Rich Legacy of Solid State Chemistry Activities

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Preamble:

Solid state chemistry has always been one of central areas of research in Chemistry Group since early days. R&D in solid state chemistry, one of the oldest activities in Chemistry Group, was introduced in the department in the 1958, the era towards the expansion of atomic energy programme in India. In 1958, three sections were created in Chemistry Division namely, Radiation Chemistry Section, High Purity Materials Section and Solid State Studies Section. The activities in solid state chemistry were carried out by "Solid State Studies Section" under the aegis of Chemistry Division. The research in Solid State Chemistry has always focused on properties of solids of either direct relevance to Indian nuclear energy programme or having prospects of technological application. Additionally, studies on solids to understand their fundamental as well as functional properties were also encouraged in the beginning era of solid state research in Chemistry Division.

Brief history and scope of solid state chemistry activities:

Even though the research in Chemistry Division started in later half of 1950s, it was only in 1971, that the detailed Annual Divisional Report was compiled. The exciting work carried out in the area of solid state chemistry during that time is categorically mentioned by Dr. Jagdish Shankar, then Head, Chemistry Division, in the foreword of Divisional Annual report (1971) as follows:

"*The thing worthy of mention is work which has been initiated during the last few years in the field of high temperature chemistry and the rather sophisticated techniques which have been developed and set up in the Division*".

(Reproduced from foreword by Dr. Jagdish Shankar, Head, Chemistry Division (Annual Report, Chemistry Division, 1971)).

The work highlights mentioned in the annual reports of Chemistry Division and various conferences and journal publications in that period amply reflect the extraordinary works carried out on fuel, fertile materials and cladding as well as on conventional solid state chemistry for crystallographic and magnetic phase transitions, thermodynamics and thermal analysis of high temperature materials, preparation and properties of thin films, semiconductors, X-ray crystallography, Mössbauer studies, effect of neutron irradiation on materials among others. All these activities were pursued under the leadership of Dr. M. D. Karkhanawala, Head, Solid-Sate Studies Section. An important aim of activities in solid state chemistry and crystallography was to understand the processes taking place at the atomistic level during phase transitions in solids. These were pursued by employing techniques like thermo-gravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), dilatometry and high temperature X-ray diffraction (HT-XRD). Magnetic and electrical properties of various binary compounds of metal- metalloid using electrical conductivity and magnetic susceptibility measurements were studied during that period. In addition, a considerable work was initiated in the direction of thermodynamics of high temperature materials using (a) transpiration technique to estimate the vapour pressures of materials in controlled atmospheres and high temperatures (b) solid state galvanic cell measurement(to determine free energy changes for various cell reactions). The activities on materials research were focussed on electronic and ionic conductors, magnetic materials, thermoelectric materials, phosphors and dielectrics. A lot of efforts had also been directed towards design and development of equipments in that period, and that manifested in many indigenous instruments and techniques developed during the initial decades of Chemistry Group. In fact, the first Annual report published in 1971 has a dedicated section on this aspect. The section had also established number of indigenous facilities for experimental work like differential thermal analyser, dilatometer, equipments for electrical conductivity, Hall mobility, Magnetic susceptibility as well as Mössbauer Spectroscopy. Many scientists significantly contributed to the growth of the research activities in the section. In fact, in sixties and seventies, the Division was a prominent centre of X-ray crystallography and thermal analysis in the country. In late 1980s and early 1990s, high Tc oxide superconductors attracted the attention of solid state chemistry fraternity in Chemistry Group. Early 2000s witnessed the renaissance of solid state chemistry activities wherein several new projects were initiated to include futuristic materials envisaged for back end and front end of nuclear cycle. Typical examples are pyrochlores and zirconolite type materials for nuclear waste immobilisation, materials for extreme conditions, materials with tailored thermal expansion behaviour etc. Several host materials were developed to incorporate minor actinides. Rational design of materials was adopted to prepare newer and superior functional materials. The concepts like tuning of radius ratio, degree of disorder, distortion, point defects engineering, unusual polyhedral sharing, unusual coordination numbers and counter-ion polarisability were used to prepare many new materials with desired functional properties.

Over the years, the activities saw a huge expansion matching shoulder-to-shoulder with the developments happening in the international scientific community to cover areas such as high temperature superconductors, ionic conductors, dielectric and ferroelectric relaxors, materials for solid state lighting, research on inorganic fluorides, spintronic materials, radiation stability studies in Pelletrons, energy materials and so on. Some notable examples are described in the following sections that provide glimpses of research in solid state chemistry over last few decades.

Phase transition studies:

Phase transition was one area of research that caught the fancy of Solid State Studies Section quite early due to its technical significance. In early 1970s, an interesting result was the observation of unusual behaviour of phase transition from orthorhombic to trigonal in KNO_3 at 129°C.The correlation between shape of single crystal of Na_2SO_4 with its crystalline polymorph had been unravelled. It was pointed out that Na_2SO_4 when grown at temperature above 38°C show needle shaped crystal for Na_2SO_4(III) while prismatic for Na_2SO_4 (V). Extensive characterization of Na_2SO_4(III) had been carried out by using single crystal X-ray diffraction, dilatometry as well as DSC. The superiority of DSC in detecting magnetic and structural phase transition was demonstrated on a variety of oxides, alloys and compounds. Another example of an interesting finding of the early research of the section was the observation of phase transition in anhydrous sodium sulphate induced by simple mechanical grinding. The entire mechanism had been deciphered using then available facilities like DTA, dilatometry and HT-XRD in the section. In addition, significant research efforts had also been made on magnetic transitions in Fe-Ge binary compounds. During 1982-84, activity on synthesis and properties of various stable and metastable polymorphs of various materials had been initiated. Some of the examples are crystalline and amorphous polymorphs of zirconium phosphates, stabilized zirconia, etc. This work is continued till now, and in the last two decades, lot of efforts have been directed towards the synthesis and understanding the stability of metastable phases and their properties. Some of the examples of the recent studies are: composition and temperature dependent phase evolution of materials in CeO_2- Gd_2O_3, CeO_2- ZrO_2 systems etc. A number of metastable phases such as $CeCrO_3$, $CeScO_3$, $La_{1-x}Ce_xCrO_3$ and framework-type $K_2Ce(PO_4)_2$ have been isolated in recent years by carefully modifying the synthesis route. Gel combustion has been employed to obtain various metastable phases in $REInO_3$ system (RE: rare earth ions) by virtue of the non-equilibrium nature of synthesis conditions. Interesting structure driven properties have been observed in some of these phases. Another example of stabilization of metastable phase is tetragonal $ThSiO_4$ by substitution of Ce^{4+} in monoclinic phase that was carried out in 2005.

Radiation effect on materials:

Right from the beginning, Chemistry Division had a rich tradition of research on radiation effects on solids. Most of the works in early and late 1970s were devoted on vanadium and stainless steel. In a typical study, formation of point defects in vanadium on irradiation by fast neutrons of fluence of about 1x 10^{18} $n/cm^2/s$ was studied. Studies on annealing of the point defects had shown a distinct recovery stage at 170°C. Also, the effect of dislocations on recovery of irradiated samples had also been studied. Extensive use of electron microscopy had been carried out to observe and understand the defects in irradiated metals and alloys. In 1971-72, studies on damage in stainless steel (SS)on neutron irradiation to understand the effect of extremely high fluences (10^{24} $ions/cm^2$) of neutron as expected in fast reactors over a period of three years. The studies concluded the formation of voids in SS even at moderately higher fluence. These were also supported by theoretical studies wherein the relations for variation of $\Delta V/V$ with flux at different temperatures had been derived. In 1980-82, neutron damage and recovery studies were also done on V- 2at% Nb, V- 2at% Al and V-2 at% Zr. Subsequently, the studies were extended by irradiation with helium ions at

VECC, Kolkata using the degraded beam of 3 - 5 MeV. A notable example of this study is TiC coated 304 stainless steel. Many studies were carried out with emphasis on radiation-generated electron/hole trapping state and emission centres in solids especially in wide band gap materials like calcites, barites, alumina, and magnesium oxide. Irradiation facilities such as Co^{60} γ- irradiation cell (Chemistry Division), neutron beam source at CIRUS and α-particle beam at Van de Graff accelerator were utilized for these studies. For this work an instrumental set-up for recording thermoluminescence (TL) emission that was equipped with a photomultiplier tube and a temperature programming facility was developed indigenously *(A BARC report highlighting the simplicity and good efficiency of this low-cost indigenous instrument was also published)*. Later on, the TL work was supplemented by Electron Spin Resonance (ESR) and Photoluminescence (PL) measurements, utilizing the facilities available in other divisions of BARC. These studies resulted in several publications in the reputed international journals.

In context of materials under extreme conditions, 2005 onwards, several pyrochlore-based materials were irradiated at pelletron at Inter University Accelerator Centre, Delhi (IUAC) with low energy heavy elements (to mimic alpha recoils) and high energy heavy elements (to mimic fission fragments). The pre- and post- irradiated samples were investigated, by various techniques such as Grazing incident x-ray diffraction (GI-XRD), Raman spectroscopy, Rutherford backscattering, X-ray photoelectron spectroscopy (XPS), Positron annihilation spectroscopy (PAS) etc. to understand bulk and local radiation damage evolution. In case of pyrochlores, radius ratio of the cations was found to be a predominant factor directing the radiation response. In case of redox active material like CeO_2, it was concluded that reducible nature of ion along with vacancy prevalence influences the radiation response. In addition to the effect of energy of radiation, the radiation response as a function of particle size has also been studied and that has given very important guidelines to design materials for tailored radiation response.

Thermodynamics and thermochemistry of high temperature materials:

Since beginning, studies on thermochemistry and thermodynamics were an integral part of Solid State Research in Chemistry Division. Heat transport studies on a variety of materials including rare earth cobaltates ($RECoO_3$), cuprates (RE_2CuO_4) and nicklates (RE_2NiO_4), semiconducting $Gd_{2-x}Sr_xCuO_4$, etc, added value towards understanding of fundamental heat transport mechanisms (via electrons, phonons, excitons, etc.) in solids. For $LaCoO_3$, it was concluded that the excitonic mode is the dominant mode of heat conduction at high temperature. Valuable thermodynamic data for materials, like CoO-Co_3O_4, $LaCrO_3$, $LaCoO_3$, considered suitable for high temperature applications had been determined by EMF measurement using solid electrolyte galvanic cells. Entire thermochemistry data on Zr-Nb in the Zr-rich region refractory alloys prepared by electron beam melting has also been generated.

Research on optical materials and phosphors:

The studies on solids were also expanded to insulators and materials with wide band gap for enhancing the optical transparency. The studies received prominence from the point of view of developing radiation dosimeters, and that paved ways to explore variety of materials as ASO_4 and AF_2, A = Ca, Sr and Ba, and minerals such as MgO, silica and barite for their importance in thermoluminescence dosimetry. The glow curves and emission spectra from various impurity doped $BaSO_4$ phosphors have been standardized to use them as radiation dosimeter in department. The coloration of diamond by defect control was also explored. The study of thermoluminescence behaviour of different inorganic materials (minerals and phosphors) was also performed to understand the underlying mechanism of thermoluminescence and the role played by various chemical impurities and lattice imperfections. Additionally, modelling and computer-based analysis procedures for interpreting glow peaks have been developed to obtain the thermoluminescence parameters from phosphors. In 2006-2008, the optical properties of solids regained attention, with the aim to develop phosphors for solid state lighting and daylight generation, development of laser or luminescent crystal, multiphoton excitations, tagging of molecules for biological applications, display device, optical markers, etc. Wide varieties of oxides, like $ZnGa_2O_4$, $BiPO_4$, TiO_2, $LaPO_4$, YPO_4 etc. have been extensively studied in this period. Vast amounts of studies were carried out on rare-earth based nano-fluorides for solid state lighting in view of their wide band gap and sharp emissions. Many of them such as CeF_3 were also developed as polymer composites for practical applications. Further, the studies were also extended to organic luminescent materials as well.

High Tc oxide superconductors:

Research on solid state chemistry of oxides got a tremendous boost by the advent of high Tc oxide superconductors ($La_{1.85}Ba_{0.15}CuO_4$) reported towards end of 1986. In early 1987, $YBa_2Cu_3O_{7-\delta}$ (also termed as Y123 oxide) was discovered which led to an intense flurry of activities in the field of oxide superconductors in different Divisions of Chemistry Group. Several cationic and anionic substituted Y123 oxide-derivatives were prepared and characterised. Several superconductors with electrons as charge carriers were also synthesized. Research was also diversified towards synthesis of Bi and Tl based oxide superconductors. A novel matrix assisted synthesis route was developed to prepare these superconductors. Successful attempts were made to fabricate thin films of Y123 oxides by Laser assisted routes. Subsequently, in 2012-13, thick discs of Y123 oxides were also fabricated for various applications. Another interesting work was on synthesis of nano-crystalline Pb by chemical methods which is a Type-I superconductor. In context of this work, several state-of-the-art facilities such as VSM and XRD were also installed in Chemistry Group.

Thoria-based systems and potential materials for minor actinide transmutation:

In recent years, extensive work had been done in establishing phase relations and thermophysical properties in thoria and thoria-based systems. The activities were taken as a part of thoria task force constituted in 1998 by Dr. Anil Kakodkar, then Director, BARC, towards mandate of utilisation of thorium. A large number of binary and ternary systems were synthesized by high temperature synthesis, characterised by XRD and investigated for linear and bulk thermal expansion. In the beginning of 2000, activity towards the understanding of phase relations in the systems that have potential as inert hosts for minor actinide transmutation (Inert matrix fuel) was initiated. These studies led to development of extensive and novel ternary phase relations in oxides such as ceria, thoria, zirconia, RE_2O_3(RE: Gd, Dy). Bulk/lattice thermal expansion of several single-phasic compositions were investigated in this activity. Later on, the inert matrix work has been expanded to included garnets ($Y_3Al_5O_{12}$) and composites for obtaining better thermally conducting potential inert candidates. This work has not only resulted in building up of a vast database of structural, phase relations and thermophysical properties of thoria-based systems and potential candidates for minor actinide immobilisation and transmutation but also has given a thorough understanding of solid-state chemistry of these materials. More details on these activities are included in a dedicated chapter on nuclear materials.

Solid inorganic fluorides:

In early 1980s, another new activity on synthesis of solid inorganic fluorides was initiated at Chemistry Group. Initially the synthesis approach involved use of NH_4HF_2 and KHF_2 as the fluorinating agents to prepare fluorides of different types of oxides e.g. Cr_2O_3, ThO_2, UO_2, RE_2O_3 etc. In fact, NH_4HF_2 was also used to prepare fluoride containing oxides superconductors. By mid 1990s, the work was diversified to various ternary/ quaternary fluorides prepared by high temperature solid state route. Some of the examples are Li_3TiF_6, Li_3CrF_6 etc. In several cases, the structure was solved using single crystal X-ray diffraction technique. Subsequently, an extensive research programme was launched to establish phase relations in REF_3-MF_2systems (RE: rare earth ion; M: Alkaline earth ion/ Pb^{2+}). It resulted in the preparation of superior fluoride ion conductors in $Pb_{1-x}Y_xF_{2+x}$ system. In addition, these studies yielded an extensive understanding of phase relations in several types of mixed fluorides systems. Some of the anion-rich systems exhibited fascinating ordered structures.

Thermal expansion studies:

Thermal expansion and phase transition of solids have been studied for many years by using in situ high temperature XRD and dilatometry. In early seventies, thermal expansion of $NaNO_3$was studied using specially designed high temperature camera to record XRD data in back reflection geometry. During that period, perovskite type solids like alkaline zirconate, and nuclear fuel related materials like U_3O_8, UO_2-ThO_2, UC, UN and standard materials like Pt-Rh alloys etc. have been investigated to reveal their thermal expansion and phase transition behaviours. High temperature structure and thermal expansion behaviour of high Tc oxide superconductors like $YBa_2Cu_3O_{7-x}$, had been studied using variable temperature XRD. Subsequently, the studies were extended to materials related to AHWR, like ThO_2 and UO_2 doped with varieties of fission products and elements surrogate to actinides and various compounds of fission products. In 2000, a new automated high temperature XRD was installed which was extensively used to study lattice thermal expansion of crystalline materials. The studies were further diverted in early 2000 towards the search and understanding of negative thermal expansion materials. Varieties of materials, like $A_2(WO_4)_3$, Ln = La, Nd, Y and Al have been explored for their anomalous expansion behaviour. Studies on negative or low thermal expansion materials, like ZrW_2O_8, $HfMo_2O_8$, $NbOPO_4$,

$A_2(MoO_4)_3$, A = trivalent cations,$Al_{1-x}Ga_xPO_4$, BPO_4etc. have also been carried out. Composites and solid solutions were also studied to develop tailored thermal expansion materials. Further a variety of low and negative thermal expansion materials were also studied at higher pressure to understand the correlation of compressibility and amorphization with structure.

Solid state chemistry of framework solids:

Studies on Solid State Chemistry of framework solids evolved from the exploration of materials for negative thermal expansion and highly compressible solids. These were further extended to design and develop materials for ionic conductors, dielectrics and ion exchanger. Flexible structure of framework materials allows to control substitution and migration of ions in the lattice. These were also very amenable to immobilize variety of ions. Several type of materials like $AMnO_2.xH_2O$, $Na_2Ti_3O_7$, $NaAlSiO_4$, $K_2Ce(PO_4)_2$, $K_2Fe_2Ti_6O_{16}$ etc. have been extensively studied for their structure, stability, ion mobility and/or ion exchange characteristics. Also, there are several zeolites, and framework type titanosilicates, like $NaTiSiO_5$, ETS-4, etc. that have been explored for their ion exchanging properties. Framework-type $Li_2Si_2O_5$, $Na_2Si_2O_5$, $Na_2Ti_3O_7$, $LiFePO_4$, $LiMnPO_4$, etc. have been explored for alkali ion diffusion at high temperature.

Electrical materials:

The studies on electrical properties of solids in Chemistry Group dates back to the early 1960s. There has been a tradition of extensive research on electrical materials both dedicated to ionic or electronic conductors as well as dielectrics. Extensive studies on electronically conducting ceramics like $LaCrO_3$, $LaCoO_3$, $LaMnO_3$, etc. and their solid solutions have been performed for the electronic conductivity at high temperature in possible application as electrodes in magneto-hydrodynamics. In mid-seventies (1975), a four-probe facility for electrical conductivity measurements at high temperature was developed in-house to measure resistivities in the range $0.1\text{-}10^6\ \Omega$ cm with an accuracy up to 3% at high temperature. Studies on lanthanum cuprate using the in-house developed four probe assembly revealed metallic conductivity along with anomaly of ionic conductivity at around 310°C. The group had also indicated that only La_2CuO_4 is metallic while all other rare-earth cuprates were semiconducting. There were also extensive studies on resistivity of Co-Ga alloys. In 1980-82, studies on electrical resistivity and magnetic properties of Cr-Mn, Cr-Ir and Co-based Heusler alloys have also been carried out.

In the area of ionic conductors, synthesis, characterisation and ionic conductivity has been explored in the systems like doped CeO_2, doped zirconia as well as pyrochlores ($RE_2Zr_2O_7$). Extensive studies relating the defects present in these materials with their ionic transport behaviour have been carried out. It has been concluded that the degree of disorder in pyrochlores obtained by isovalent cationic substitution affects both pre-exponential factor as well as activation energy. It is the relative variation in these two factors that ultimately controls the ionic conductivity. An interesting result was the optimisation of activation energy and pre-exponential factor by slightly tuning the non-stoichiometry in $Nd_2Zr_2O_7$ system (without any external doping) wherein $Nd_{1.80}Z_{2.20}O_{7.10}$ showed two-orders higher ionic conductivity as compared to stoichiometric system. A lot of work on electrical materials aimed at “Solid Oxide Fuel Cell (SOFC)” technology has also been done. Various $BaCeO_3$, $BaZrO_3$ and $Ba_2In_2O_5$ based proton conductors have been investigated for influence of dopant on lattice symmetry, chemical stability and protonic conductivity. Yttrium doped $BaCeO_3$-$BaZrO_3$ solid solution-based systems exhibit enhancement of chemical stability with increasing Zr content with marginal loss in conductivity. $BaCe_{0.4}Zr_{0.4}Y_{0.2}O_3$ and $Ba_2In_{1.7}W_{0.3}O_5$ have been identified as the most appropriate materials in terms of chemical stability and protonic conductivity. A proton conductor-based prototype button cell was developed and demonstrated with 35 $mW.cm^{-2}$ power density.

During last ten years, research on dielectric materials has been aimed at developing new ferroelectrics, dielectrics and ferroelectric relaxors materials. Some of the highlights have been introduction of relaxor properties in the incipient ferroelectric TiO_2 by substituting Fe and Ta that yielded charge neutrality but created compositional inhomogeneity in nominal composition $FeTiTaO_6$. A very high dielectric constant (10^4) material was developed by substituting 1- 5 mol% Nb^{5+} in TiO_2. A new class of relaxors was established in rare earth indates, $REInO_3$. Post 2000, studies on Bi_2O_3 based solid solutions and composites have been studied to explore for possible electrolytes for intermediate temperature solid oxide fuel cell. A large part of studies was concentrated on doped ceria and zirconia for application in SOFC. Fundamental studies on effect of oxides ion and variable oxidation state of transition metals on dielectric properties and magnetic properties of double perovskites like $Ln_2B'BO_6$ (B’ = Co, Mn, Ni), Ln = La, Nd, Y Eu etc. have been studied. Also, a number of materials like, like, $BiFeO_3$, $Nd_2Ti_2O_7$, $Pr_2Ti_2O_7$, $Bi_4Ti_3O_{12}$, $BaMnF_4$, and several types polymer or ceramic composites have been explored in the interest of ferroelectric, multiferroic and magneto-dielectric properties.

Magnetic materials:

Studies on Magnetic properties of several types of materials like intermetallics, alloys and oxides and non-oxides have been studied in late sixties and early seventies in Chemistry Division. In house facilities like VSM, as well as EPR and NMR facilities available in the country and aboard were used to study the magnetic properties of materials. During this period, optimization of DSC measurement procedures to unravel the magnetic transitions have been carried out, and that has been used to characterize several types of magnetic transitions. Some of the examples of early studies are, magnetic and electrical properties of Pt_3Mn, Co_xGa_{1-x}, $Fe_{1.67}Ge$, Cr-Ir, Cr-Mn alloys, UFe_2, UCo_2, UP, Rb_2CuF_4 etc. In eighties, the studies on magnetic materials were expanded as per the global research trend. Magnetic properties of high Tc super conductors and related oxides like La_2CuO_4, giant magneto-resistance materials, like $LaMnO_3$, $LaCoO_3$, and related oxides, soft magnetic materials like molecular magnets, binuclear compounds $MCu[(obbz)].nH_2O$ (where M: Mn/ Co; obbz=oxamido-bisbenzoato), $[Ni(OCH_2CH_2O)_2]_3[Fe(CN)_6]_2 2.5H_2O$ and $[Ni(SCH_2CH_2O)_2]_3[Fe(CN)_6]_2 7H_2O$, nanomagnetic materials g-Fe_2O_3, Mn_3O_4, spintronics and dilute magnetic semiconductors, like transition metal ion doped ZnO, TiO_2, In_2O_3 etc., multiferroic, like $BiFeO_3$, $BiMnO_3$, $CdCr_2O_4$, etc., and magneto-dielectrics like La_2CoMnO_6, Y_2NiMnO_6 etc. have been studied in due course of time. The trend continues till date to study magnetic properties of newer materials. A variety of alloys/intermetallic compounds based on transition metals and main group elements were prepared by arc/induction melting methods and characterised for their structural aspects using X-ray and neutron diffraction techniques. Typical examples include: FeSn, FeMnSn, FeGe, FeAs, FeCoMn etc. Magnetisation and Mössbauer spectroscopic studies were carried out to understand the nature of magnetic interactions existing in above mentioned alloys as well as the local environment around iron in it. Many technologically important alloys and their hydrides were synthesized and explored for their magnetic behaviour. The examples include $U(Ni_{0.85}Co_{0.15})AlH_{2.1}$ which was formed by hydridation of intermetallic compound $U(Ni_{0.85}Co_{0.15})Al$. Whereas the magnetic susceptibility and heat capacity measurements indicated paramagnetic, spin fluctuation behavior at low temperatures in $U(Ni_{0.85}Co_{0.15})Al$ alloy, the hydride, $U(Ni_{0.85}Co_{0.15})AlH_{2.1}$, in contrast, is found to order antiferromagnetically at $T_N \cong 90K$. Similarly, hydrogen induced antiferromagnetic ordering and structural studies were carried out on $U(Co_{0.3}Ni_{0.7})AlH_{2.2}$. While the hexagonal crystal structure for parent alloy $U(Co_{0.3}Ni_{0.7})Al$ was retained upon hydrogen absorption, the alloy was observed to be paramagnetic up to 2K whereas the hydride showed antiferromagnetism with a relatively high Neel temperature of 70 K.

Materials for harnessing radionuclides:

The sorbent materials used in column form considered as the heart of the radionuclide generator. To overcome the limitations of existing sorbents such as poor adsorption characteristics and elution profile, chemical instability, multiple elution steps and degradation in performance with time, several nanomaterials were developed for applications in radionuclide generators. Nanocrystalline oxides like TiO_2, ZrO_2, γ-Al_2O_3, SnO_2 and CeO_2were synthesized and evaluated as sorbent matrices for the preparation of ^{99}Mo-^{99m}Tc, ^{188}W-^{188}Re and ^{68}Ge-^{68}Ga radionuclide generators under different conditions. The enhancement in sorption properties was observed due to higher surface area, surface energy and surface charge of the nanomaterials. These oxides show improved efficiency of the generator by providing better selectivity and enhanced capacity compared to attributes of conventionally used sorbents. The enhanced mechano-chemical stability of inorganic nanocrystalline sorbents ensured the sequential elution from generator over a sustained period without bleeding of sorbent from the column materials.

Development and installation of instruments:

Development of instruments has been one of the important activities since the beginning of Chemistry Group. Annual Report of 1971 mentions that resistivity measurement equipment was developed to comply the requirements of the activities on resistivity/conductivity measurement of materials. Rod-shaped samples (~ 6mm diameter) were used to measure a voltage drop across the sample (~ 0.01 μV). A micro-thermogravimetric system to study mass change up to 1000^{o}C had been developed in the division. An assembly was setup for measuring efficiency and spectral characteristics of phosphors and nearly 100 samples of (Zn,Cd)S were tested on this facility. In addition, a DR-UV setup was also assembled to study various oxides.

In addition, Chemistry Group has very rich history and vast expertise in X-ray diffraction instrumentation and technique. It started with an XRD unit wherein data collection was done by photographic films. It was one of the first XRD units installed in BARC that served Chemistry Group from 1954 to 1968. This was followed by two XRD units that served from 1968 to 1998. An HT-XRD unit was installed in 2001 for *in situ* studies on materials at high temperature. Presently, CG has three XRD units, including one based on rotating anode, that provide supports for XRD studies to colleagues within and beyond the Chemistry Group.

Way forward:

Studies in solid state synthesis, structural analysis and property measurement have been a stronghold of Chemistry Group, and is being continued with same vigour matching the pace of domestic and global research scenario. In keeping up with the requirements, some of the activities were discontinued and certain new activities have been taken up. Some of the research directions shall be continued to align with departmental mandate while new research directions would also be progressively added to satisfy the scientific curiosity and catch up with exciting new discoveries happening worldwide.

The way forward shall include exploratory R&D for new materials for nuclear safety, accident tolerant fuels and newer fuels in ceramics/CECER/CERMET. Research would be directed towards advanced materials for front-end and back-end of nuclear fuel cycle. The solid state chemistry of materials under extreme conditions of temperature, pressure and radiation shall continue to be an integral part of activities. The work on dielectrics and ionic conductors would be directed towards short-listing better performing and cost-effective device-worthy materials for energy applications. The research shall also focus on processing of materials and technologies for conversion of nuclear waste to wealth. The focus shall be forefront areas of material science to cater to sustainable developments goals as well as viable technology development followed by transfer and deployment. The driving force remains the research towards the National mandates, departmental goals and societal benefit.