

R&D on High Purity Materials

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Preamble:

This account serves as a travelogue, chronicling the journey of high purity work within the Chemistry Group of BARC. It stands as a profound testimony to the unwavering dedication and passion exhibited by the team working tirelessly to advance various methods and technical expertise in the realm of ultrapure materials.

The evolving notion of materials purity:

The term ‘purity’ has different connotations for materials used for food, drugs, pharmaceuticals, chemical standards, electronics, nuclear, etc. Yet, in the beginning of the 20th century, only chemical- and pharmaceutical-grade purity was recognized. In present times, the horizon has expanded to semiconductor, nuclear, laser, primary chemical, nano grades etc. Nevertheless, purity of materials can be broadly clubbed into three different groups, viz. (i) isotopic purity (e.g., ²³⁵U, D₂O, etc.), (ii) phase purity (e.g., SiO₂: quartz, amorphous, silica gel, insulator layers; and for carbon: diamond, graphite, fullerene) and (iii) compositional purity. The demand for ever increasing purity, principally stem from the use of these materials in sophisticated and high-end technologies. Presence of even traces of undesirable impurities in these materials, drastically affect various desired material properties. Therefore, purification of a material for a particular application is inevitable. This, in turn, has generated improved and refined methods of achieving purity with vanishingly low level of impurities.

Early initiatives:

With the above prospective, Department of Atomic Energy felt the need for high purity materials for advanced technologies in the areas of nuclear energy, space and electronics since its inception. Accordingly, erstwhile ‘Pure Materials Section’ of Chemistry Division, Chemistry Group, BARC was created in 1958. The major R & D activities pursued are given in Table 1. In the beginning, emphasis was on preparation and purification of uranium and thorium compounds and pure oxides of zirconium, niobium, tantalum and tungsten. Having initiated a program on purification, another challenging project on separation of individual rare earths from indigenous rare earths concentrates (obtained from IRE Ltd, Alwaye) was taken up. Oxides of Y, La, Pr, Nd, Sm, Gd, Tb and Dy (99.99% pure) were separated on a pilot plant scale using ion-exchange technique. Rich concentrates (90%) of heavy rare earths

(Ho, Er, Yb) were also prepared. The know-how for rare earth separation was transferred to IRE Ltd, Alwaye in early 1960s.

Pioneering indigenous high purity materials program:

A real thrust for developing indigenous high purity materials in Chemistry Group came after Dr. Bhabha Committee Report on Electronic Commission of India in 1966 which envisaged ultra-pure materials requirement for the semiconductor industry in the country. Therefore, emphasis was laid on developing purification methods from indigenously available raw materials. The work necessitated fabrication of a series of equipments and apparatus required for ultra-purification techniques, *viz.* electrolysis, vacuum distillation of metals, zone melting, solvent extraction and ion exchange. The first automatic zone melting unit to purify kilogram quantities of materials was designed and successfully operated ~1967-1970 (Figures 1, 2). Additionally, a combination of several physico-chemical methods, such as distillation, liquid/liquid extraction, ion-exchange, iodide method, electrolysis, zone refining, etc have been adopted to develop purification methodologies for Zn, Cd, Ga, In, Sn, Pb, As, Sb, Bi, Se, Te, Ag, Au, Ta, BF₃ and POCl₃, etc. to a purity level of 5 N (99.999%) on laboratory scale. The know-how was transferred to Special Materials Plant (SMP) of NFC, Hyderabad, for upgrading production scale to meet the industrial needs. Assessment of purity at each and every stage of purification process was carried out by Analytical Chemistry Division and Spectroscopy Division in BARC. Besides these, a challenging problem of separating Ta and Nb from indigenous tanto-Coulmbite ore was also taken up and the know-how of a solvent extraction process for Ta/Nb separation was transferred to SMP. Furthermore, high pure Zr bars required for the indigenous atomic energy programme was fabricated by Van Arkel-de Boer iodide method.

Table 1: R & D on High Purity Materials in Chemistry Division, BARC

1957 - 1961
<ul style="list-style-type: none"> • Preparation and purification of uranium and thorium compounds • Preparation of pure oxides of zirconium, niobium, tantalum and tungsten.
1961-1985
<ul style="list-style-type: none"> • Work on nuclear materials continued • Separation of rare-earth from rare earth concentrate • Primary materials for semiconductor technology (Ga, In, Si, Sn, P, As, Sb, Bi, Se, Te; AlN, POCl₃, POBr₃, PBr₃) • Setting up of zone refining unit • GaP, GaAs, CdSe, ZnS, CdS • Know-how of preparation of high purity materials was transferred to Special Materials Plant (SMP), NFC, Hyderabad in early 1970 • Gallium recovery from Bayer liquor (technology transferred to Hindalco, Renukoot, U.P.)

1986-1994
<ul style="list-style-type: none"> • Zone refining • [Ph₄Ge] • CaSO₄.Dy₂(SO₄)₃ (TLD phosphor) (technology transferred to industry) • MASCOT Project for high purity Gallium and Arsenic and organometallics for MOCVD (in 1994)
1995-2000
<ul style="list-style-type: none"> • MASCOT Project for high purity Gallium and Arsenic • Preparation and purification methods for organometallic precursor for MOCVD
2000-2016
<ul style="list-style-type: none"> • Commissioning of MAT lab (2004) • MASCOT Project for high purity Gallium and Arsenic completed • Synthesis and purification methods for organometallic precursors completed • High purity Indium and Antimony • High purity Antimony rods • High purity Germanium (~8 to 9N)
2019-2023
<ul style="list-style-type: none"> • Hyper pure Germanium of detector grade purity

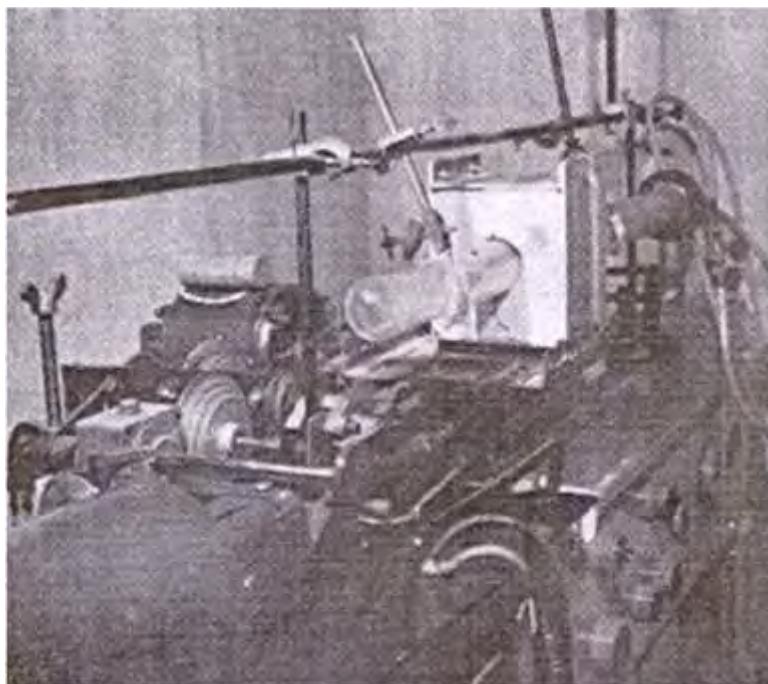


Fig. 1.: First indigenously fabricated horizontal automatic zone refining unit in 1967 (Adapted from A.J. Singh, SMC Bulletin, 6 (No.3) (2015) 1-14)

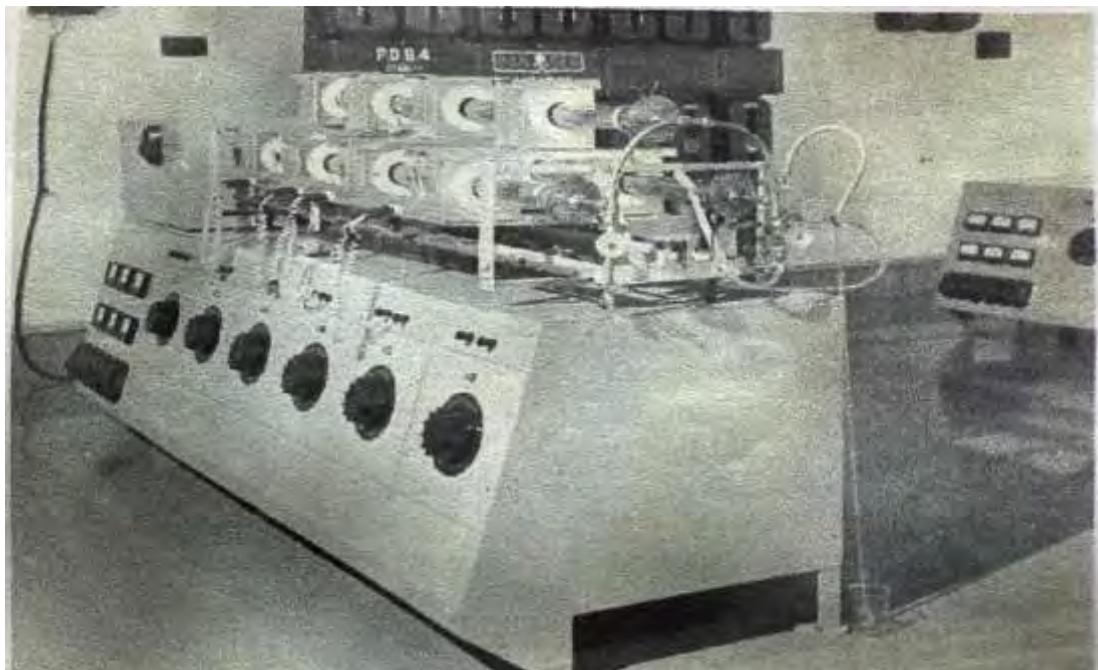


Fig. 2.: Indigenously built multiple-zone refining unit for use at NFC Hyderabad in 1973

During 1970s, methods were developed for recovering germanium from fly-ash, tellurium from slimes of copper industry, tungsten from wolframite, tungsten alloy scrap and carbide residues, and gallium from Bayer liquor of aluminium industry. The know-how for gallium recovery from Bayer liquor was transferred to M/s Hindustan Aluminium Company (Hindalco) by setting up an electrolytic production unit at the company's site at Renukoot (UP). For in-house requirements of high purity materials, processes for several relevant products were developed. These include production of several kilograms of nuclear grade cadmium, pure antimony with less than 100 ppm of arsenic required for fabrication of antimony-beryllium neutron source, etc. Apart from successfully obtaining high purity elements as mentioned above, the zone refining unit was also employed for ultra purification of organic compounds, such as C-120 dye (7-amino-4-methyl coumarin) resulting in enhancement of lasing efficiency and tetraphenyl germane [Ph_4Ge] for radiation and photochemical studies.

Development of semiconductor materials:

A logical extension of the processes developed for the preparation of high purity materials was to demonstrate their utility for the synthesis of compound semiconductors. Accordingly, methods for the synthesis of III-V (GaP, InP, GaAs, InSb), II-VI (CdSe, CdTe), IV-VI (PbSe, PbTe), V-VI (As_2S_3 , Sb_2S_3 , Bi_2Te_3) and chalcopyrites (AgGaS_2 , AgGaSe_2) on a laboratory scale were developed and demonstrated using in-house prepared high purity materials. The experience and expertise generated during the processes development for high purity materials were helpful in conceptualizing the synthesis of these binary and ternary

semiconductors directly from the constituent elements. The synthesis of GaP, for instance, was performed using high purity gallium and phosphorus at high temperatures (~1500 °C) and high pressure (35 - 40 atmosphere). An autoclave for performing high temperature and high-pressure experiment was designed and fabricated indigenously. Several single crystals of GaP (8-10 mm diameter and 10-15 mm length) were grown by liquid encapsulation vertical Bridgman technique. Similarly, single crystals of several other materials were grown from their melts.

Preparative methods for high purity phosphors like ZnS, Cd:Ag (used in infrared image converters), phosphor grade CdS and ZnS and CaWO₃:W phosphor (for X-ray screens) were developed. A preparative method for Dy-doped calcium sulfate, used for TLD badges for dosimetry, was developed. The know-how has been transferred to industries for commercial production (M/s Rementech Chemical Pvt. Ltd, Mumbai in 1992; M/s Avanttec Medical System Pvt. Ltd., Chennai in 2005 and M/s Ultra-Tech Laboratories Pvt. Ltd., Mumbai in 2012).

Having successfully concluded all the projects on high purity materials, there was a lull period where further progress was not foreseeable in the Group. Nevertheless, even greater challenges were on their way for the scientific community in BARC. With rapid advancement and miniaturization of electronic devices, the need for higher order of purity of materials was not only inevitable but also led to the development of new growth processes (CVD methods) which need high purity organometallic precursors.

Establishment of clean laboratories:

When Dr. A.P.J. Abdul Kalam was Secretary, Department of Defence R&D, assessment and requirement of various high purity materials for electronic industry in India was made. It was realized that efforts should be made to develop processes for ultra-high-purity materials (i.e., 6N) as these materials are precursors in the production of electronics hardware. Accordingly, MASCOT project was conceived in 1994 with a primary objective to develop methods for ultra-high purity gallium and arsenic (6N purity) and their organometallic compounds. Such stringent purity requirement needed clean laboratories for process development. Under this program, a clean room facility (10,000 class)–MAT lab of approximately 725 square meters (~7800 sq. feet), was created (Fig. 3). The Lab is located near Van-de-Graff Building, BARC. It consists of 6 clean rooms (10,000 class) housing work-benches (1000 class) and glove boxes, a service area, two fume-hood labs, office area, corridors, air filter room and hold-up tank. The foundation stone was laid by Dr. Anil Kakodkar, Director, BARC on 7th April 1997. The lab was formally inaugurated by Dr. Kakodkar, Chairman, AEC and Secretary, DAE, Govt. of India on July 9, 2004 in the presence of Dr. S. Banerjee, Director, BARC. Other required infrastructure was also developed. The newly inducted manpower for the project was given in-house training for working in clean laboratories and for handling ultra-high purity materials.



Fig. 3: MAT Lab (10000-class clean laboratories) of Chemistry Division, BARC. The Lab was commissioned in 2004.

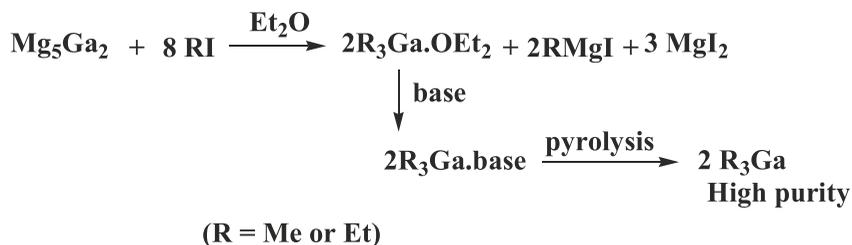
Under this program, methodologies for the preparation of high purity gallium (7N; 99.99999%) by electro-winning process and arsenic (6N, 99.9999%) by hydrogen reduction of purified As_2O_3 were developed (Figure 4). Arsenic being highly toxic, extraordinary precautions were taken during handling and processing. The purity of these materials was not only ascertained by NCCCM, Hyderabad but also from external agencies abroad. The single crystal of GaAs grown from BARC purified materials showed better properties than the one grown from imported gallium and arsenic. The high purity antimony was prepared by vacuum sublimation of commercial antimony and the resulting material was casted in rod form for applications in reactors. Indium was also purified by electro-winning process.



Fig. 4: (a) 6N Arsenic and 7N Gallium prepared at MAT Lab, BARC, (b) Gallium arsenide single crystal grown at SSPL, Delhi from BARC supplied material (weight ~4 Kg)

Development of metal organic precursors:

New growth processes such as chemical vapour deposition (CVD) techniques emerged as a powerful growth tool for micro-electronics which require high purity organometallic compounds for deposition of semiconductor materials at micron (or even nano) levels. The volatile organometallic compounds are highly air and moisture sensitive and several of them are pyrophoric and extremely toxic (in particular organo-arsenic compounds). Methodologies for the synthesis (Scheme 1) and purification of organo-gallium and-indium compounds using locally available chemicals were developed. The process involves gallium/ magnesium alloys, instead of metal chlorides. The method is very convenient and economical giving high yields of $R_3M.OEt_2$ ($M = Ga$ or In ; $R = Me$ or Et). High purity trimethyl gallium prepared in MAT lab was evaluated for deposition of thin films of GaAs at TIFR; the material showed similar behaviour as that one procured from imported sources (Figure 5). Several organo-arsenic and antimony compounds and their purification methods have been developed. Organo-arsenic compounds can be purified by pyrolysis of their palladium adducts such as $[PdCl_2(AsPr^i_3)_2]$ which release pure Pr^i_3As .



Scheme 1: Methodology for the synthesis of high purity trialkylgallium compound.

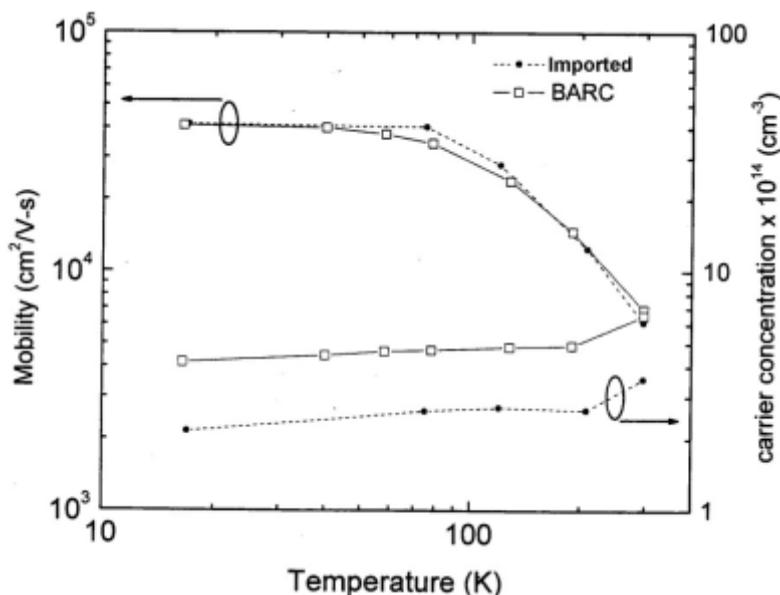


Fig. 5: Comparison of Hall mobility data of BARC trimethylgallium (TMG) vs imported TMG (courtesy Prof. B. M. Arora, TIFR, Mumbai)

As a natural extension of the program on development of organometallic precursors for MOCVD, single source molecular precursors for the synthesis of inorganic materials were conceptualized. In conventional MOCVD approach volatile compounds are used for deposition of thin films of inorganic materials, but there are several disadvantages in their use. These include (i) pyrophoric nature, (ii) most of the hydrides (e.g., Groups V and VI) are toxic gases, (iii) high pressure and excess of precursors are usually required, (iv) only limited number of materials can be prepared. To overcome these drawbacks, the use of single source molecular precursor was considered. Metal chalcogenides represent an important family of semiconductor materials which are core in numerous electronic devices. During this time numerous single source molecular precursors for metal chalcogenides were developed and their utility was demonstrated not only for deposition of thin films but also for the preparation of metal chalcogenide nano-crystals. Precursors for I-VI, II-VI, III-VI, IV-VI and V-VI materials were designed and developed.

The quest for detector grade purity:

In the XII-Plan a multi-Divisional program for HPGe detector was conceptualized and this needed ultra-high purity germanium. Accordingly, work on high purity germanium from commercially available metal (4 - 5N) was initiated. The process parameters for zone refining of germanium were worked out. Zone refining unit (Figure 6) fabricated indigenously during MASCOT project was used for this purpose. With step-by-step improvisation in processing parameters, purity levels also improved from 5-6 to 7-~8N, a limit of chemical analysis was

reached. Several kilograms of ~8 to 9N pure metal were supplied to TPD for single crystal growth (Figure 7). The real challenging task was to achieve detector grade purity germanium from ~9N level. The detector grade purity could be realized by modified zone refining unit with the required interfacing as shown in Figure 8 and subsequent optimization of the zone refining conditions. Analysis of germanium samples beyond 9N purity in general are carried out by electrical measurements (e.g., resistivity, carrier concentration and carrier mobility, etc.). The Hall measurement data of zone refined germanium sample of Chemistry Division compared with that of commercial germanium Single Crystal. The data clearly indicates that detector grade purity germanium has been achieved. The difference in resistivity and carrier mobility for zone refined Ge can be attributed to the polycrystalline nature of the sample.

In addition to afore-mentioned important jobs, commercial CsI (3N pure) has been purified to 5N pure CsI by employing repeated recrystallization method and delivered to erstwhile Technical Physics Division for CsI crystal growth. Besides, CsI nanoparticles were also supplied to NPCIL for CsI aerosol dispersion studies to understand the distribution pattern of CsI aerosols released in the nuclear reactor under accidental conditions.



Fig. 6: Zone refining (ZR) unit with induction heating designed and fabricated indigenously in 2012.



Fig. 7: (A) ~8 to 9N pure germanium ingot from Zone-refining unit, and (B) Single Crystal (<100>) of germanium (950 g) grown by TPD from ~8N pure germanium supplied by Chemistry Division.



Fig. 8: (A) Zone refined detector grade purity germanium ingot.

Way forward:

This travelogue not only showcases the remarkable achievements and breakthroughs but also provides a profound insight into the core values that underpin the endeavours of the Chemistry Division team. This account further reflects that team has responded to the need of the hour. With each passing decade purity of materials of interest has moved from 4N to 5N-6N and 7N and so on. Similarly work on organometallic compounds, required for CVD and related processes, has not only been initiated but also in consonance with the progress in

growth process for microelectronics. Among all the aforementioned high purity work, highly challenging and noteworthy achievement is the zone refined germanium of detector grade purity.

The future prospects of achieving high purity work rely not only on technological advancements but also on improving analytical techniques to assess sample purity. Current evaluation of purity is limited by the minimum detection limits of analytical methods. For example, HR-GDMS can detect elements at parts per trillion (ppt) levels. Interestingly, there exists a direct relationship between technological advancements and the demand for high purity materials. As futuristic technologies rely on the precise properties of extremely pure materials, they drive the development of advanced instruments capable of surpassing current detection limits. These next-generation instruments play a vital role in identifying impurities in high purity materials, ultimately providing impetus for further improvements in materials purity. This creates a cycle of progress. Achieving ever-higher materials purity enables the development of sophisticated technologies, which, in turn, push the boundaries of detection limits and facilitate even purer materials for future applications.

The relevance of this pursuit is underscored by their significance in several key areas including nuclear programs and development of sophisticated technologies. Nevertheless, the future scope for purification activities in Chemistry Group is certainly dependent on the requirements of Department of Atomic Energy (DAE), India pertaining to nuclear programme.