



**INTERNATIONAL SOLVOTHERMAL AND HYDROTHERMAL
ASSOCIATION**

ISHA NEWSLETTER, November/December 2008

No.3, Volume 3, 2008

Dear Friends and Colleagues,

**WE WISH ALL OUR MEMBERS AND READERS HAPPY AND
MOST PROSPEROUS YEAR 2009**

We are happy to present this Issue No. 3, Vol. 3, 2008, of ISHA Newsletter. We thank the readers for their continuous support and encouragement for ISHA Newsletters. Several readers are coming forward to submit their articles and general information to share with the ISHA community. The activities of ISHA are growing, and we had the most successful first ISHA International Conference during September 08-10, 2008, at the University of Nottingham, UK. We would like to share some experiences of delegates in the Nottingham conference.

The membership drive is still on, and several new members from multi-disciplinary branches of science are getting enrolled regularly. ***Please encourage your friends and fellow researchers to join our association and also contribute to the ISHA Newsletter.***

The new President of ISHA has initiated the publication of bibliography from the current issue for the benefit of readers. ISHA would like to publish regularly the reports on conferences, workshops, symposia and seminars being held in different parts of the world. The members are requested to submit a small report giving the highlights of any such event(s) they participate with one or two photographs taken during the event. The members are hereby requested to provide information on the calendar of events in their regions or countries for publication in ISHA Newsletters. We appeal to ISHA members to write small articles of general interest or reports of their activities for publication in ISHA Newsletters. As it was mentioned in the previous ISHA Newsletter, we would like to publish the availability of Research Positions like Assistantships, Post-Doctoral Fellowships and Associates positions in different laboratories all over the world. This would encourage the young researchers to read ISHA Newsletters regularly.

ISHA has the following Founding Committee:

PATRONS	:	Prof. R. Roy, USA Prof.S. Somiya, Japan
President	:	Prof.Masahiro Yoshimura, Japan
Vice Presidents	:	Prof.G. Demazeau, France Prof.N. Yamasaki, Japan
General Secretaries	:	Prof.K. Byrappa, India Prof.T. Adschiri, Japan
Executive Members	:	Prof. S. Komarneni, USA Prof.R.E. Riman, USA Prof.L.N. Demyanets, Russia Prof.M. Goto, Japan Prof.T. Funazukuri, Japan Prof.S. Feng, China

ISHA had established two important awards recently. The recipients of these two important awards are as follows:

- 1) ISHA-SAWYER Lifetime Achievement Award to the senior researcher in the area of Hydrothermal, Solvothermal and Supercritical Hydrothermal research areas. This award has been established in collaboration with Sawyer Technical Materials, LLC (formerly Sawyer Research Products, Inc.), Eastlake, Ohio, USA. Prof.Rustum Roy of Penn State University, USA was awarded this prestigious life time achievement award and the extracts of his presentation are given in this Newsletter.
- 2) Roy-Somiya Medal in honor of our two Patrons viz. Prof. Rustum Roy and Prof. Shigeyuki Somiya. The Roy-Somiya Medal was awarded to Prof.Brian Korgel of Texas University, USA for his outstanding research contribution in the field of Hydrothermal and Solvothermal Research below the age group of 45 years for the innovative research contribution with a high impact on the field.

Important ISHA News

The ISHA Council met on 9th September 2008 in Nottingham, UK and discussed various issues related to its present and future activities. The bye laws are under preparation. It was also decided to rotate the president and the Council Members once in two years. Prof.M. Yoshimura served as the Founder President of ISHA for Two years and did a commendable job as a senior researcher in the field of Hydrothermal and Solvothermal research. The members have proposed

Prof. Gerard Demzeau, University of Bordeaux, France as the successor of Prof. M. Yoshimura and requested Prof. Yoshimura to continue in ISHA as the Consultant in future. His expertise can be utilized in future also for the growth of ISHA, as a consultant. All the Council Members thank Prof. M. Yoshimura for the excellent job as the President, and welcome our new President Prof. G. Demazeau, who is one of the most active researchers of solvothermal technology in particular.

The Council also recommended Prof. S. Komarneni, Penn State University, USA, as the Vice President for the place of Prof. G. Demazeau, who has become the President of ISHA. Similarly, Prof. Edward Lester from the University of Nottingham, UK has been nominated as the Council Member in the earlier position of Prof. S. Komarneni.

The New ISHA Executive Committee is given below:

PATRONS	:	Prof. R. Roy, USA Prof. S. Somiya, Japan
President	:	Prof. G. Demazeau, France
Vice Presidents	:	Prof. N. Yamasaki, Japan Prof. S. Komarneni, USA
General Secretaries	:	Prof. K. Byrappa, India Prof. T. Adschiri, Japan
Executive Members	:	Prof. R. E. Riman, USA Prof. L. N. Demyanets, Russia Prof. M. Goto, Japan Prof. T. Funazukuri, Japan Prof. S. Feng, China Prof. Edward Lester, UK
Consultant	:	Prof. M. Yoshimura, Japan.

Here the editors of this Newsletter briefly introduce our New President of ISHA to the readers.

Gérard Demazeau was born in St-Pierre les Eglises (near Chauvigny, Vienne) on June 7th, 1943. He studied chemistry at the University of Poitiers and received the *Lauréat de la Faculté des Sciences* in 1967. In the same year, Gérard joined the *Laboratoire de Chimie du Solide* in Bordeaux where Professor Paul Hagenmuller offered him the opportunity to obtain his thesis in the field of preparative high-pressure chemistry. In December 1969, Gérard defended his *Thèse de 3ⁱème Cycle* with the title *Réalisation d'une unite de haute pression en milieu fluide. Application à la synthèse de nouveaux composés oxyfluorés et hydroxyfluorés*. He continued research in solid-state chemistry and completed a *Thèse de Doctorat d'Etat* in October 1973 entitled *Réalisation de hautes*

pressions d'oxygène. Préparation et étude physique de nouveaux composés oxygénés du cobalt, du nickel et du cuivre au degré d'oxydation +III. While carrying out his doctoral research, Gérard was already engaged in teaching at the University of Bordeaux I as a *Maître Assistant Stagiaire*. In 1978 he was appointed *Maître de Conférences*, he became a full professor in 1979, and a *Professeur de Classe Exceptionnelle – 1er échelon* in October 1996. Gérard was



awarded the *Prix Paul Pascal de l'Académie des Sciences* in 1986 and *Chevalier dans l'ordre des Palmes Académiques* in 1996, in recognition of his contributions to teaching and research. In addition, Gérard has accepted many varied administrative duties for the University of Bordeaux I. Gérard created an internationally respected high pressure research group which recently became the *Centre de Ressources Hautes Pressions* within the *Institut de Chimie de la Matière Condensée de Bordeaux* (the former *Laboratoire de Chimie du Solide –LCS*). With his colleagues and many external collaborators, Gérard's research has ranged broadly across the field of high-pressure science, including solid-state chemistry, materials science, geosciences, biosciences, and environmental studies. The laboratory acquired a corresponding variety of technical facilities, ranging from autoclaves for reactions in fluids (aqueous solutions, hydrogen fluoride, liquid ammonia, hydrazine and oxygen gas), a Belt, a hexaeder press and diamond anvil cells, to pilot equipment for high-pressure food treatment. Gérard's principal research topic in the field of solid-state chemistry was the stabilization of unusual, high oxidation states of transition metals under high pressure conditions and the investigation of their electronic and magnetic properties. Prominent examples are the synthesis of novel perovskite-related phases such as LaCuO_3 , and the rare earth nickelates RENiO_3 , TiNiO_3 , and LaPdO_3 . Other projects included work on magnetic pigments based on chromium dioxide and Fe_4N . Many of these new materials were doped with Mössbauer-active nuclei for spectroscopic characterization. More than 100 publications resulted from these transition-metal projects. The Demazeau group also synthesized a novel family of high-pressure phyllosiloxides and new compounds of light elements, with a particular focus on carbon nitride, C_3N_4 . Phase transformations in geochemically relevant materials were also studied.

An equally important theme of G´erard’s research has been the investigation of solvo- and hydro-thermal reactions to grow crystals and to understand crystallization processes under high-pressure conditions. Important examples are the flux growth of diamond, gallium nitride, cubic boron nitride and the piezoelectric α -quartz, SiO₂. The reduction of crystal defects was a particularly important task for the application of the latter material in high-frequency devices, and G´erard worked closely with industrial partners on several technological projects. The biosciences research concerned the conservation of food and the destruction of pathogenic micro-organisms using high pressures at mild temperatures (sometimes referred to as ‘Pascalization’). *Sauternes* (sweet white wine) and *Foie gras* were among many foodstuffs conserved in a pilot project at Bordeaux. G´erard’s broad, interdisciplinary approach to science has resulted in almost 500 scientific publications to date. He has also supervised 49 doctoral theses, several *en cotutelle* through many external collaborations in France and beyond. His passion for science, his receptiveness and chemical creativity gave rise to many of these collaborations when he was visiting high-pressure and solid-state chemistry laboratories around the world. The scientific contribution of G´erard Demazeau is not only measured by his research output, but also by his engagement in creating local, national, and international networks for teaching and research. He has organized several high-pressure and materials-science research summer schools for doctoral students, and he coordinated the Pierre Duhem seminar from 1994 to 1997. In 1990 and 2003, he organized the combined European (EHPRG) and International (AIRAPT) high pressure conferences in Bordeaux, both attracting more than 300 participants. G´erard has also recently directed a European Science Foundation COST D30 network on *High Pressures in Materials Chemistry*, to promote the future of high-pressure materials synthesis by linking laboratories in Germany, Spain, and the UK with Bordeaux.

G´erard is also an oenophile and a distinguished expert in Bordeaux wines. His other hobbies are cooking and gardening, especially in the summer residence at *La Teste* in the *Bassin d’Arcachon*, where Colette and G´erard spend many weekends and holidays. There they have hosted many excellent dinners enjoyed by friends and colleagues from around the world. G´erard, we wish you a happy birthday, good health, and continuing scientific creativity for the years to come.

J. Paul Attfield, Hubert Huppertz, and Rainer Pottgen,
Edinburgh, Mnchen, and Mnster, June 2008.

Comments on ISHA Awards

It was my honor and a happy to hear the news of establishment of the Roy-Smiya Medal for young persons under 45 years old at the International Solvothermal and Hydrothermal Association (ISHA). Professor Rustum Roy, the Pennsylvania State University, U.S.A., received the ISHA Sayer Lifetime Achievement Award. I would like to express my congratulation to Professor Rustum Roy. He has studied hydrothermal works with Professor E. F. Osborn

since 1946 at the Penn. State. Professor Rustum Roy has studied clay minerals, zeolite, and fine powders and single crystals. And also he has made high pressure-high temperature equipments so called a test tube-type bomb. The test tube-type bomb is used up to present time, more than 60 years. It is an amazing long life.

Congratulations, Professor Brian Korgel to receive the Roy-Somiya Metal. You were the first winner of the Roy-Sômiya Medal. I hope you keep condition of healthy and high research activities in your fields.

I have worked under high gas pressure of oxygen for Cr-O system. There was explosion. It was a dangerous thing for human bodies. I had to stop these experiments.

In 1975, I received a scientific research budget from the Ministry of Education, Science and Culture, in Japan to study on the hydrothermal works. It was about one hundred million yen for one laboratory for 3 years. This was a starting point of my hydrothermal works. At that time, the world was not so active to study on hydrothermal works. Therefore, my hydrothermal laboratory was one among the top 5 in the world. Hydrothermal reactions are not high speed reactions, but instead consume longer durations. We need a lot of test tube-type bombs. This is one of the characteristics of the hydrothermal research. Even a bomb, this is a special steel and/or heat resistance alloys. It is difficult to make a long hole in the bomb. These are the reasons why hydrothermal bombs are so expensive. Safety of my students was another big problem. I have experienced explosions twice in my laboratory. One was already mentioned in high oxygen gas experiment, and the second one was 10 Kb high Ar gas pressure apparatus. Safety is one of the most important things for high pressure experiments.

I hope the International Solvothermal and Hydrothermal Association will grow year after year in a big way.



Professor Shigeyuki Sômiya

AWARDS PRESENTATION

I. ISHA-SAWYER LIFETIME ACHIEVEMENT AWARD

Prof. Rustum Roy, Penn State University, USA was awarded the prestigious ISHA-SAWYER Lifetime Award in recognition of his contribution to the field of Hydrothermal and Solvothermal Research. Here is the wonderful Award Lecture presented at the First ISHA Conference held in Nottingham. Unfortunately, Prof.

Roy could not be present personally in ISHA-2008, and the voice mixed Video presentation of his lecture was shown to the audience. The video presentation demonstrated his great contribution to this field for the past 60 years.

I.S.H.A.

First International Conference

Nottingham, United Kingdom

September 8-10, 2008



Shown with largest
cZ diamond:
still growing them
for 50 years
including
hydrothermal

Rustum Roy

Evan Pugh Professor of the Solid State Emeritus
Professor of Science Technology and Society Emeritus
The Pennsylvania State University

Distinguished Professor of Materials
Arizona State University

Visiting Professor of Medicine
University of Arizona



**Diamond Jubilee
of**

**Hydrothermal/Solvothermal
Research
at Penn State**

1948-2008

July 1, 1948

Rustum Roy appointed
as
Research Associate in Geochemistry
ONR Contract

GOAL: Mineral Synthesis and Phase Equilibria
in
the System $\text{Al}_2\text{O}_3\text{-SiO}_2$ (+ H_2O ...)



BACKGROUND I:

Roy was sent to U.S. to study the mica industry, one of India's biggest exports.

Fluoromicas had been made in Japan, Germany in WWII.

Why not Hydroxylmicas?



BACKGROUND II:

G.W. Morey at Geophysical Lab in D.C. had designed in the 1930's his

HYDROTHERMAL BOMB in determining phase equilibria in H_2O systems.

Morey Bombs limited to $\approx 450^\circ\text{C}$ and pressure only calculated as S.V.P.



BACKGROUND III:

E.F. Osborn, Roy's mentor, had come from the same lab as Morey and there was a strong link to PSU;

And Roy had already used Morey bombs in his Ph.D. work on phase equilibria in $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$

The unsolvable problem:

How to make Al_2O_3 and SiO_2 react, **at all**, at the lower temperatures (400 C) where most clay minerals like kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), etc., are obviously stable

Solving this one problem led to two major discoveries

Designing: The simple pump for water
The test-tube bomb

Inventing: The sol-gel process
Essential to solvothermal basic research

Roy's Key Hydrothermal Advances

- ▶ Roy, R. and E. F. Osborn, "Some Simple Aids in the Hydrothermal Investigation of Mineral Systems," *Econ. Geol.* 47:717-721 (1952)
- ▶ Roy, R., "Aids in Hydrothermal Experimentation: II. Methods of Making Mixtures for Both "Dry" and "Wet" Phase Equilibrium Studies," *J. Am. Ceram. Soc.* 49:145-146 (1956)

Roy's Evolution In Hydro/Solvo-thermal Research driven by fundamental science/practical exploitation

- Only** route to:
Phase Equilibria and synthesis in...
- ▶ systems involving volatile components (e.s, H_2O , CO_2 , NO_3 , S)
 - ▶ systems involving very stable (high ΔH_f) phases*

* SiO_2 (quartz), Al_2O_3 (rubies), C (diamonds):
all very early targets only SiO_2 great success

Experimentation Advances Needed what we helped make

1. Develop simple pressure source
2. Develop simple higher T (>500 C) higher P vessel
 - a) Test-tube "bombs"(10 kb)
 - b) Opposed anvils.....(200 kb)
3. Develop techniques for precise HPHT research
 - a) quenching; gold tubes for composition control

The "Test-Tube Bomb"

Work-horse of World Wide Solvothermal Research

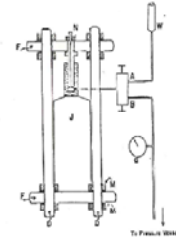
- ▶ Evolved between 1948-51
- ▶ Based on Tuttle's idea in Geophysical Lab
- ▶ Developed by Roy at Penn State (upside down made quenching possible, new alloys);
 - multiple 'bomb' racks using same pump; use of gold tubes for multiple samples per run;
 - use with other solvents, N₂, NH₃, CO₂, alkali + useful solution.
 - use of electric fields, added.

First Advance: Simple Pump

Reprinted from Economic Geology, Vol. 47, No. 7, November, 1952
Printed in U. S. A.

SOME SIMPLE AIDS IN THE HYDROTHERMAL INVESTIGATION OF MINERAL SYSTEMS.

KUSTOM ROY AND R. F. OSBORN.



Next was the test tube "bomb"

Commercial version



* See reverse side for list of dimensions and capacities. Pressure and temperature limits are also shown.

Commercial version by TEM-PRES



Prof. Della Roy using a rack of T.T. vessels and furnaces (c. 1955)



Grad School: Hydrothermal Research

And adds ball-milling in Morey bombs



1957:
Roy and Tuttle formed the "Tem-Pres" Co.

To make high pressure pumps (>KB)
high pressure T. T. bombs
(up to 1100°C: 5 k bars)

This tiny company serviced the world wide
solvothermal community for 50 years.

First Major Industrial Application

Growth of Quartz crystals

Bell Labs: research
Sawyer at Brush Development



The Sol-Gel Process was a synthesis of 4 separate advances.

- ▶ Mix via solution not solid powders
- ▶ Preserve homogeneity by gelation
- ▶ Use organic pre-cursors
- ▶ Use pre-made sols for some compounds

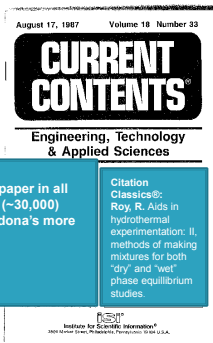
The sol-gel process

became essential for ALL low-temperature
hydrothermal phase-equilibria studies;
in the 1950s.

in addition to "dry" reactions
...for ALL ceramics nowadays.

NOW UNIVERSAL

The sol-gel paper in
J. Am. Cer. Soc., 1956,
became the 1st citation
classic in ceramics as
noted by →



Is possibly the most cited paper in all
materials science formally (~30,000)
and informally (see M. Cardona's more
precise criteria) ~500,000

Citation
Classics®:
Roy, R. Aids in
hydrothermal
experimentation: II,
methods of making
mixtures for both
"dry" and "wet"
phase equilibrium
studies.

1952-1970s at Penn State

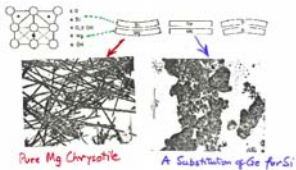
H-T, H-P used by dozens of PhD students under Roy,
Tuttle, Burnham, Barnes, etc., for...

- Synthesizing clays, zeolites, and determining stability
in many different geological problems
- Low temperature equilibria in oxide systems,
impossible by any other way
- Epitaxy on substrates (e.g. GeO₂) stable at low temp

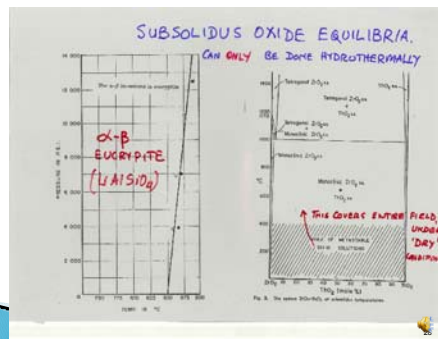
Hydrothermal even made first synthetic (morphology (controlled) nanotubes (chrysotile) in 1950

ELIMINATE LATTICE STRAIN IN CHRYSOTILE ASBESTOS BY
SUBSTITUTING Ge FOR Si — FINE CURLED TUBES
BECOME FLAT PLATES.

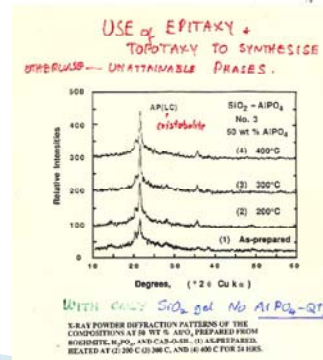
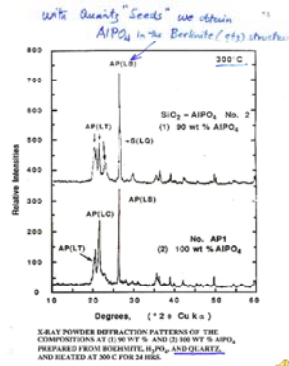
Note:
nanotubes



(ONLY) Method For Low Temp Equilibria



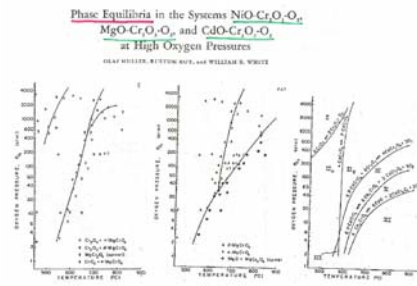
Hydrothermal invaluable for low-T epitaxy



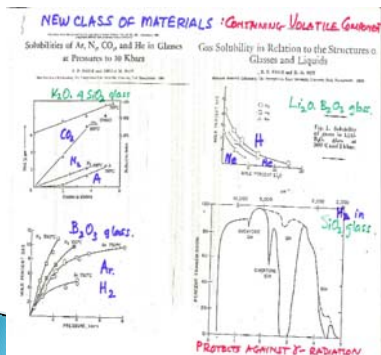
Solvothermal (up to 5 kbars, 1000°C)

- CO₂ Equilibria systems. Goldsmith, Tuttle, Wyllie, Burnham
- O₂ Roy and White used same bombs for equilibria in: Pb-O, Cr-O, etc. Growing selenium single crystals
- NH₃ Growing selenium single crystals
- A } Dissolving vapor into glasses to make unique ceramics
- H₂ }
- N₂ }

OXYGEN PRESSURES TO 5 KBARS



Dissolving Vapor into Glass



2b. EXAMPLES OF HYDROTHERMALLY CATALYZED ANHYDROUS REACTIONS

- CRYSTALLIZING GELS OR GLASSES IN 1, 2, 3, 4 COMPONENT SYSTEMS TO ANHYDROUS SELS OF PHASIS. SiO_2 , $MgO-SiO_2$, $MgO-Al_2O_3$ ETC.
- ENSOLUTION OF CRYSTALLINE SOLUTIONS TO EQUILIBRIUM VALUES. $CaO-ZrO_2$, $MgAl_2O_4$, Al_2O_3 ETC.
- SITE ORDER-DISORDER IN OXIDES:
 - $MgAl_2O_4$ spinel
 - all feldspars
 - micas

THE EXPERIMENTAL DATA ARE ENORMOUS, BUT MECHANISM IS NOT CLEAR.

Next we added electric field to H-T (multi-energy) 1962

B.1. HYDROTHERMAL + ELECTRIC FIELD, Electrolytic Synthesis of Kaolinite Under Hydrothermal Conditions

Table I. Chemical Composition of Glasses Studied (Weight %)

Element	Structure	Density (g/cm ³)	Specific heat (cal/cm ³ °C)
SiO ₂	3.24	1.87	2.27
Na ₂ O	2.89	3.00	2.04
PbO	3.47	8.39	9.20
CaO	1.71	7.85	7.00
MgO	2.09	6.74	4.00
Al ₂ O ₃	15.75	10.42	16.12
B ₂ O ₃	69.62	17.52	16.12
Total	99.70	99.05	98.99

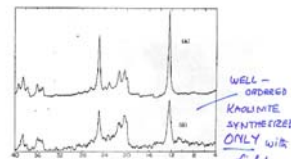


Fig. 1. X-ray diffraction patterns of (A) well-ordered natural kaolinite and (B) synthetic kaolinite.

Multi-Energy Processing

- H-T was the very first world recognized success: involves P, T, and chemical potential
- In 1962 we had added electric fields
- In 1980s microwave hydrothermal was commercialized (every analytical lab in the world must use it)
- In 2008 Roy, Rao, and Kanzius confirmed atomic dissociation of H₂O in polarized RF beam

Hence, in solvothermal's future

We will...

add other variables,
especially
electric/magnetic fields.



Prof.S. Komarneni (from Penn State University, USA) - a collaborator and a close associate of Prof.Rustum Roy, receiving the ISHA-SAWYER Lifetime achievement award – huge synthetic quartz crystal and a plaque, from the President of ISHA Prof.M. Yoshimura and General Secretary Prof.K. Byrappa, on 10th September 2008, in Nottingham, UK on behalf of Prof.Roy, who could not come to Nottingham.

II. ROY-SOMIYA MEDAL

The first ever Roy-Somiya Medal was awarded to a young scientist of below 45 years - Prof.Brian Korgel of the The University of Texas at Austin, USA in recognition of his research contribution to the field of hydrothermal and solvothermal research. The award committee unanimously selected Prof.Brian Korgel for this prestigious award. Prof.Brian Korgel received this Roy-Somiya Medal and also a plaque from Prof.M. Yoshimura, President of ISHA and Prof.K. Byrappa, General Secretary, ISHA, on 10th Sept. 2008. After receiving this award, Prof. Brian Korgel delivered his award lecture to the delegates of ISHA. His award lecture is given here for the benefit of the readers.

Synthesis of Semiconductor Nanowires in Supercritical Solvents (Acceptance Address for the ISHA Roy-Somiya Medal)

Brian A. Korgel

Department of Chemical Engineering,
Texas Materials Institute,
Center for Nano- & Molecular Science and Technology
The University of Texas at Austin
Austin, TX 78712
USA

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First of all, I would like to thank the International Solvothermal and Hydrothermal Association (ISHA) for this award. I have enjoyed many interactions with members of ISHA over the last several years and this award means a lot to me and I greatly appreciate the support of our work.

When I started as an Assistant Professor in the Department of Chemical Engineering at the University of Texas at Austin (UT Austin) in July, 1998, I was not working on hydrothermal or solvothermal systems. In fact, I was not at all familiar with the research area. I had spent my PhD and post-doc working on nanocrystals and developing their synthesis using wet chemical, solution-based methods. My first efforts as a PhD student at UCLA working with Hal Monbouquette involved the synthesis of CdS nanocrystals at room temperature in water within phospholipid vesicles—the vesicles served as reaction compartments to control the size of the nanocrystals. I studied the photocatalytic properties of these nanocrystals, their doping with impurities and core-shell heterostructure growth. After that I spent a year-and-a-half as a post-doc at University College Dublin in Ireland working with Donald Fitzmaurice, where I focused on the synthesis of organic monolayer-stabilized gold and silver nanocrystals and understanding their self-assembly. I was utilizing room temperature solvents under ambient conditions to synthesize the nanocrystals by arrested precipitation, which is an approach that relies on capping ligands like dodecanethiol that stick to the nanocrystal surface and provide a steric barrier to aggregation to control the nanocrystal size.

In 1998, I was fascinated by the idea of using nanocrystals as “building blocks” to construct different kinds of electronic and optical devices and as a material that could be interfaced with biological systems. At that time, the field of nanocrystal chemistry had advanced tremendously from the end of the 1980’s, but the library of compounds that could be synthesized was quite limited. The goal of my research program was to develop the materials chemistry needed to provide a library of nanocrystal materials, ranging from metals to semiconductors to magnets, which could be applied to a wide variety of technologies, including

general illumination, solar energy utilization, information technology, and medicine.

In 1998, I met Keith Johnston, Professor in Chemical Engineering at the University of Texas at Austin, and a post-doc working with him, Justin Holmes. They were working towards developing supercritical solvents as a medium for nanoparticle synthesis and they introduced me to their field of supercritical solvents. At the time, Justin was working on a project to make CdS nanocrystals in supercritical carbon dioxide (sc-CO₂).¹ They were precipitating the CdS nanocrystals within the water droplets of water-in-CO₂ microemulsions. The research infrastructure at UT Austin has since improved tremendously, but in 1998 at UT Austin there was no electron microscopy facility and I was one of only 2 or 3 people on the entire campus who could do transmission electron microscopy (TEM), so I helped Justin get some TEM images of his nanocrystals. This was the beginning of a long and fruitful collaboration with Keith Johnston.

One day while we were talking in the lab, I was describing the separation procedure that we used to narrow the size distribution of our nanocrystals, called size selective precipitation. In this process, hydrophobic nanocrystals are dispersed in an organic solvent, like toluene, and then a more polar, miscible solvent like ethanol, is slowly added until the dispersion becomes slightly opalescent. The change in turbidity occurs because the larger nanocrystals aggregate while the smaller diameter nanocrystals remain suspended in solution and can be isolated from the mixture. Using this process, the size distribution can be narrowed to obtain nanocrystals with standard deviations about the mean diameter of less than $\pm 10\%$. Keith pointed out an interesting feature about supercritical fluids that I was not aware of, and that is, that by changing the pressure and temperature (or density) of the solvent, the solvation strength changes rather dramatically, and this might be a property that could be utilized for size selective precipitation. Instead of adding a non-polar solvent, which is *not a reversible process*, the pressure could be increased or decreased in very controlled manner to selectively precipitate nanocrystals in a precise, larger size range. Keith also pointed out that sc-CO₂ was a good solvent for organic molecules like dodecane and should disperse the hydrophobic nanocrystals. For me, this was a very exciting idea.

We first tested this idea with some dodecanethiol-stabilized silver nanocrystals that I made. Justin took the nanocrystals and tried to disperse them in sc-CO₂. The nanocrystals did not disperse, and at the time, this was a big surprise. I did not understand how the molecule itself—dodecane—could be very soluble in sc-CO₂, but when tethered to the surface of the nanocrystals, would not provide nanocrystal dispersibility. I was fascinated by this. This was my first introduction into the world of supercritical CO₂, and the beginning of my research effort into the fascinating and always surprising arena of hydrothermal and solvothermal chemistry. Even now, 10 years later, steric stabilization of nanocrystals in sc-CO₂ is only very qualitatively understood. Over the years, we have examined a variety of different ligands and found that fluorocarbons are the

best ligands for steric stabilization in sc-CO₂, but the chemistry is still not so obvious, and perfluorinated alkanes work well, but fluorocarbons with more polar groups added in the core of the ligand work even better.^{2,3} The best ligand for steric stabilization that we have identified over the last 10 years has been a thiolated fluoro-octylmethacrylate (FOMA-SH), like the one shown in Figure 1.

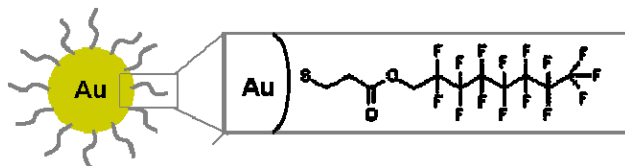


Figure 1. A Au nanocrystal coated with the CO₂-philic ligand, thiolated fluoro-octyl methacrylate (S-FOMA). (Image courtesy of Aaron Saunders).

During the past 10 years, Keith and I have collaborated to examine sterically-stabilized nanocrystals in a wide variety of different supercritical solvents, including CO₂, ethane, and water. The concept of density-tunable dispersibility does indeed work, but it took some backtracking and an examination of a simpler supercritical fluid—ethane—to begin to get a handle on the systems and confirm our initial ideas. Parag Shah spent his PhD studying these issues and he set out to understand dispersibility of sterically-stabilized nanocrystals in supercritical solvents. Prior to Parag's efforts, a variety of nanoparticles of various materials had been made in solvothermal and hydrothermal solvents, but the particle size control was relatively poor. The concept of arrested precipitation using ligands to control particle size had not been tested in any hydrothermal or solvothermal system. In five years, Parag carved a path into a new frontier in nanocrystal science in supercritical media, demonstrating: (1) density-tunable dispersibility of hydrophobic alkyl-stabilized silver and gold nanocrystals in supercritical ethane; (2) steric stabilization of metal nanocrystals in supercritical CO₂ (by using perfluorinated CO₂-philic solvents); (3) arrested precipitation of nanocrystals in supercritical CO₂ and ethane; and (4) controlled deposition of monolayers of sterically-stabilized nanocrystals onto substrates from supercritical CO₂ by lowering the solvent density in a controlled manner. Working in parallel with Parag, Kirk Ziegler, demonstrated the arrested precipitation of copper and copper oxide nanocrystals in supercritical water. And another PhD student, Aaron Saunders followed up on Parag's work with quantitative measurements of interparticle interactions of CO₂-dispersible nanocrystals as a function of ligand chemistry and solvent density by making use of small angle X-ray scattering (SAXS) techniques. His data still represent the most quantitative information about steric stabilization in sc-CO₂ in the literature.³

Another aspect of solvothermal chemistry has also consumed me for much of the past ten years: the use of high temperature (>350°C) supercritical organic solvents as a reaction media for nanomaterials synthesis. This research effort was sparked by a simple question that my department chair, John Ekerdt, has posed to me in the hall one day in 1999, "Can you make silicon

nanocrystals?” That simple question sparked the beginning of a nearly 10-year research effort in my group.

The synthesis of Si nanocrystals in solution is a daunting challenge. First of all, Si crystallization requires high temperatures; for example, crystalline Si films are typically deposited by chemical vapor deposition (CVD) at temperatures greater than 550°C to avoid the deposition of amorphous Si films. Unlike ionic solids like CdSe, Si has a relatively stable amorphous structure that is not easy to crystallize. The boiling temperature limitation of solvents at ambient pressure is a significant problem for Si synthesis; for example, trioctylphosphine oxide (TOPO)—a common solvent for CdSe nanocrystal synthesis—is only ~360°C. So, after John sparked my interest in Si nanocrystals, I began to think about different ways of making Si nanocrystals, including gas-phase methods. As I thought about how to make Si nanocrystals using a solution-based approach, it suddenly dawned on me that a high temperature supercritical organic solvent would provide *unprecedented access to a high-temperature window* for nanocrystal synthesis that had never before been studied. Would it be possible to synthesize crystalline Si nanocrystals in toluene for example at 500°C by arrested precipitation?

Keith Johnston’s group had spent many years studying supercritical water and had a reaction cell available built to withstand the high temperatures and pressures needed to carry out the reactions. I talked to Keith about whether it would be possible to feed organic solvents into the supercritical water reactor and although they had never done it before, he didn’t see any reason why it couldn’t be done. This is where Justin Holmes again made the essential contribution. Justin and I had become very good friends and when I told him about the idea he was really excited to try it. He had never used the supercritical water setup before, so he had to ask Kirk Ziegler, the student currently using the apparatus, if he could teach him how to use it. Justin was also good friends with Kirk and he was happy to show him how to use the apparatus—it pays to have good friends in science! Justin was now all set to try a reaction.

The next consideration was the chemistry itself, which uncharted territory. One of the major challenges of Si nanocrystal synthesis in solution is the reactant: it is not at all obvious what to use to generate Si atoms in solution that will ultimately form nanocrystals. Furthermore, there was no knowledge about silane decomposition in hot supercritical solvents. Although a tremendous body of literature exists on Si chemistry in solution, it’s devoted to relatively low temperature (<300°C) reactions generally aimed at making organosilane or silicon halide compounds. The knowledge of high temperature silane decomposition was isolated to relatively high temperature gas-phase conditions with very dilute silane concentrations, as in the case of CVD reactions. I decided to talk to Ekerdt about this to see if he had any ideas—and brought the Aldrich catalog. We thumbed through the catalog and discussed some options and

finally he turned a couple of pages and put his finger down on diphenylsilane...“this one.” I ordered it.

The capping ligand chemistry is the other important consideration for Si nanocrystal arrested precipitation. It was also not obvious what to use to stabilize particle growth. Self-assembled monolayers on Si surfaces had been extensively studied, but this information provided only a rough guideline in terms of what might work for nanocrystal synthesis. A ligand was needed that would bond to the Si surface of the growing nanocrystals, but would also release from the surface to allow growth. If the ligand bonded irreversibly to the Si surface, the nanocrystals would not grow. The most common passivation scheme on Si was alkene hydrosilylation, which leads to a molecular layer bound via a covalent Si-C bond. The problem with this chemistry is that the ligands most likely would not desorb from the nanocrystal surface to allow for growth. Although alkenes were an option, I was worried that they would not work for this reason. There was some precedent for stabilizing aerosol-generated Si nanocrystals using glycerol, so I decided to try a version of this approach using a long chain alcohol, octanol, as the capping ligand.

Justin had ordered all of the chemicals and set up for the reaction. I was in the lab hovering over his shoulder—I couldn't help it, it was a really exciting experiment and I couldn't wait to see what happened. We let it run for about 30 minutes and then shut down the reactor. Something had definitely happened...the solution turned a dark yellow/orange color. I placed a drop of the reaction product on a TEM grid and imaged it (Figure 2). There were nanocrystals there; the lattice spacings matched Si and EDS confirmed that only Si was present. The reaction had worked.⁴

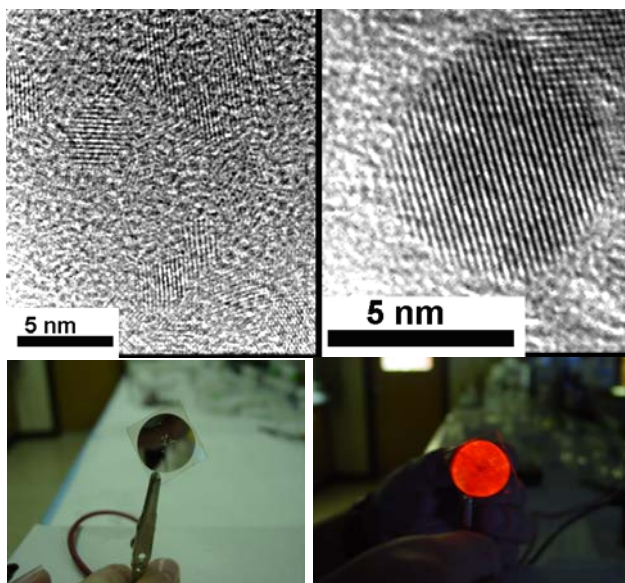


Figure 2. (Top) TEM images of Si nanocrystals synthesized by arrested precipitation in supercritical toluene at 450°C. (Bottom) Si nanocrystal light emitting diode (LED). (Images courtesy of Lindsay Pell and Chris Doty).

As Justin was working to optimize the Si nanocrystal reaction conditions, I came across a recent paper from Charles Lieber's group in *Accounts for Chemical Research*, "Chemistry and Physics in One Dimension: Synthesis and Properties of Nanowires and Nanotubes," which described the synthesis of semiconductor nanowires by a process called vapor-liquid-solid (VLS) growth. In VLS, Si is added via a vapor phase reactant to a system with gold at a temperature exceeding the Au:Si eutectic temperature at 360°C. Under these conditions, Si dissolves into the gold to form a liquid solution that then seeds Si crystallization into the form of nanowires. I was fascinated by this concept and it occurred to me that we could do something similar in our reaction system. The Si reaction we were using was perfectly suited for this purpose—after all, we were making Si at temperatures above the eutectic temperature. We could carry out the same reactions we were studying for nanocrystal growth, but leave out the capping ligands and add in gold nanocrystals. By feeding gold nanocrystals smaller than 10 nm in diameter into the reactor, Si nanowires should form with diameters less than 10 nm. Like the Si nanocrystal reactions, this was another case of carrying out an exploratory reaction and then looking by TEM to see if it worked. When I looked at the sample, there were nanowires there—it worked.⁵

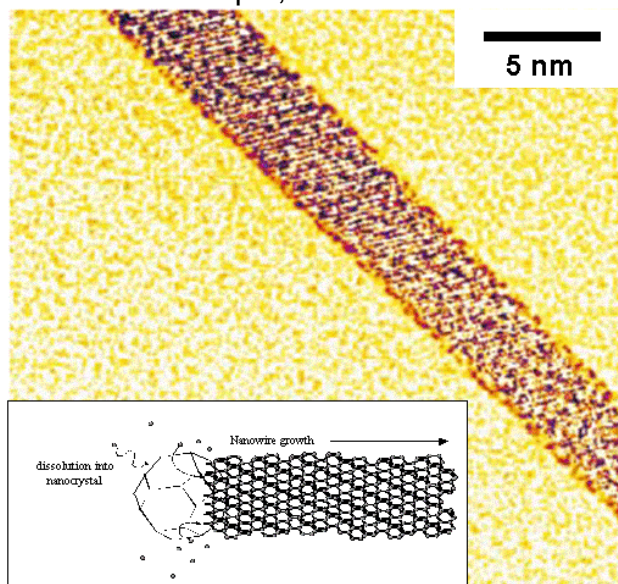


Figure 3. TEM image of a silicon nanowire made by the supercritical fluid-liquid-solid (SFLS) process. The inset depicts how nanowires grow: a silicon reactant decomposes to silicon atoms in the *supercritical fluid* and then dissolves into the gold nanocrystals to form a *liquid melt*; the *solid* silicon nanowire then crystallizes from the melt.

In approximately one year, we had tapped a new field of research—the use of high temperature organic supercritical solvents as a reaction media for nanocrystals and nanowires. These early results were very exciting, but the reactor configuration was difficult to use and produced very little material. The reactor volume was only 300 μl and consisted of two thick sandwiched sapphire windows that often cracked during the reactions. In the fall of 2000, Tobias Hanrath joined my group as a PhD student to work on extending the SFLS

synthesis to Ge. Tobias recognized the problems with the reactor and built a new 1 ml volume reactor that carried him through much of his PhD. He published his first paper as a student only a year after he started in *JACS*.⁶ By the end of his PhD, he had further scaled up the system to obtain ~1 g of Ge nanowires in a single reaction (Figure 4). This magnitude of nanowire production was unprecedented by any method and he was demonstrating the potential of the process to scale up to more than kg/day scale production.

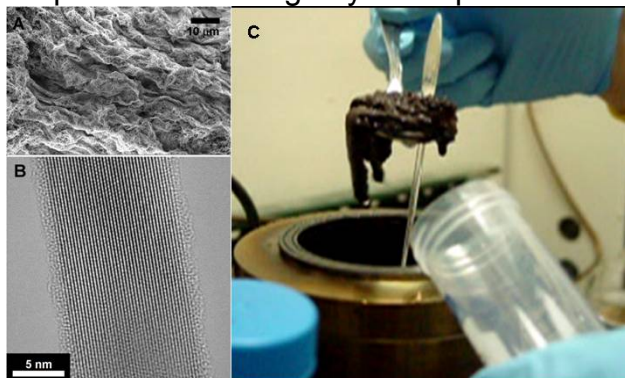


Figure 4. (A) SEM and (B) TEM images of Ge nanowires; (C) ~1/2 g of Ge nanowires synthesized in a 250 mL Parr reactor by the SFLS process (Images courtesy of Vince Holmberg and Tobias Hanrath).

From 1999 to the present, a series of very talented students has worked to understand and develop the SFLS process. Tobias Hanrath developed the SFLS growth of Ge nanowires and scaled it up to pilot-scale quantities; he developed the passivation of their surfaces with organic monolayers;⁷ fabricated field effect transistors (FETs) and was the first in the nanowire field to report the importance of surface states on nanowire FET performance;⁸ and performed electron energy loss spectroscopy (EELS) on individual nanowires to examine the size dependence of their electronic properties.⁹ Doh Lee systematically studied the SFLS growth of Si nanowires and developed a fundamental understanding of silane reactant decomposition in hot supercritical organic solvents,¹⁰ which has been applied by two of my newer students, Reken Patel and Andy Heitsch, to reach reaction yields on the order of Si, of about ½ a gram per reaction. Doh also demonstrated the multiwall carbon nanotubes could be grown in supercritical toluene at 625°C—a solution synthesis of carbon nanotubes,¹¹ which Danielle Smith later improved upon to obtain very pure nanotube product with narrow size distributions by subtle changes in the reaction parameters.¹² Hsing-Yu Tuan joined the research group just after Doh and demonstrated that seed metals other than gold, such as cobalt, nickel and copper, were very effective nanowire growth catalysts and furthermore revealed that these transition metals could yield nanowire growth by solid-phase seeding and that the seed metal could catalyze the decomposition of various Si reactants;¹³ he also revealed an unexpected and remarkable solvent dependence on the Si reaction yields.¹⁴ Hsing-Yu also discovered that under certain oxidizing conditions, the Si growth process would yield silica nanotubes.¹⁵ Tripp Davidson demonstrated that SFLS could be used to make Group III-V semiconductors,¹⁶ such as GaAs

and GaP and discovered that crystallographic twins on the (111) planes are common extended defects in semiconductor nanowires, particularly in III-V nanowires and explained their formation with a new model for twin formation.¹⁷ And two of my current students, Vince Holmberg and Damon Smith, are examining in detail the influence of Ge nanowire surface passivation chemistry on their chemical, electronic, optical and mechanical properties and revealing many interesting new information.¹⁸ The science and engineering of the SFLS process and the properties of the nanowires continues to be an exciting endeavor for my research group.

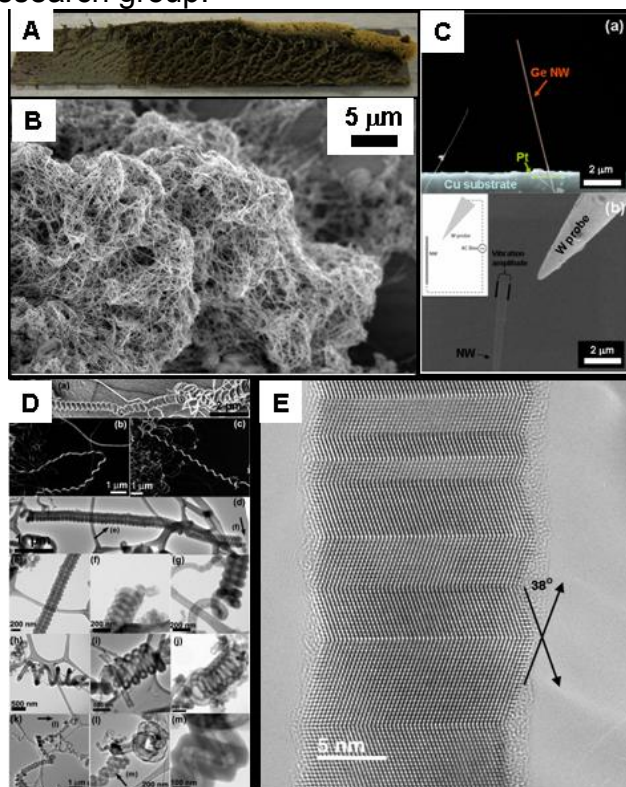


Figure 5. (A) Photograph and (B) SEM image of Si nanowires produced by the SFLS process; (C) a Ge nanowire cantilever and its vibrational resonance induced by an AC potential by STM probes; (D) silica nanotubes; (E) a twinned GaP nanowire. (Images courtesy of (A) Andy Heitsch, (B) Reken Patel, (C) Damon Smith, (D) Hsing-Yu Tuan, (E) Tripp Davidson).

I have been fascinated by the usefulness of solvothermal systems during the past 10 years for nanomaterials synthesis and processing. Initially, the goals were modest and exploratory deriving from simple questions: Could nanocrystal dispersibility in supercritical solvents be tuned by changing solvent density? Is it possible to synthesize nanocrystals by arrested precipitation in supercritical solvents? Is it possible to grow semiconductor nanowires by a VLS-like process using size-controlled metal seed particles? These efforts have convinced me that solvothermal and hydrothermal media provide unique systems for carrying out chemical transformations. The “VLS”-like synthesis of silicon and germanium nanowires is one example. These systems are also scalable and can be applied

in industrial processes. In fact, two startup companies, Innovalight and Piñon Technologies, now employ these processes to make nanomaterials.

This discussion brings me to reflect on ISHA itself as an organization and its mission. ISHA is a relatively new society, formed by bringing together the solvothermal and hydrothermal communities, which have each in their own right a very rich history and tradition of research and technology development. To those outside the field, solvothermal and hydrothermal systems can perhaps appear to be relatively specialized, requiring complicated equipment that operates under extreme pressure and temperature. But in fact, solvothermal and hydrothermal systems are not complicated; for example, every biology lab in the world uses hydrothermal technology—in the form of an autoclave—to sterilize glassware. Solvothermal and hydrothermal systems are applicable to many different fields, such as nanomaterials chemistry, making it a highly interdisciplinary research area. This interdisciplinarity can lead to challenges disseminating knowledge widely to researchers across scientific borders, as well as within the solvothermal and hydrothermal community itself. Therefore, I believe that ISHA has an important mission to widely disseminate old and new knowledge from the solvothermal and hydrothermal community to those not currently engaged in research in the area to teach the broader international science and engineering community about the potential of these systems. I am certainly a believer. So, I would like to thank the ISHA committee again for this honor of the Roy-Somiya Medal. The award has special significance as it has come from a community that understands deeply the chemical systems that have empowered some of the most exciting research in my career.

References

1. J. D. Holmes, P. A. Bhargava, B. A. Korgel, K. P. Johnston, "Synthesis of Cadmium Sulfide Q-Particles in Water-in-CO₂ Microemulsions," *Langmuir*, 15 (1999) 6613-6615.
2. P. S. Shah, J. D. Holmes, R. C. Doty, K. P. Johnston, B. A. Korgel, "Steric Stabilization of Nanocrystals in Supercritical CO₂ Using Fluorinated Ligands," *J. Am. Chem. Soc.*, 122 (2000) 4245-4246.
3. For a review, see P. S. Shah, T. Hanrath, K. P. Johnston, B. A. Korgel, "Nanocrystal and Nanowire Synthesis and Dispersibility in Supercritical Fluids," *J. Phys. Chem. B*, 108 (2004) 9574-9587.
4. J. D. Holmes, K. J. Ziegler, R. C. Doty, L. E. Pell, K. P. Johnston, B. A. Korgel, "Highly Luminescent Silicon Nanocrystals With Discrete Optical Transitions," *J. Am. Chem. Soc.*, 123 (2001) 3743-3748.
5. J. D. Holmes, K. P. Johnston, R. C. Doty, B. A. Korgel, "Control of the Thickness and Orientation of Solution-Grown Silicon Nanowires," *Science*, 287 (2000) 1471-1473.
6. T. Hanrath, B. A. Korgel, "Nucleation and Growth of Germanium Nanowires Seeded by Organic Monolayer Coated Gold Nanocrystals," *J. Am. Chem. Soc.*, 124 (2002) 1424-1429.
7. T. Hanrath, B.A. Korgel, "Chemical Surface Passivation of Ge Nanowires," *J. Am. Chem. Soc.*, 126 (2004) 15466-15472.

8. T. Hanrath, B. A. Korgel, "The Influence of Surface States on Electron Transport Through Intrinsic Ge Nanowires," *J. Phys. Chem. B*, 109 (2005) 5518-5524.
9. T. Hanrath, B.A. Korgel, "A Comprehensive Study of Electron Energy Losses in Ge Nanowires," *Nano Lett.*, 4 (2004) 1455-1461.
10. D. C. Lee, T. Hanrath, B. A. Korgel, "Role of Precursor Decomposition Kinetics in Silicon Nanowire Synthesis in Organic Solvents," *Angew. Chem. Intl. Ed.*, 44 (2005) 3573-3577.
11. D. C. Lee, F. V. Mikulec, B. A. Korgel, "Carbon Nanotube Synthesis in Supercritical Toluene," *J. Am. Chem. Soc.*, 126 (2004) 4951-4957.
12. D. K. Smith, D. C. Lee, B. A. Korgel, "High Yield Multiwall Carbon Nanotube Synthesis in Supercritical Fluids," *Chem. Mater.*, 18 (2006) 3356-3364.
13. H.-Y. Tuan, D. C. Lee, B. A. Korgel, "Nanocrystal-Mediated Crystallization of Silicon and Germanium Nanowires in Organic Solvents: The Role of Catalysis and Solid-Phase Seeding," *Angew. Chem. Intl. Ed.*, 45 (2006) 5184-5187.
14. H.-Y. Tuan, B. A. Korgel, "Importance of Solvent-Mediated Phenylsilane Decomposition Kinetics for High Yield Solution Phase Silicon Nanowire Synthesis," *Chem. Mater.*, 20 (2008) 1239-1241.
15. H.-Y. Tuan, A. Ghezlbash, B. A. Korgel, "Silicon Nanowires and Silica Nanotubes Seeded by Copper Sulfide Nanocrystals," *Chem. Mater.*, 20 (2008) 2306-2313.
16. F.M. Davidson, A.D. Schricker, R. Wiacek, B.A. Korgel, "Supercritical Fluid-Liquid-Solid Synthesis of Gallium Arsenide Nanowires Seeded by Alkanethiol-Stabilized Gold Nanocrystals," *Adv. Mater.*, 16 (2004) 646-649.
17. F. M. Davidson, D. C. Lee, D. D. Fanfair, B. A. Korgel, "Lamellar Twinning in Semiconductor Nanowires," *J. Phys. Chem. C* 111 (2007) 2929-2935.
18. D. A. Smith, V. Holmberg, D. C. Lee, B. A. Korgel, "Young's Modulus and Size-Dependent Mechanical Quality Factor of Nanoelectromechanical Germanium Nanowire Resonators," *J. Phys. Chem. C* 112 (2008) 10725-10729.



Prof. Brian Korgel receiving Roy-Somiya Medal and Plaque from ISHA President: Prof. M. Yoshimura and ISHA General Secretaries Prof. K. Byrappa and Prof. T. Adschiri on 10th Sept. 2009, in Nottingham, UK.

III. BIBLIOGRAPHY

A GLANCE TO THE SCIENTIFIC ACTIVITY INVOLVING SOLVOTHERMAL PROCESSES

Through a rough analysis of the bibliography during the first 10 months of this year 2008 (close to 280 papers involving Hydro/Solvothermal were published).

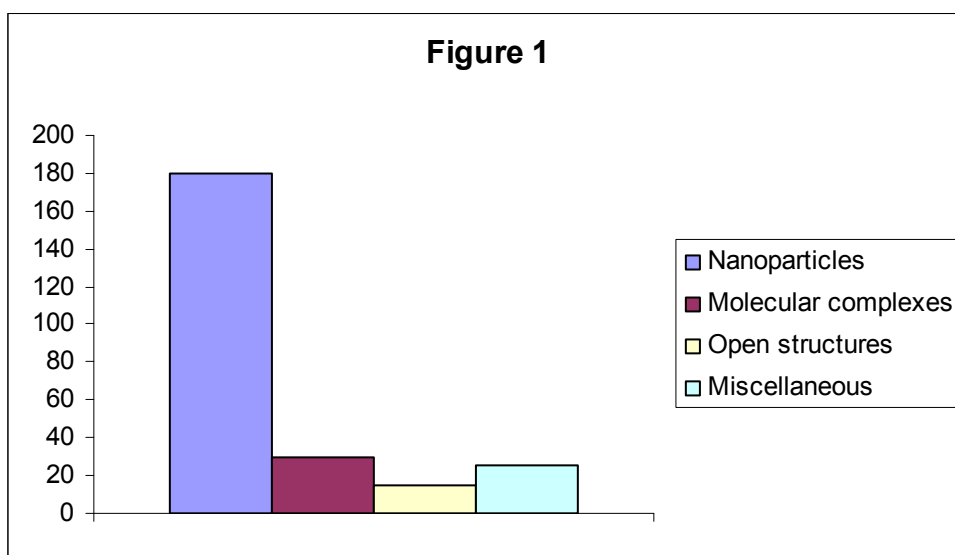


Figure 1 The main topics concerned by this bibliography.

Through this first analysis , approximatively 70 % of the papers deal with the elaboration of nanoparticles.

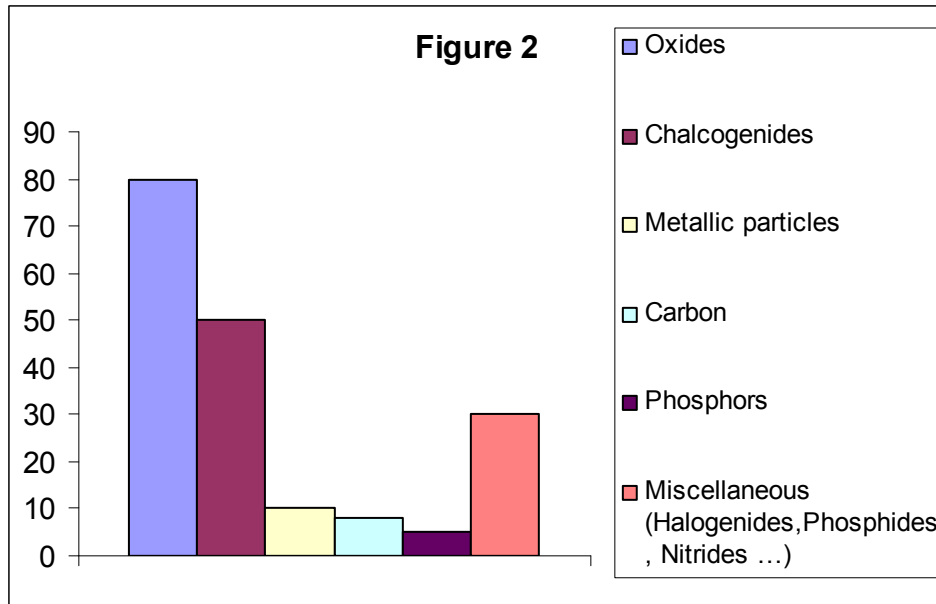


Figure 2 Different research areas concerning the Solvothermal preparation of nanoparticles.

Globally concerning Solvothermal Processes, two main features can be underlined:

1) ***The development of new assisted processes :***

- processes using a specific technology (ultrasonic, magnetic fields,...),
- processes developing a particular chemical approach (microemulsion, phase transfer catalysis, ionic liquids...).

2) ***The development of specific topics.***

Some illustrations:

1) ***The development of new assisted processes***

Solvothermal Processes using a specific technology

Sonochemical synthesis and photocatalytic activity of meso- and macroporous TiO₂ for oxidation of toluene.

Y. LIU ,Y. LI Y. WANG ,L. XIE, J. ZHENG ,X. LI
J. Hazardous Materials **150** (2008), 153-157.

Magnetic-field-assisted solvothermal growth of single-crystalline bismuth nanowires.

Y. XU ,Z. REN ,W. REN, G. CAO, K. DENG ,Y. ZHONG.
Nanotechnology **19**(2008), 115602 (5 pages)

Solvothermal Processes developing a particular chemical approach

Solvothermal synthesis and characterization of Ln(Eu³⁺, Tb³⁺) doped hydroxyapatite.

(involving microemulsion mediated processes)

C. YANG , P. YANG , W. WANG, J. WANG , M. ZHANG , J. LIN
J. Colloid and Interface Science , **328**, (2008), 203-210.

Microemulsion –mediated solvothermal synthesis and photoluminescent Property of 3D flowerlike MnWO₄ micro/nanocomposite structure

Y. XING, S. SONG, J. FENG, Y. LEI, M. LI , H. ZHANG.

Solid State Sciences **10** (2008) , 1299-1304

Microemulsion-mediated solvothermal synthesis of tin(IV) hydrogen phosphate.

H. YANG , X. HE , M. CAO.

Mater. Res. Bull. (online doi:10.1016/j.materresbull.2008.07.009)

Phase transfer catalysis : synthesis of monodispersed FePt nanoparticles and its electrocatalytic activity

M. WEN , H. QI , W. ZHAO, J. CHEN , L. LI, Q. WU

Colloids and Surfaces A: Physicochem. Eng. Aspects **312** (2008), 73-78

Ionic liquid-assisted complex-solvothermal synthesis of ZnSe hollow microspheres.

X. LIU , J. MA, P. PENG , W. ZHENG

Materials Sciences and Engineering B **150** (2008) , 89-94

2) The development of specific topics.

Solvothermal processes for preparing nano-composites systems.

Synthesis and characterization of 1D Co/CoFe₂O₄ composites with tunable morphologies

L. ZHAO , H. ZHANG , L. ZHOU , Y. XING , S. SONG , Y. LEI

Chem. Commun. (2008), 3570-3572.

Direct Solvothermal formation of nanocrystalline TiO₂ on porous SiO₂ adsorbent and photocatalytic removal of nitrogen oxides in air over TiO₂-SiO₂ composites.

H. KOMINAMI , K. YUKISHITA , T. KIMURA , M. MATSUBARA,

K. HASHIMOTO , Y. KERA, B. OHTANI

Top Catal. **47** (2008) , 155-161

One-pot synthesis of CoO/C hybrid microspheres as anode materials for

lithium- ion batteries.

H. QIAO, L. XIAO ,Z. ZHENG , H. LIU ,F. JIA, L. ZHANG
J. Power Sources **185** (2008), 486-491.

SnO₂@C core-shell spheres : synthesis, characterization and performance in reversible Li-ion storage

H. QIAO ,Z. ZHENG ,L. ZHANG ,L. XIAO.
J. Mater. Sci. **43**(2008) ,2778-2784.

Preparation of magnetic nanoparticles encapsulated by an ultrathin silical shell via transformation of magnetic Fe-MCM-41.

M. ARRUEBO ,W.Y. HO , K.F. LAM ,X. CHEN ,J. ARBIOL,
J.SANTAMARIA ,K.L. YEUNG.
*Chem. Mater.***20** (2008) ,486-493.

Solvothermal synthesis of carbon nanotube-B₂O₃ nanocomposite using tributyl borate as boron oxide source.

A. OKI , L. ADAMS , Z. LUO.
Inorg. Chem. Communications **11** (2008) , 275-278.

Comparison of microwave assisted solvothermal and hydrothermal syntheses of LiFePO₄/C nanocomposite cathodes for lithium batteries.

A. VADIVEL MURUGAN , T. MURALIGANTH ,A. MATHIRAM.
J. Physical Chemistry.C **112** (2008) ,14665-14671

Fabrication of CdS nanowires decorated with TiO₂ nanoparticles for photocatalytic hydrogen production under visible light irradiation.

J. S. JANG , H. G. KIM, U.A. JOSHI, J.W. JANG , J.S. LEE
Intern. J. hydrogen Energy **33** (2008) ,5975-5980.

Fabrication of high aspect ratio core-shell CdS-Mn/ZnS nanowires by a two step solvothermal process.

S. KAR , S. SANTRA, H. HEINRICH.
J. Physical Chemistry C **112** (2008), 4036-4041.

All these papers , concerning different domains of applications ,underline that Solvothermal process can manage all chemical mechanisms governing each step of the fabrication of the corresponding nanocomposite.

Solvothermal processes for preparing new phosphors.

Highly enhanced blue-emission of LnOCl:Tm prepared by dehydration of Ln(OH)₂Cl :Tm (Ln=La and Gd)

S.S. LEE , C.H. JOH ,S.H. BYEON
Materials Science Engineering B **151** (2008), 163-168.

Evidence of trivalent europium incorporated in anatase TiO₂ nanocrystals with multiple sites.

W. LUO ,R. LI, G. LIU, M.R. ANTONIO ,X. CHEN
J. Physical Chemistry C **112** (2008) , 10370-10377.

Solvothermal synthesis , controlled morphology and optical properties of Y₂O₃:Eu³⁺ nanocrystals.

M.K. DEVARAJU , S. YIN , T. SATO
J. Crystal Growth ,(on line doi:10.1016/j.crysgro.2008.09.139)

Synthesis , characterization and luminescent properties of Pr³⁺-doped bulk and nanocrystalline BaTiO₃ phosphors.

Z. FU ,B.K. MOON ,H. K. YANG , J.H. JEONG
J. Physical Chemistry C **112** (2008) ,5724-5728

Polyol –mediated synthesis and luminescence of lanthanide-doped NaYF₄ nanocrystal upconversion phosphors.

Y. WEI , F. LU, X. ZHANG , D. CHEN
J. Alloys Compounds **455** (2008) , 376-384.

If oxides , halogenides are always the main matrixes , sulfides could be developed in the near future.

Advances in sulfides phosphors for displays and lighting

D. POELMAN , J.E. Van HAECKE , Ph. F. SMET
J. Mater. Sci. : Mater. Electron. (on line: doi 10.1007/s10854-007-9466-3)

Solvothermal synthesis of new materials

This topic is always developed . It is possible to give some illustrations concerning the structure and the composition.

Cobalt (ethylenediamine) sulphate: a pillared layered coordination polymer.

S. LAUCHAN , T. J. PRIOR, S. MEANSIRI ,A. RUJIWATRA
J. Inorg. Organomet. Polym. **18** (2008) , 352-357

The synthesis and crystal structure of [BiI₂(tpy)₂][Bi₂I₇(tpy)]: A new metal halide material

M.A. TERSHANSY , A.M. GOFORTH , M.D. SMITH , H-C zur LOYE
*J. Chem. Crystallogr.***38** (2008), 453 -459.

The rough analysis of the bibliography during these last months underlines that Solvothermal processes are more and more developed and involved in different research areas.

***Bordeaux November 18 ,2008
Gérard DEMAZEAU***

Conference Reports

1. XXI International Union of Crystallography Congress and General Assembly , August 22-31, 2008, Osaka, Japan

The XXI IUCr Congress and General Assembly was a well organized scientific event with a participation of over 2600 delegates from all over 66 countries bridging major fields such as biology, chemistry, physics, mineralogy, and earth science ranging from academic research to industrial/medical applications. Its scientific program in 7 days was very rich and exciting with 2 Plenary Lectures, 36 Keynote Lectures and as many as 98 Microsymposia. A special attention for programming has been paid to promote interdisciplinary fields in crystallography including health, environment, energy and information.

The author of this report was the Chair of the Microsymposium MS4 : Hydrothermal Growth of Crystals, with Prof. Shouhua Feng from China as a Co-Chair. The Chair and Co-Chair had carefully selected the speakers to cover all the broader areas of hydrothermal growth of crystals with an emphasis on the recent trends. The Chair Prof. K. Byrappa gave a nice brief introduction to the audience on the topic of each invited speaker in order to introduce the subject and its evolution. Some of the major breakthrough or results in this session were the use of ecofriendly processes to grow crystals. Also perfect blend of size and morphology greatly influence the properties. During the inaugural session and also 60th anniversary of the International Union of Crystallography, Prof. Edward N. Baker, gave a wonderful and highly thought provoking talk on the topic "Crystallography and the world around US.

The symposium organized by the present author of this report was very well attended by a good number of delegates. We had 5 speakers who presented the latest trends in Hydrothermal Growth of Crystals covering all the aspects. These topics and the speakers were carefully selected to cover all the aspects of hydrothermal growth of crystals starting from hybrid crystals (that is the latest trend), gallium nitride (a hot topic in Materials Science), ZnO (a popular material, but this speaker presented the new dimension for this material in terms of its biological applications), the use of eco-friendly precursor in the hydrothermal processing of materials was also presented, and lastly the use of hydrothermal technique for the growth of perfect fibers and nanotubes. On the whole the microsymposium was a great success. After several years, a Microsymposium on Hydrothermal Growth of Crystals was held in the IUCr Congress. The delegate met various other delegates from different countries and exchanged the subject matter with them. It was an excellent academic interaction which was useful to learn the recent trends in crystallography.

The Ewald Prize – the highest prize in crystallography was awarded to Dr D. Sayre (Department of Physics, State University of New York, Stony Brook, USA) has been awarded the eighth Ewald Prize for the unique breadth of his contributions to crystallography, which range from seminal contributions to the

solving of the phase problem to the complex physics of imaging generic objects by X-ray diffraction and microscopy, and for never losing touch with the physical reality of the processes involved. In addition to all these, there were several satellite meetings of interest, and some of them were attended by the delegate. On the whole the arrangements were excellent in this congress, except for the lack of visits to the research laboratories and Universities and research institutes. However, at the end of the congress, a visit to Spring-8 was arranged, and that was an excellent trip and most useful especially for the students.

2. The First International Solvothermal and Hydrothermal Association Conference (ISHA 2008), Nottingham, UK, Sept. 8-10, 2008.

www.isha2008.org

The University of Nottingham has successfully hosted the first joint meeting of the International Solvothermal & Hydrothermal Association (ISHA) Conference at the University of Nottingham.

The conference took place 7th -10th September 2008 and featured over 80 talks with delegates from over 25 countries. There were multiple sessions covering 10 different technical areas from nanoscience to origins of life and from clean technology to clean up technology. The event was hosted by Dr Ed Lester from The Engineering Faculty (Chemical and Environmental Engineering).



The event was supported by Promethean Particles Ltd (a Nottingham Spin out company working in Nanomaterials) and DICE – Driving innovation in chemistry and engineering – the EPSRC/HEFCE funded Innovation award bringing together Chemists and Chemical Engineers- headed by Professor Martyn Poliakoff CBE. All four DICE lecturers – Dr Pete Licence, Dr Wim Thielemans, Dr Darren Walsh and Dr Derek Irvine also gave lectures on their current research activities. DICE visiting professors Professor Tadafumi Adschiri (Tohoku University) and Professor Viktor Bagratashvili (Moscow State University) also attended the event.

There were three Plenary lectures from Masahiro Yoshimura on 'The Feature and Future of Hydrothermal Processing for Materials Science', Martyn Poliakoff on 'Rolling the DICE - Will Green Science save the day?' and Rik Riman on 'Thermochemical Design of Solvothermal Processes: Current Status and Future'.

The conference included networking opportunities with a trip to Belvoir Castle and a banquet on the second evening. Delegates tried out archery, falconry, a tour of the castle and a jousting display from the Knights of Nottingham.

The final day's events included prizes and awards for lifetime achievement award and an award for an outstanding researcher under 45.

The Sawyer Award to recognize unique and outstanding lifetime contributions in the research, development, or production of materials by hydrothermal or solvothermal techniques or to recognize leadership or entrepreneurship within profit or non-profit organisations in all areas of solvothermal and hydrothermal technology. This prize went to Professor Rustum Roy, Pugh Professor of the Solid State Emeritus, Professor of Science Technology and Society Emeritus, The Pennsylvania State University

The Roy-Somiya Medal (named after our two Patrons viz. Prof.R. Roy and Prof.S. Somiya) for an outstanding researcher in the field of Hydrothermal and Solvothermal Research below the age group of 45 years for the innovative research contribution with a high impact on the field. This year's award went to Brian Korgel Cockrell School of Engineering Temple Professor #1 & Matthew Van Winkle Regents Professor of Chemical Engineering, Department of Chemical Engineering from The University of Texas at Austin.

[ISHA2008 website](#). If you would like to know more please email [Dr Ed Lester](#).

Some Photos from ISHA-2008:



Prof. Dermot O'Hare Oxford University



Attendees during a session
(Martyn Poliakoff left of centre)



Standard British transport to Belvoir Castle



Professor Youn Woo Lee with Ed Lester



Archery practice by the ISHA delegates



Minstrels introducing the Knights of Nottingham

Calendar of events for 2009-2010:

- 1) Nanobiophysics, Nanochemistry, Nanomedicine & Nanotoxicology Conference, to be held on the shores of the Caribbean sea, in Bolans Village, Antigua and Barbuda, between January 21 and January 25 2009.
<http://www.zingconferences.com/z.cfm?c=44>
- 2) Solid State Chemistry conference, in Playa del Carmen, Mexico, February 25 to February 28 2009.
- 3) **Hybrid Materials 2009**
Tours, France, March 15 – 19, 2009
Homepage: www.hybridmaterialsconference.com.

- 4) **The International Nanotechnology Conference (Nanolsrael 2009)**
Jerusalem, Israel, March 30-31, 2009.
Contact Address: Nanolsrael_2009@mail.vresp.com
- 5) **First International Conference on Nanostructured Materials and Nanocomposites (ICNM – 2009): April 10,11 and 12, 2009, Kottayam, Kerala, India**
E-mail: icnm2009@gmail.com and icnms2009@gmail.com
- 6) **9th International Symposium on Supercritical Fluids (ISSF2009)**
New Trends in Supercritical Fluids: Energy, Materials, Processing
May 18-20, 2009, Bordeaux, France.
Website: <http://www.issf2009.cnrs.fr>
- 7) **8th PACIFIC RIM CONFERENCE ON CERAMIC AND GLASS TECHNOLOGY**
May 31 – June 5, 2009, Hyatt Regency Vancouver
Vancouver, British Columbia, Canada
www.ceramics.org/pacrim8
- 8) **International Conference on Materials for Advanced Technologies 2009, ICMAT 2009**
28 June-03 July, 2009, Singapore
Homepage: <http://www.mrs.org.sg>

Symposium S

Novel Routes of Solution Processing

Chairs : K. BYRAPPA, University of Mysore, India

Gregory K.L. GOH, *IMRE, Singapore*

Co-Chairs:

- Richard E. RIMAN, *Rutgers University, USA*
- Shouhua FENG, *Jilin University, China*
- Tadafumi ADSCHIRI, *Tohoku University, Japan*

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(Last date to submit abstracts is fast approaching. List of Speakers is given in the website)

Scope of Symposium

This symposium provides a perfect platform for academics, researchers, technologists and industrial players to meet and discuss the latest developments in the area of novel routes of solution processing to fabricate advanced materials covering polyscale crystals, particles, films, composites, nanostructures, patterned materials, etc. The symposium will focus also on the in situ fabrication and intelligent engineering of functional materials, thermochemical modelling, reactions kinetics, transport kinetics and crystallization kinetics.

Symposium Topics

- Nature inspired, Biomimetic, Bio-inspired, Geomimetic Solution Processing, Geothermal reactors.
- Solution processing - Conventional Methods and Novel Methods including CBD, Soft Solution Processing, Spray Pyrolysis, Solution Plasma Processing, High Temperature Solution, Wet Chemical Processing, Hydrothermal, Solvothermal, Supercritical Fluid Technology, Ammonothermal, Glycothermal, methods, Hydrothermal-epitaxy, Direct write technology, etc.
- Multi-Energy Solution Processing of Materials: Mechanochemical, Sonochemical, Microwave, Electrochemical, etc., in combination with conventional solution routes.
- *In situ* fabrication of functional products from Novel Solution Routes.
- Thermochemical modeling, Reaction Kinetics, Transport Kinetics, Crystallization Kinetics.
- Solution processing of Technological Materials and their applications including semiconductor, ceramic, optoelectronic, photonic, negative index, catalysis, treatment, sensors, biomedical and next generation display applications; Polyscale Crystals - Bulk single crystals, Fine crystals, Nanocrystals; Thin Films; Fibers; Nanomaterials - nanotubes, nanosheets, nanosphere, nanowires, nanoprobes, nanoscale films, nanocarriers, Composites – bulk to nano size, organic-inorganic composites; Patterned materials, etc. Solution routes for recycling, green chemistry.

For more information on various conferences please refer to:

- 1) <http://www.zingconferences.com/>
- 2) Elsevier Conferences <conferences@mail.elsevier-alerts.com>

If the members have some suggestions and announcements to be included in the *next ISHA Newsletter due in March 2009*, please contact the Secretaries: Prof.K. Byrappa or Prof.Tadafumi Adschiri.

We sincerely hope that you would enjoy reading this [No.3, Vol.3 \(2008\)](#) [ISHA Newsletter](#) and send us your feedback.

November/December 2008 ISHA Newsletter was prepared by ISHA Secretaries:



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