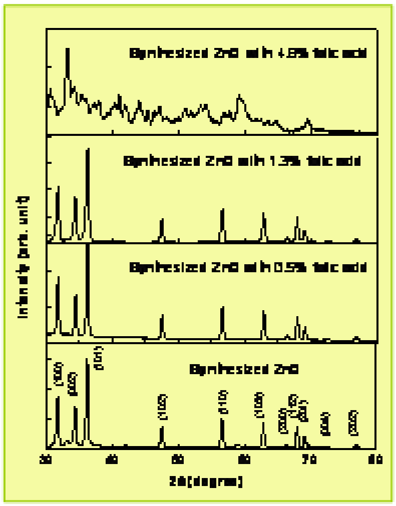
c) Perturbed Angular Correlation (PAC) studies, positron annihilation spectroscopy(PAS) also will be very helpful, besides the X-ray diffraction data and microscopic studies (SEM/TEM) often needed to examine the irradiation effects for morphological characterization. We may do positron annihilation spectroscopic studies, at least Doppler broadening of the 511 keV line shape can be done (because it is simpler)and life time analysis can be done either indirectly or through the help of other collaborating groups in the vicinity.

Some of the important results of the ZnO nano particles synthesized: Some of the characteristic results are given below for the as grown particles.

FIG. 1.

Powder X-Ray diffraction Study

Type of Diffractometer : **Seifert XDAL 3000 diffractometer with CuK$_\alpha$ radiation.**
Scanning Range : **2θ range 30° – 80° with a step size of 0.02°.**



- All XRD peaks are good agreement with hexagonal wurtzite structure of ZnO.
- There is crystalline phase except the ZnO sample having 4.8% concentration of Folic acid.
- No excess peaks detected.
- This result confirmed that ZnO was successfully synthesized.
- Partial crystallinity has been found in ZnO, having 4.8% concentration of folic acid.
- The amorphous nature is only due to folic acid. *[Thermochimica Acta 392–393 (2002) 209–220]*

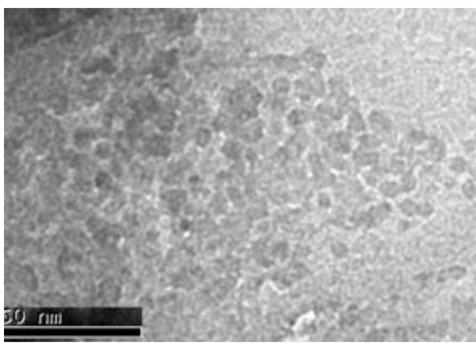


Fig.2a TEM Study of pure ZnO

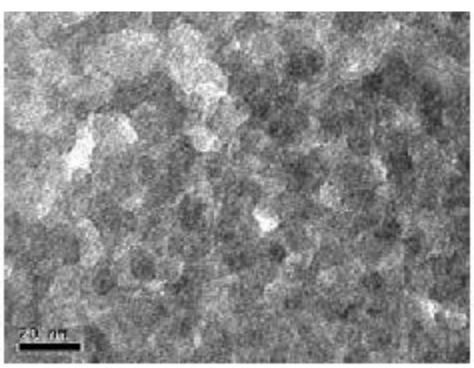


Fig. 2b TEM Study of ZnO in 1.3% Folic acid .

III Results Envisaged : Doped ions will bring about a change in crystal structure and may create structural defects and may induce phase transitions. There could be radiation effects too. Thus a thorough study of the physical properties of the system has to be made. The doped material effectively will be a new system with unstable valency state of the radioactive ions, which will propagate further changes in the system, hither to unknown. Further, Cd^{+2} (Z=48) doped/substituted ZnO generally show a distortion in the lattice due the variation of the ionic radii: $r_{Zn}{}^{+2}$=0.074nm < $r_{Cd}{}^{+2}$=0.097 nm, also there could be a lowering in the band gap, but it is important from the point of solar cell application[10]. However not much is known about the variable valency state of Cd^{+n} ions as a dopant to ZnO nano system.

III Application of such studies : ZnO is an important non-toxic LED material useful in medicine and biotechnology, it is anticipated the result of the doped and modified material will emerge in a new way into the unknown properties of the material, hopefully useful in medicine and biology. The radio tracers (short lived) can be useful in nuclear medicine diagnostic studies such as in PET as ^{68}Ga is a short lived (half-life 67.7 min) positron emitter. Cu and Ga ions used here as dopant are also physiologically active elements and can be helpful in medical application in various ways. The doped Cd ions in the system will bring about toxic change in the biological compound. As an impurity, it will impart either defects or changes in the crystal structure, size effect etc and semiconductor band gap properties which perhaps can be suitably utilized.

SUMMARY OF THE REQUIRED SHIFTS :

We ask for total of 18 shifts of Beam time for year 2012 to 2013 due to diverse nature of study involved

Required isotope ISOLDE beam	Intensity at/µC	Target	Ion Source	Shifts
^{67}Cu (Z=29)	5e8	UCx /ZrO2/YO	RILIS / HP/HP	6
^{68}Ga (Z=31)	5e8	UCx /ZrO2/YO	RILIS / HP/HP	6
^{111m}Cd	5e8	Sn	HP	6

IV References :

[1] S. Dutta et al., Prog Mater Sci 54 (2009) 89.

[2] S. Liu et al., Small 5 (2009) 2371.

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[4] K. Senthilkumar et al., physica status solidi (b) 246 (2009) 885.

[5] J. W. Rasmussen et al., Expert Opin Drug Deliv 7 (2010) 1063.

[6] S. Dutta et al., J Appl Phys 100 (2006) 114328.

[7] S Dutta and B Nandi Ganguly, 2nd Nano Today Conference Hawaii Dec 11-15, 2011.

[8] Comprehensive Inorganic Chemistry , Eds : J.C. Bailar, H.J. Emeleus, Sir Ronald Nyholm, A.F Trotman –Dickenson, vol 1 and 3 Pergamon press Ltd.1973

[9] B.N. Ganguly et.al. Jr. Nucl.Radioanal.Chem. 279 (2009) 685-698

[10] Fahrettin Yakuphanoglu , et al. Super lattices and Micro structure47 (2010) 732.

Appendix

DESCRIPTION OF THE PROPOSED EXPERIMENT

The experimental setup comprises: *(name the fixed-ISOLDE installations, as well as flexible elements of the experiment)*

Part of the Choose an item.	Availability	Design and manufacturing
SSP-GLM chamber +biophysics chamber	☒ Existing	☒ To be used without any modification
PL apparatus in building 507	☒ Existing	☒ To be used without any modification ☐ To be modified
	☐ New	☐ Standard equipment supplied by a manufacturer ☐ CERN/collaboration responsible for the design and/or manufacturing
PAC apparatus in building 115	☒ Existing	☒ To be used without any modification ☐ To be modified
	☐ New	☐ Standard equipment supplied by a manufacturer ☐ CERN/collaboration responsible for the design and/or manufacturing
[insert lines if needed]		

HAZARDS GENERATED BY THE EXPERIMENT

(if using fixed installation) Hazards named in the document relevant for the fixed [COLLAPS, CRIS, ISOLTRAP, MINIBALL + only CD, MINIBALL + T-REX, NICOLE, SSP-GLM chamber, SSP-GHM chamber, or WITCH] installation.

Additional hazards:

Hazards	*GLM chamber*		*Building 115*
Thermodynamic and fluidic			
Pressure	1e-6 mbar pressure		
Vacuum			
Temperature	[temperature] [K]		
Heat transfer			
Thermal properties of materials			
Cryogenic fluid	[fluid], [pressure][Bar], [volume][l]		
Electrical and electromagnetic			
Electricity	[voltage] [V], [current][A]		
Static electricity			
Magnetic field	[magnetic field] [T]		
Batteries	☐		
Capacitors	☐		
Ionizing radiation			
Target material	[material]		
Beam particle type (e, p, ions, etc)			
Beam intensity			

Beam energy			
Cooling liquids	[liquid]		
Gases	[gas]		O2, H2, Ar
Calibration sources:	☐		
• Open source	☒		
• Sealed source	☐ [ISO standard]		22Na sources provided by RP services at CERN, used at building 115
• Isotope	• 111Cd (100MBq) • 67Cu (0.9MBq) • 68Ga (50MBq)	• LA ~ 100MBq(estimated) • LA = 9MBq • LA = 60MBq	Isotopes all within allowance for working in a Class C environment.
• Activity			
Use of activated material:			
• Description	☐		
• Dose rate on contact and in 10 cm distance	[dose][mSV]		
• Isotope			
• Activity			
Non-ionizing radiation			
Laser			
UV light			
Microwaves (300MHz-30 GHz)			
Radiofrequency (1-300MHz)			
Chemical			
Toxic	[chemical agent], [quantity]		
Harmful	[chemical agent], [quantity]		
CMR (carcinogens, mutagens and substances toxic to reproduction)	[chemical agent], [quantity]		Acetone (ICSC: 0087), ethanol (ICSC: 0044), methanol (ICSC: 0057). Less than few centilitres per chemical, used on cleaning samples on ventilated fume hood on building 115. The respective ICSC forms have been printed and will be handled during preparation and experiments.
Corrosive	[chemical agent], [quantity]		
Irritant	[chemical agent], [quantity]		
Flammable	[chemical agent], [quantity]		
Oxidizing	[chemical agent], [quantity]		
Explosiveness	[chemical agent], [quantity]		
Asphyxiant	[chemical agent], [quantity]		
Dangerous for the environment	[chemical agent], [quantity]		
Mechanical			
Physical impact or mechanical energy (moving parts)	[location]		
Mechanical properties (Sharp, rough, slippery)	[location]		
Vibration	[location]		
Vehicles and Means of Transport	[location]		

Noise			
Frequency	[frequency],[Hz]		
Intensity			
Physical			
Confined spaces	[location]		
High workplaces	[location]		
Access to high workplaces	[location]		
Obstructions in passageways	[location]		
Manual handling	All samples and sample holders are manually handled either by long tweezers to insert and extract the sample holder into and out of the SSP implantation chamber at GLM, or when manipulating the samples and sample holders inside glove boxes or fume houses in building 115 R-007.		Chemical treatments after collections will be performed in the fume cupboard, and/or in the glove boxes in building 115.
Poor ergonomics	[location]		

0.1 Hazard identification

3.2 Average electrical power requirements (excluding fixed ISOLDE-installation mentioned above): *(make a rough estimate of the total power consumption of the additional equipment used in the experiment)*

No special power requirements for this experiment.