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Preparation of Thermoelectric Materials from Melts

The most common methods to prepare semiconductors are based on use of melts or vapor phase. A strong tendency to use thin film structures in modern semiconducting devices brought a variety of technologies based on vapor phase deposition. However, in case of thermoelectric materials the bulk ingots are used almost always and the stage of melting the materials is nearly inevitable. Manufacturing of the most common thermoelectric materials (bismuth-antimony tellurides, silicon-germanium alloys) is based on cold- or hot-pressing of the powders but the powders are prepared from the ingots of melted down and crystallized elements. Thus, the methods of preparation of materials from melts remain vital especially in technology of thermoelectrics.

Synthesis/Alloying

Modern thermoelectric materials, from a technological point of view, can be roughly divided into three categories: low-temperature materials (e.g., group V chalcogenides based on Bi_2Te_3), middle-temperature materials (e.g., group IV chalcogenides based on PbTe), and high-temperature materials (e.g., Si-Ge solid solutions). The melting points and approximate total pressures of volatile elements over the melts of the major phases are shown in Table 1

Table 1. Melting Temperatures and Total Vapor Pressures of Major Thermoelectric Materials

Temp. Range	Low Temperature Materials			Middle Temperature Materials				High Temperature Materials
	Bi_2Te_3	Sb_2Te_3	Sb_2Se_3	PbTe	PbSe	GeTe	SnTe	$\text{Si}_{80}\text{Ge}_{20}$
$T^M, ^\circ\text{C}$	585	621	612	917	1076	725	806	1350
$p^{\text{tot}}, \text{ torr}$	at T^M			10	100	40	1	$\ll 1$

The preparation of chemical compounds and solid solutions from a melt begins with melting the elemental constituents together, a process that can be called synthesis or *alloying*. It is essential to use high-grade elements of guaranteed purity and to take all necessary precautions to prevent contamination during handling, synthesis, and crystal growth. A common way to perform a synthesis of the chalcogenides is to use sealed clear quartz ampoules of up to 25-mm bore. The preweighed materials are placed into the tube, followed by a quartz plug. The tube is then pumped down to between 10^{-5} and 10^{-6} torr and sealed circumferentially with a hydrogen torch.

Most of the high-purity commercially available elements are oxidized on the surface, and it is essential to remove the oxides from the ingredients before synthesis. This can be done by etching or by reduction of the element. For example, lead placed in an alumina or graphite boat can be reduced at 700°C in a stream of pure hydrogen. The presence of oxygen causes the solidifying ingot to stick to the quartz walls due to a chemical reaction between PbO and silica. This introduces stresses into the material and can even break the ampoule and expose the hot ingot to the air. In addition, any oxygen in the chalcogenides changes the electrical properties of the final product. To prevent sticking alone, quartz containers can be coated with carbon by pyrolytically cracking acetone or toluene.

The synthesis (alloying) of Si-Ge alloys is a more complicated procedure. The most efficient thermoelectrics in this system, both n- and p-types, contain about 800/Oat of Si and 200/Oat of Ge ($\text{Si}_{80}\text{Ge}_{20}$). The high liquidus point of this composition, 1350°C , does not allow the use of vacuum-sealed silica tubes for processing. The quartz glass softens at 1250° to 1300°C , resulting in collapse of the ampoule. Also, due to the very large gap between the liquidus and solidus points of this composition ($1350 - 1280 = 70^{\circ}\text{C}$) and very low diffusion rates in the solid alloys, a heavy segregation occurs during crystallization, resulting in separation of the solid Si-rich and Ge-rich grains. The usual metallurgical homogenization by annealing cannot be performed in a reasonable period of time. Additionally, the extremely high affinity of silicon for oxygen makes unreasonable a preliminary etching of the Si. As soon as Si is exposed to air or water after etching, a thin film of oxide forms on the surface immediately. Therefore the use of large pieces of Si (and Ge) to minimize the surface area is recommended.

Alloying of $\text{Si}_{80}\text{Ge}_{20}$ is done in an RF furnace¹. The large pieces (10 to 20 mm) of Si and Ge, together with dopant, B for p-type and P for n-type materials, are placed into an open quartz crucible. Improved n-type alloy can also be doped with GaP. The crucible is inserted into a graphite susceptor in the furnace chamber, and the chamber is vacuum pumped. After purging of the chamber by Ar, a slight overpressure of Ar is established (1.1 atm), and the temperature is raised to between 1370° and 1400°C within 2 to 3 hours. Eddy currents develop an intensive stirring motion so that the homogenization of the melt can be done in 40 to 50 minutes at maximum temperature. After this, the melt is cast inside the chamber into the water-cooled copper mold, resulting in 12.5-mm-diameter by 10(-)-mm-high ingots with fine grains. The bulk wet chemical analysis of the ingots shows reasonable agreement with nominal composition. An example is shown in Table 2.

Table 2

Comparison of nominal and actual SiGe bulk precursor composition

Composition\Element	Si	Ge	Ga	P
Nominal, at. %	77.5	18.5	2.00	2.00
Actual, at. %	77.5	19.0	1.75	1.75

This material, with still segregated microstructure but fine grains, serves as a precursor for the homogeneous ingot preparation.

Crystal Growth

To allow good characterization of the material, the specimens need to be as free of defects as possible. One of the major obstacles to achieving that goal is grain boundaries. The only way to eliminate these defects is to grow single crystals. The alternative is to minimize them by growing polycrystalline ingots with very large grains.

Crystal growth, which is the next step in material preparation from the melt, can be performed in many different ways. The same material can be grown by different methods with different levels of success. Bearing in mind preparation from **melts**, we divide all possible processes into two large categories for convenience of consideration, with the understanding that this categorization is not absolute.

Category 1: Growth from stoichiometric melts, i.e., from melts with the composition of certain stoichiometric compounds, resulting in a crystal of the same (or nearly the same) composition.

Methods of growth to be considered for this category are:

- Bridgman method (Br)
- Gradient Freeze (GF)*
- Czochralski method (Cz)
- Zone Melting (ZM)

Category 2: Growth from nonstoichiometric melts, i.e., from melts with composition that does not correspond to the grown material. This process may equally result in either stoichiometric (e.g., chemical compound) or nonstoichiometric (e.g., solid solution) crystal growth.

Methods of growth to be considered for this category are:

- Gradient Freeze (GF)*
- Zone Leveling (ZL)*
- liquid Phase Epitaxy (LPE)*
- Traveling Solution Method (TSM)*

All methods listed above are well known and we are not going to describe their principles here. Many of them (marked with asterisk) were intensively used at JPL in the past years for different thermoelectric materials preparation. We are going to concentrate on JPL results because they were published in different journals or conference and meeting proceedings and are not easily available for scientific community everywhere.

Gradient Freeze (GF)

The gradient freeze process eliminates any moving parts in the apparatus, ampoule, or furnace. Instead of lowering the crucible through the temperature gradient (Fig. 2), the frozen temperature gradient extended over the whole ampoule length, is moved electronically, rather than physically, in contrast to the typical Bridgman apparatus. Correspondingly, the liquid-solid interface is translated up and crystal growth occurs. Such a system can be used not only vertically, but horizontally as well, and is sometimes called *horizontal Bridgman* (1B).

The GF vertical arrangement has been recently used for growth of promising new high-temperature materials.^{2,3} A refractory compound, Ru_2Si_3 , congruently melting at 1700°C (Fig. 3), has been grown. High-purity Ru and Si, in stoichiometric ratio, were placed in pyrolytic boron nitride crucible with pointed bottom. Boron nitride was found to be the most appropriate container material for ruthenium silicide, in spite of some dissociation and consequent contamination of the melt and crystal by boron. After synthesis of the compound at a minimum of 1765°C, the temperature gradient of 30° to 320/cm was stabilized and growth occurred at rates of 0.8 to 3 cm/day. Single crystalline ingots of the compound with typical dimensions of 12 mm in diameter by 20 mm high were obtained and their thermoelectric properties measured.

The electron analogue of ruthenium silicide, ruthenium sesquigermanide Ru_2Ge_3 , has been similarly grown in the same furnace^{4,5}. The germanide is a non-congruently melting compound and decomposes peritectically at 1470°C (Fig. 4) but the crystal growth can be achieved from off-stoichiometric Ge-rich solutions. Single crystals of this compound were grown in 12 mm inside diameter graphite or glassy carbon cylindrical crucibles with a conical bottom. The preferential direction of growth was found to be [110] and crystals exhibited a reversible gradual diffusionless phase transformation within 400-600°C (tetragonal at high and orthorhombic at low temperatures). Both of the phases were p-type semiconductors with bandgaps of 0.58 and 0.71 eV, respectively. Maximum ZT value for this material was found to be about 0.4 at 500°C (Fig. 5).

Similar furnace configuration was used to grow single crystals of some thermoelectric compounds with skutterudite structure, $CoSb_3$ and $RhSb_3$ ^{6,7}. Related phase diagrams (fig.

6) suggest that growth can be performed from Sb-rich solutions. The single crystals were obtained by slow crystallization of solutions of Co and Rh in Sb (3-9 and 3-14 at%, respectively) in sealed carbon-coated quartz ampoules. A temperature gradient of about 40-50°C/cm was maintained at the growth interface and the growth rate was about 0.7°C/hr (Fig 7).

All as-grown samples were p-type with Hall carrier concentration in the 10^{16} to 10^{19} cm⁻³ range for CoSb₃ and between 2 and 7×10^{18} cm⁻³ for RhSb₃. It was found that, for the CoSb₃ ingots, the Hall carrier concentration of the samples decreases from the tip to the top of the ingots. Because the ingots were grown from non-stoichiometric melts, during the growth the melt became richer in Sb and the stoichiometry of the samples could gradually change along the ingot, resulting in carrier concentration variations. These stoichiometric deviations might be very small and were not detected by microprobe. The addition of Te (between 0.1 and 0.2 at.%) into the original melts resulted in n-type electrical conductivity.

Exceptionally high p-type Hall mobilities were obtained on RhSb₃ and CoSb₃ samples. The Hall mobilities of the two skutterudite compounds are significantly higher than those of Si, Ge and GaAs in the 10^{17} to 10^{19} cm⁻³ carrier concentration range. A maximum Hall mobility of about $8000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ was obtained for RhSb₃ at a carrier concentration of 3.5×10^{18} cm⁻³.

From the variations of the resistivity with temperature in the intrinsic regime, the band gap of CoSb₃ and RhSb₃ was estimated at 0.56 and 0.80 eV, respectively. The high hole mobilities measured on the skutterudite compounds CoSb₃ and RhSb₃ even at high temperatures make these materials interesting new semiconductors and we are planning further studies to investigate their thermoelectric and electronic properties.

Zone Leveling (ZL)

ZL is one of the versions of Zone Leveling well described in the literature. As opposed to several reciprocating zone passes, this version is performed using only one zone pass and is based on the phase relationship shown in Figure 8. We consider this process as a crystallization of metal solution because "dilute" liquid solution crystallizes, resulting in "concentrated" solid solution x . It is obvious that if the liquid a composition, which loses component B during crystallization, is constantly replenished by B, the crystallizing composition x is the only product of the process.

ZL of a very difficult and most important high-temperature material, Si₈₀Ge₂₀ solid solution, is a perfect example of the use of this technique. It was described in 1957⁸, investigated in more detail and applied later⁹, and more recently applied again with some changes. Figure 8 represents the principle of the process. Two precursors of SiGe are prepared: $a(\text{Si}_{52.5}\text{Ge}_{47.5})$ for zone melt, and $x(\text{Si}_{80}\text{Ge}_{20})$ for homogenization, e.g., composition leveling. They are loaded into the processing boat (graphite, glassy carbon, carbon-coated quartz), sealed under vacuum in a quartz tube, and zone melted (Fig. 9) at a constant temperature. One pass of the zone was usually employed. Two processes take place simultaneously during the zone passing on both liquid-solid interfaces: melting of

inhomogeneous precursor x , on the right interface, and crystallization of homogeneous composition x , on the left interface. At each given time the quantity of crystallized material is equal to the quantity of melted precursor. Therefore a constant composition of the melt is maintained, and a perfectly homogeneous $\text{Si}_{80}\text{Ge}_{20}$ solid-solution ingot is yielded. It was found⁸ that an RF coil used as a zone heater, instead of the conventional resistance furnace, helps to avoid deterioration of the quartz ampoule (Fig. 10). In this case the graphite boat (crucible) also played the role of an RF susceptor. Two resistance furnaces mounted on both sides of the RF coil maintained sufficiently high pressure in the ampoule, when P (or GaP) was a dopant, and suppressed phosphorus deposition on the tube wall during the process. In this case the whole heating assembly was stationary and the ampoule was translated. The travel rate was about 2 mm/hr, which was slow enough to provide homogeneous recrystallization of the charge. Thus, intercrystalline liquation was avoided.

One more advantage of this version of ZL should be noted: The process is performed at a much lower temperature than T^{liq} of $\text{Si}_{80}\text{Ge}_{20}$. The processing temperature corresponds to T^{sol} of the alloy (1280°C) versus $T^{\text{liq}}=1350^\circ\text{C}$, and the sealed quartz container can easily survive even when a conventional heater is used.

Liquid phase epitaxy (LPE)

Liquid phase epitaxy (LPE) is the growth of a material epitaxially on an oriented, single-crystalline substrate seed from the solution of the material in an appropriate solvent. Usually the material is grown in the form of a thin (10 nm to 100 nm) layer over the polished and etched wafer. The layers reproduce the structure of the substrate (*epitaxy*) as in any other seeded crystal growth. The basics of the process are illustrated by Figure 11. A mixture of solvent and soluble is heated to certain temperature. At this temperature, melt is brought into contact with substrate. According to the phase diagram, melt and substrate are in thermodynamic equilibrium, and no changes are expected at this temperature. By lowering the temperature, dissolved material precipitates from the melt and grows epitaxially on the substrate until the substrate is withdrawn from the melt. By introducing a dopant into the melt, the doped layer can be grown on an undoped substrate.

The major obvious advantages of LPE are: (1) LPE can be performed at substantially lower temperatures than bulk growth of the same material from a stoichiometric composition; (2) consequently, the vapor pressures over the melts can be much lower during LPE, thus eliminating a big loss of volatile elements and simplifying the process; (3) solid solutions of certain composition can be grown. LPE has been so widely used in research and manufacturing of semiconductors that a huge number of apparatus designs have been developed. A horizontal configuration of LPE apparatus is shown in Figure 12.

The use of LPE in thermoelectric research can be illustrated by developing improved SiGe material. It has been found^{10,11} that Si-Ge solid solutions can be more

heavily doped when crystallized from metallic liquid solutions, at lower temperatures than T^{liq} (Fig. 13). In this case the use of a solvent, which is also a dopant, is beneficial because the solvent-dopant atoms are incorporated in the SiGe alloy, according to their solid solubility at the temperatures of growth. $Si_{80}Ge_{20}$ layers 10 to 100 μm thick were grown from solution in Ga with GaP addition on (111) oriented Si substrates. Temperatures of growth ranged from 750° to 900°C with cooling rates of 30° to 40°C/hr (compared to $Si_{80}Ge_{20}$ $T^{liq}=1350^{\circ}C$). These low growth temperatures were used because of the selected melt composition of $Si_{7.7}Ge_{24.8}Ga_{67.5}$, which produced a $Si_{79.9}Ge_{19.9}Ga_{0.2}$ crystalline layer at 900°C (Fig. 14). LPE experiments proved the feasibility of enhancing the P-dopant solid solubility in SiGe material in the presence of (is. This multiple doping had improved the thermoelectric energy conversion efficiency of $Si_{80}Ge_{20}$, which is widely employed in radioisotope thermoelectric generators (RTGs).

Traveling Solution Method (TSM)

The traveling solution method (called sometimes traveling heater method, TLM) is one of the Zone Melting techniques, and the process can be described in almost the same words as Zone Leveling. It is the recrystallization of a concentrated solution through a dilute solution and is usually carried out vertically with one pass of the molten solution zone. The vertical configuration of the apparatus (Fig. 15) provides a more symmetrical thermal field applied to the charge and better uniformity of composition and properties in grown ingot cross sections. TSM has been successfully employed for crystal growth of several well established thermoelectric materials, resulting in high-quality samples. In this case, as in Zone Leveling, the processing temperature can substantially be brought down. At JPL, solvents such as Ga and Sn were used for growth of bulk ingots of $Si_{80}Ge_{20}$, with growth temperatures between 800° and 900°C (compared to $T^{liq} = 1350^{\circ}C$ for $Si_{80}Ge_{20}$).

Concluding Remarks

A brief review has been given of the preparation of thermoelectric materials from melts. The emphasis was given to works performed at JPL, within the past 8 years. The results were published in different Journals, Conference and Meeting Proceedings and it was our intention to put them together to illustrate the JPL achievements.

Acknowledgments

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Figures

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Vacuum Furnace for Si-Ge
Precursors Preparation
(schematic)

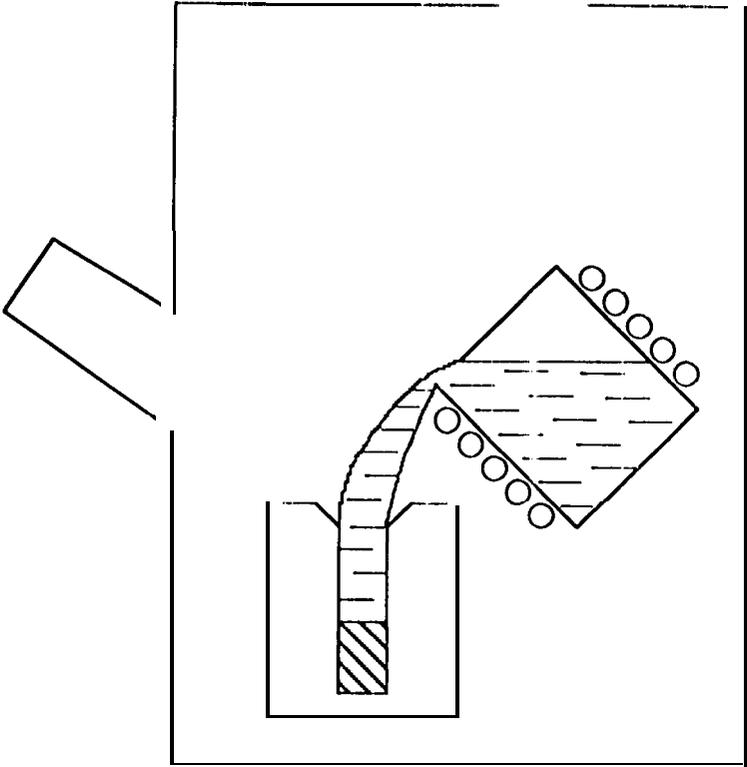


Figure 1

Two-zone Furnace for Gradient Freeze Process

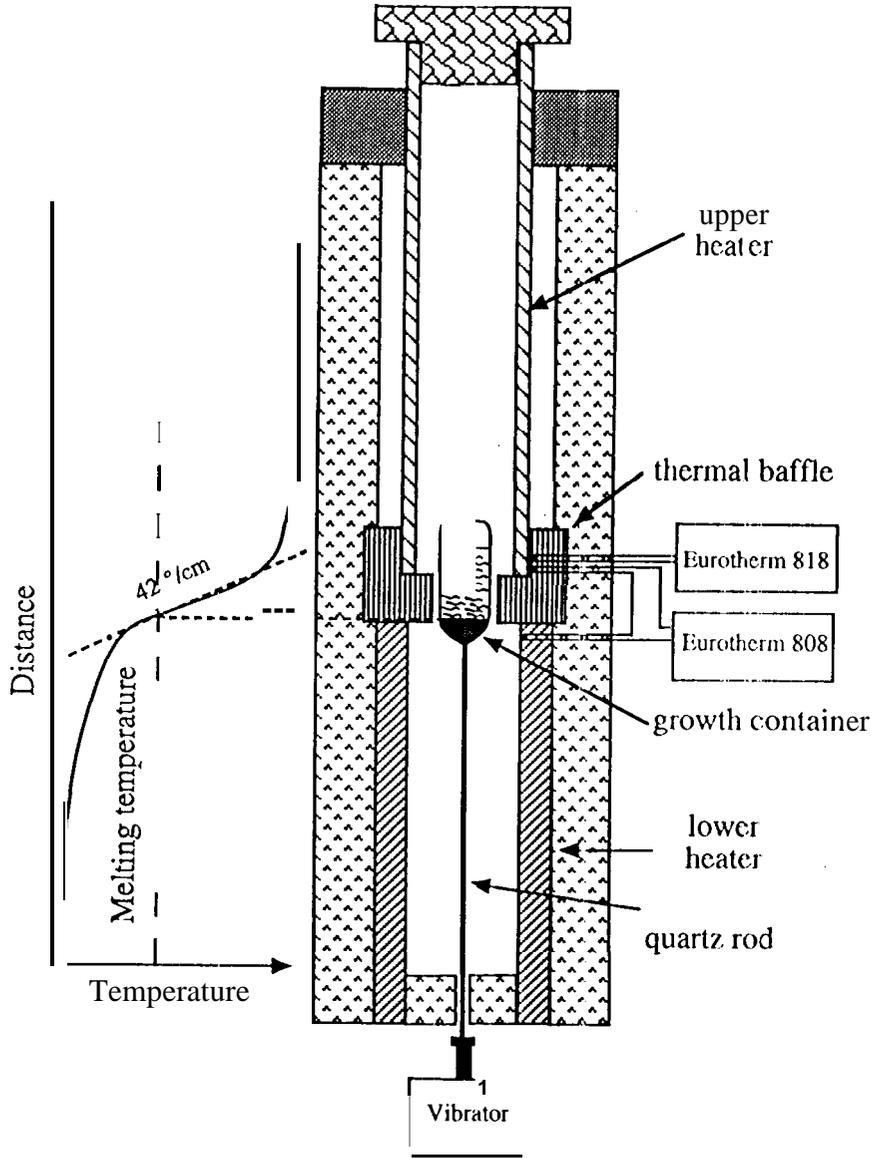


Figure 2

 Ru-Si Phase Diagram

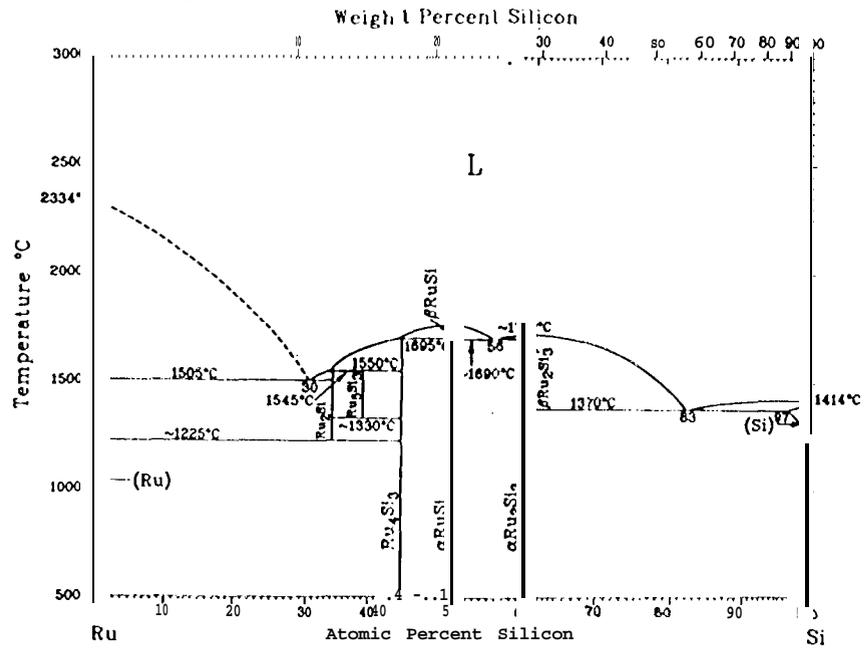


Figure 3

Ge-Ru PHASE DIAGRAM

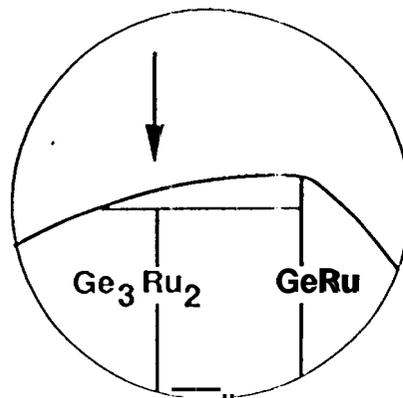
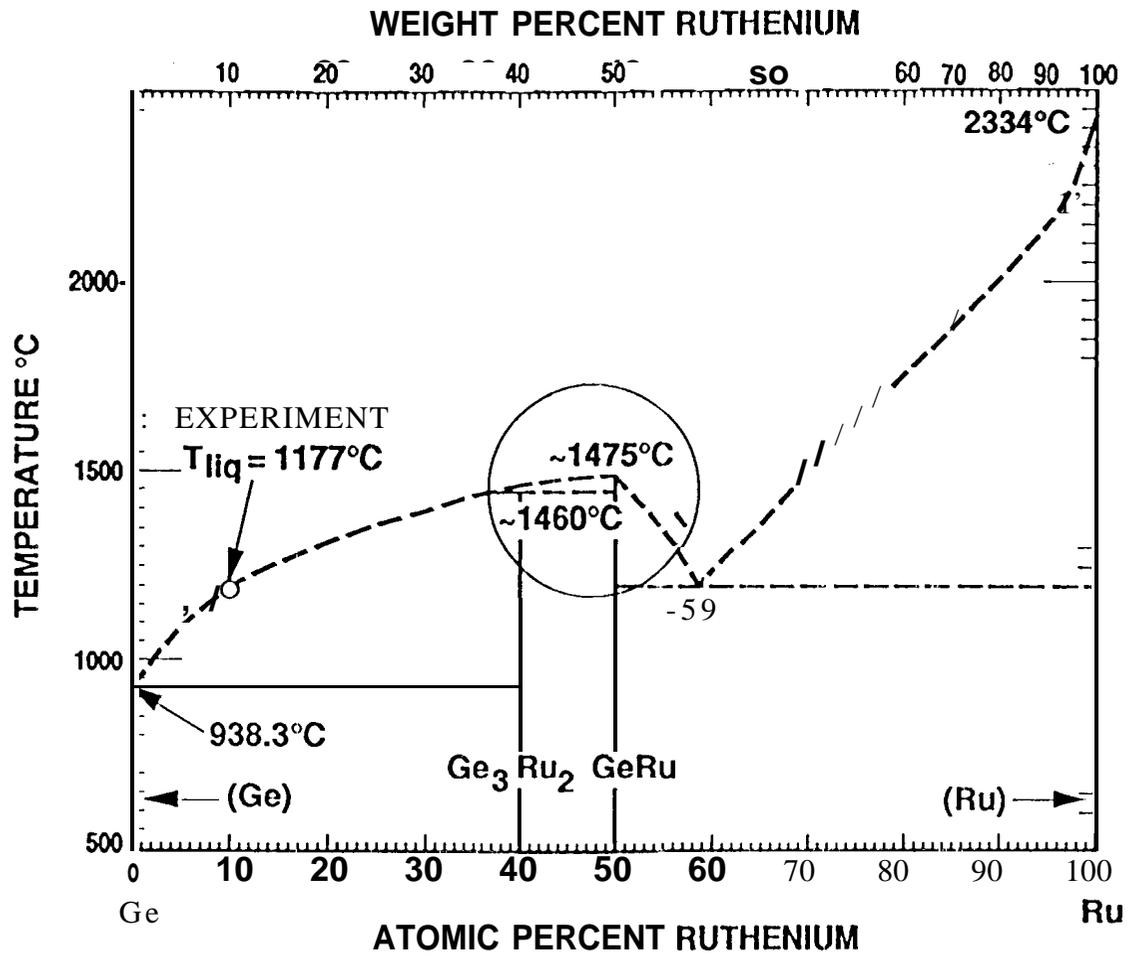
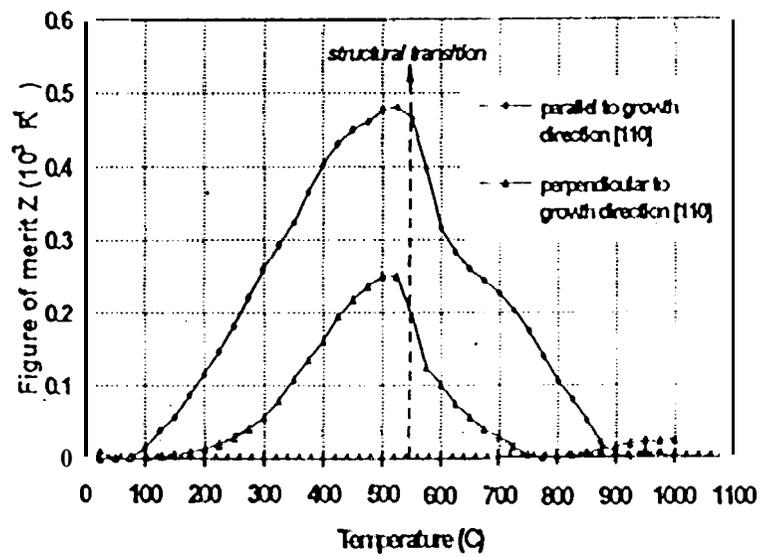


Figure 4

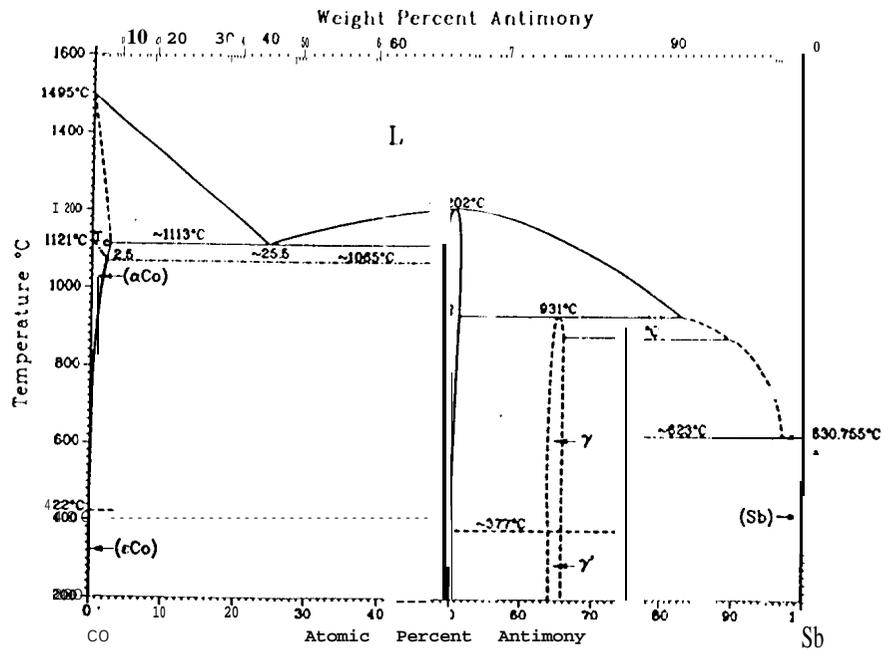


Calculated ZT values versus temperature for In-doped Ru_2Ge_3 samples. Results for directions \parallel and \perp to the [110] direction of crystal growth are plotted.

Figure 5



Co-Sb Phase Diagram



Rh-Sb Phase Diagram

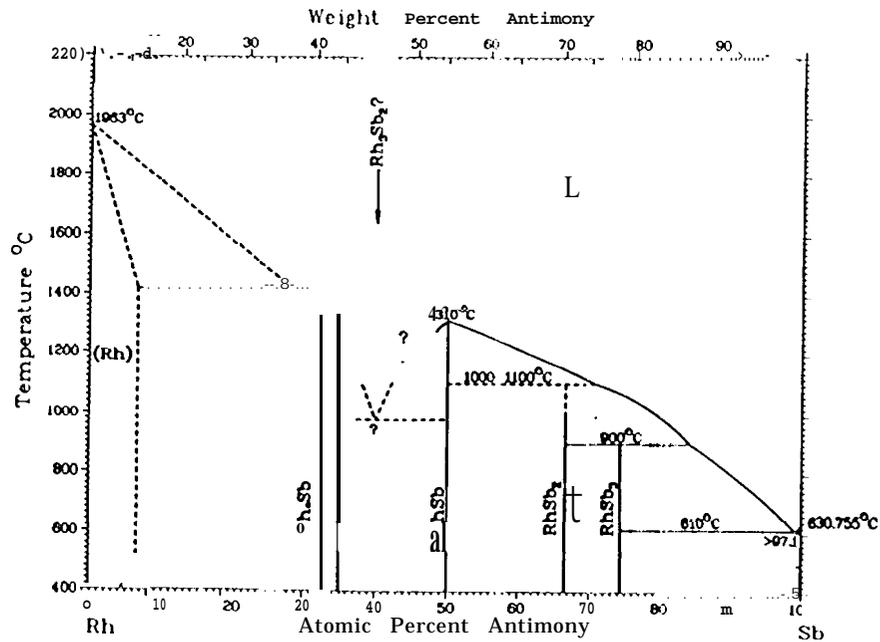
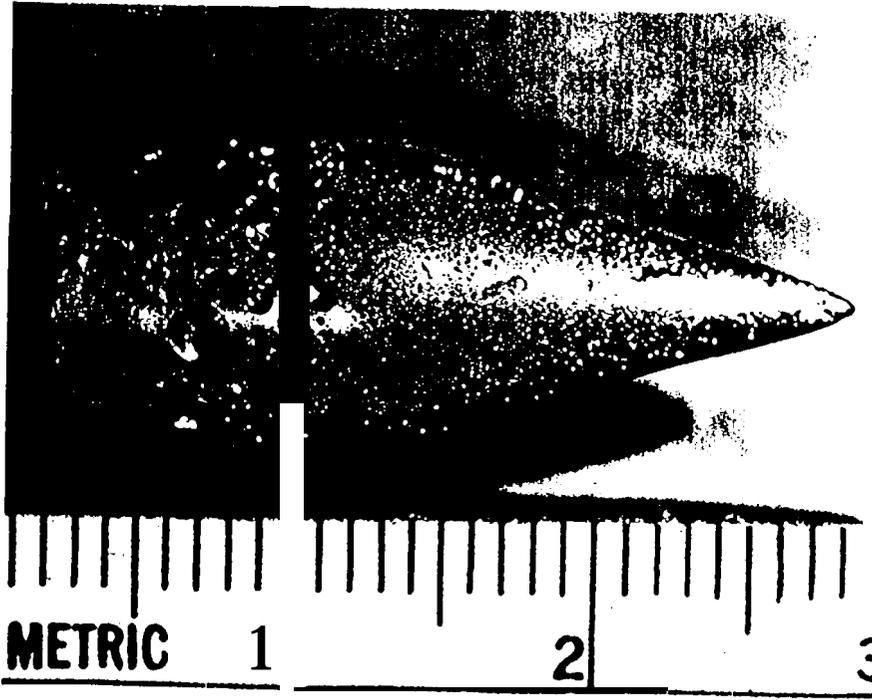


Figure 6

CoSb_3



Ingot



Interface

Figure 7

Zone Leveling

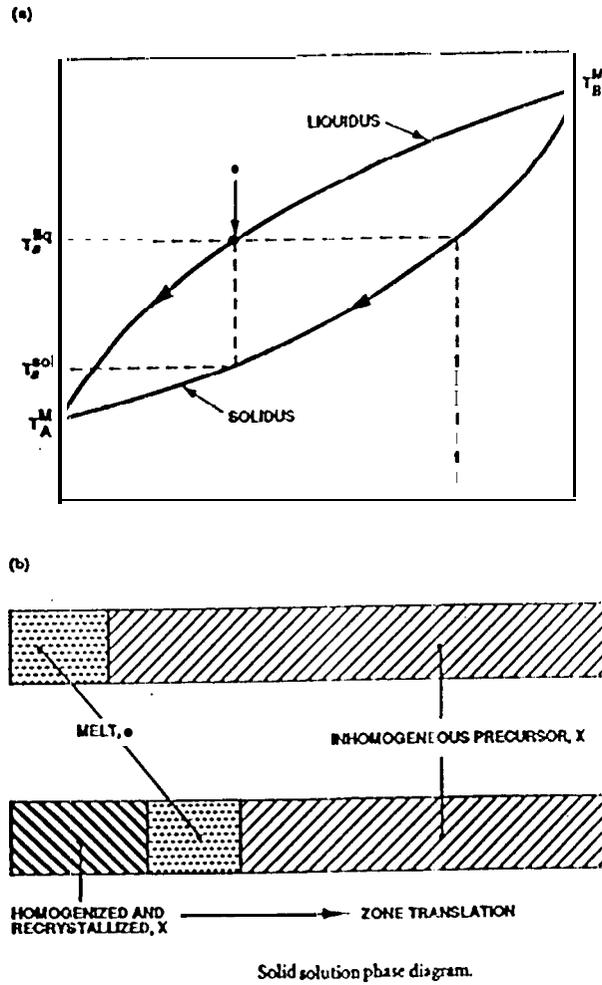


Figure 8

Zone Leveling (temperature profile)

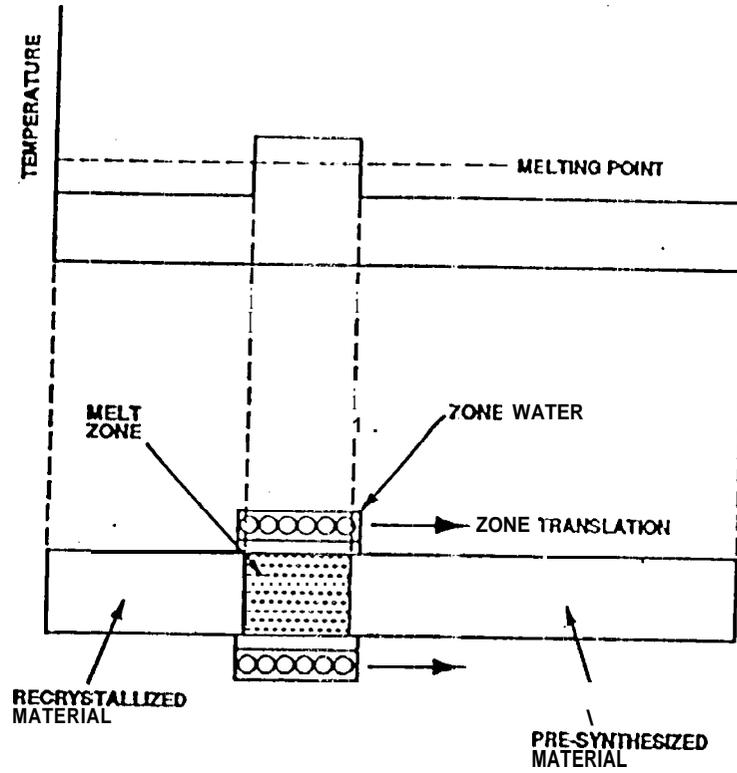
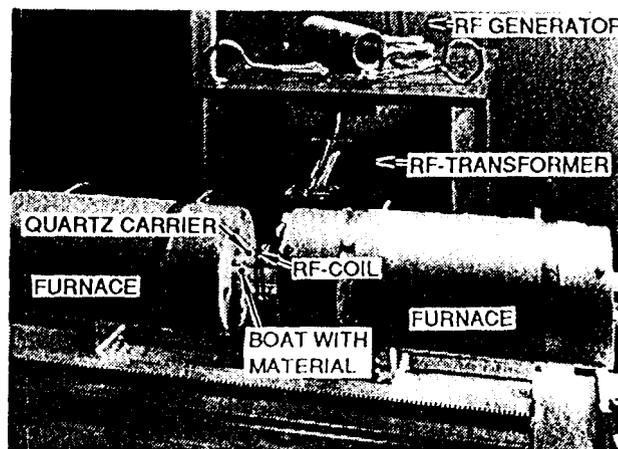


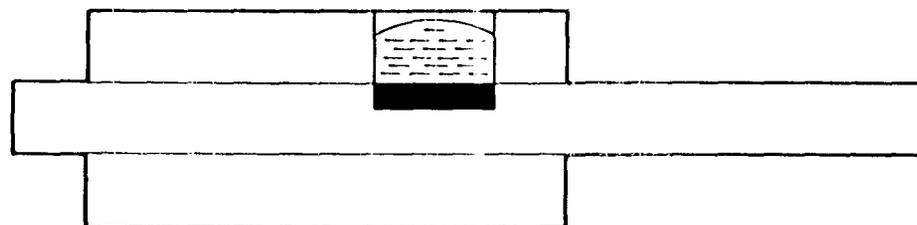
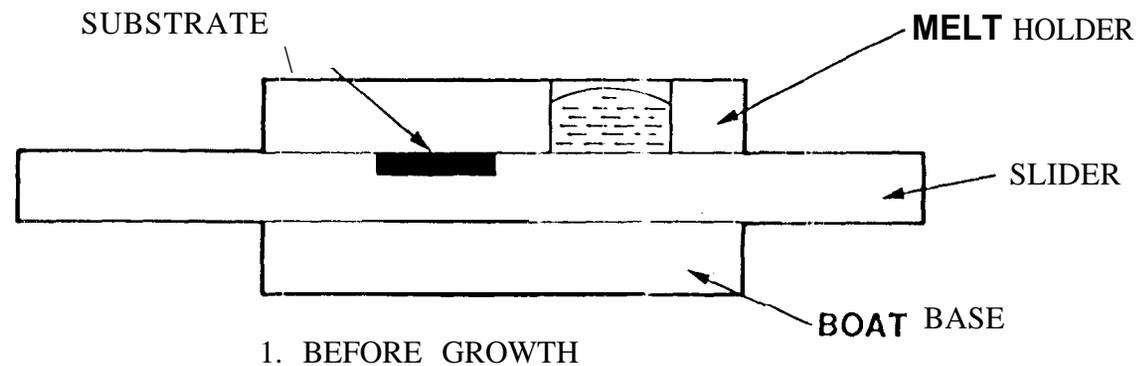
Figure 9

Zone Leveling Apparatus



. Figure 10

JPL LIQUID PHASE EPITAXY (LPE)



2. GROWTH

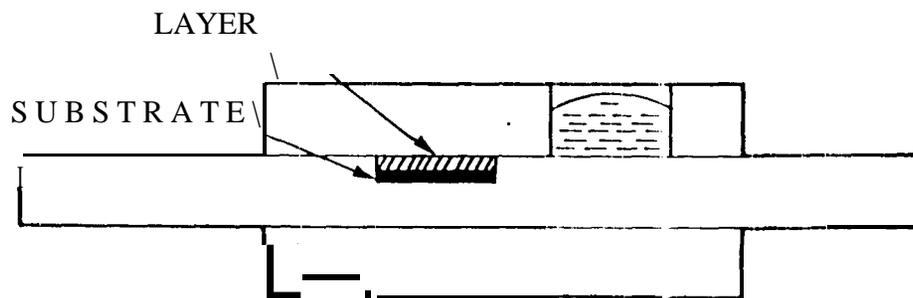


Figure 11

LPE System

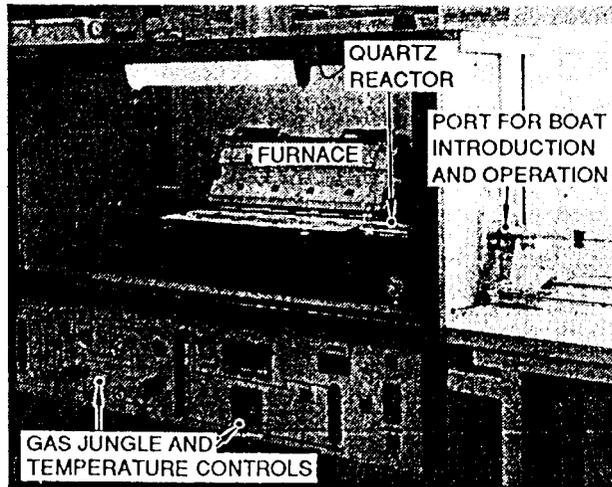
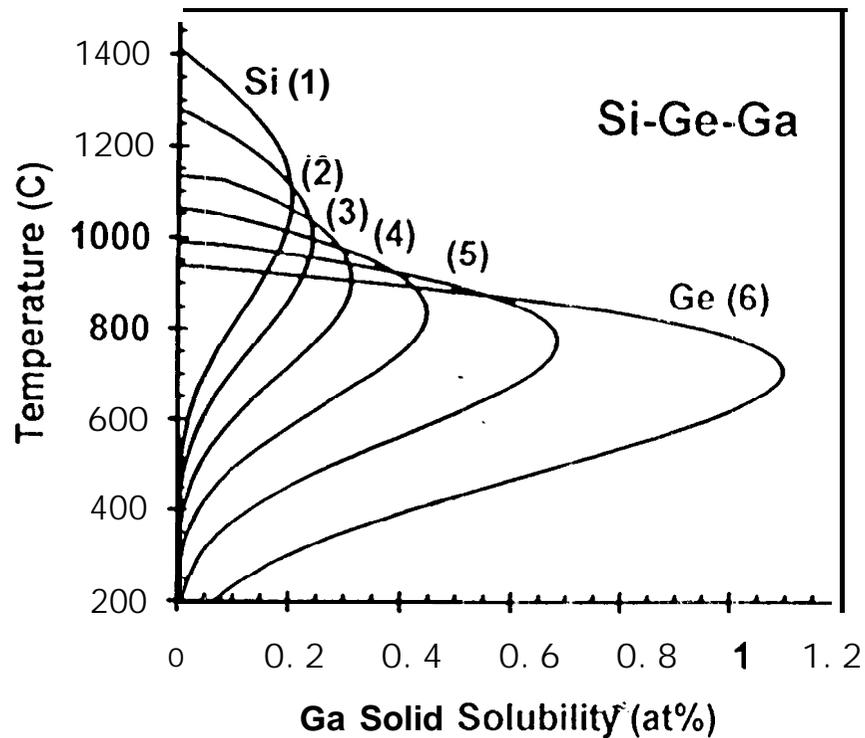


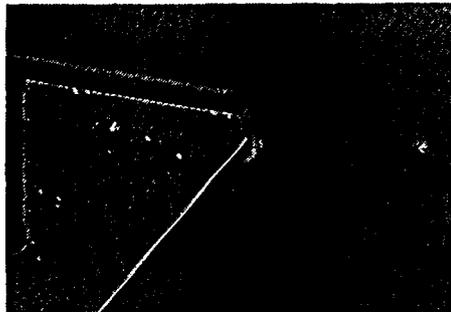
Figure 12



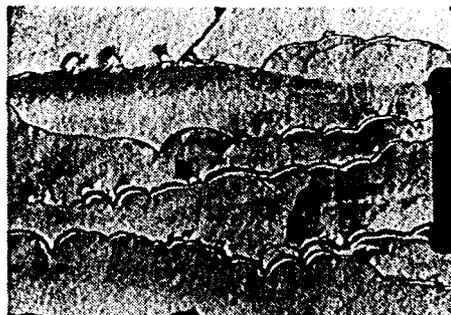
Calculated Ga solid solubility curves as a function of temperature for various Si-Ge alloy compositions in at%: (1) Si; (2) 80% Si; (3) 60% Si; (4) 40% Si; (5) 20% Si; (6) Ge.

Figure 13

LPE-GROWN $\text{Si}_{82}\text{Ge}_{18}$ ON (111) Si
MAGNIFICATION ON 35mm FILM



INITIAL STAGES OF GROWTH



x 62.5 TERRACED MORPHOLOGY OF COMPLETED LAYER

Figure 14

JPL
**TRAVELING SOLVENT
METHOD (TSM)**
APPARATUS SCHEMATIC

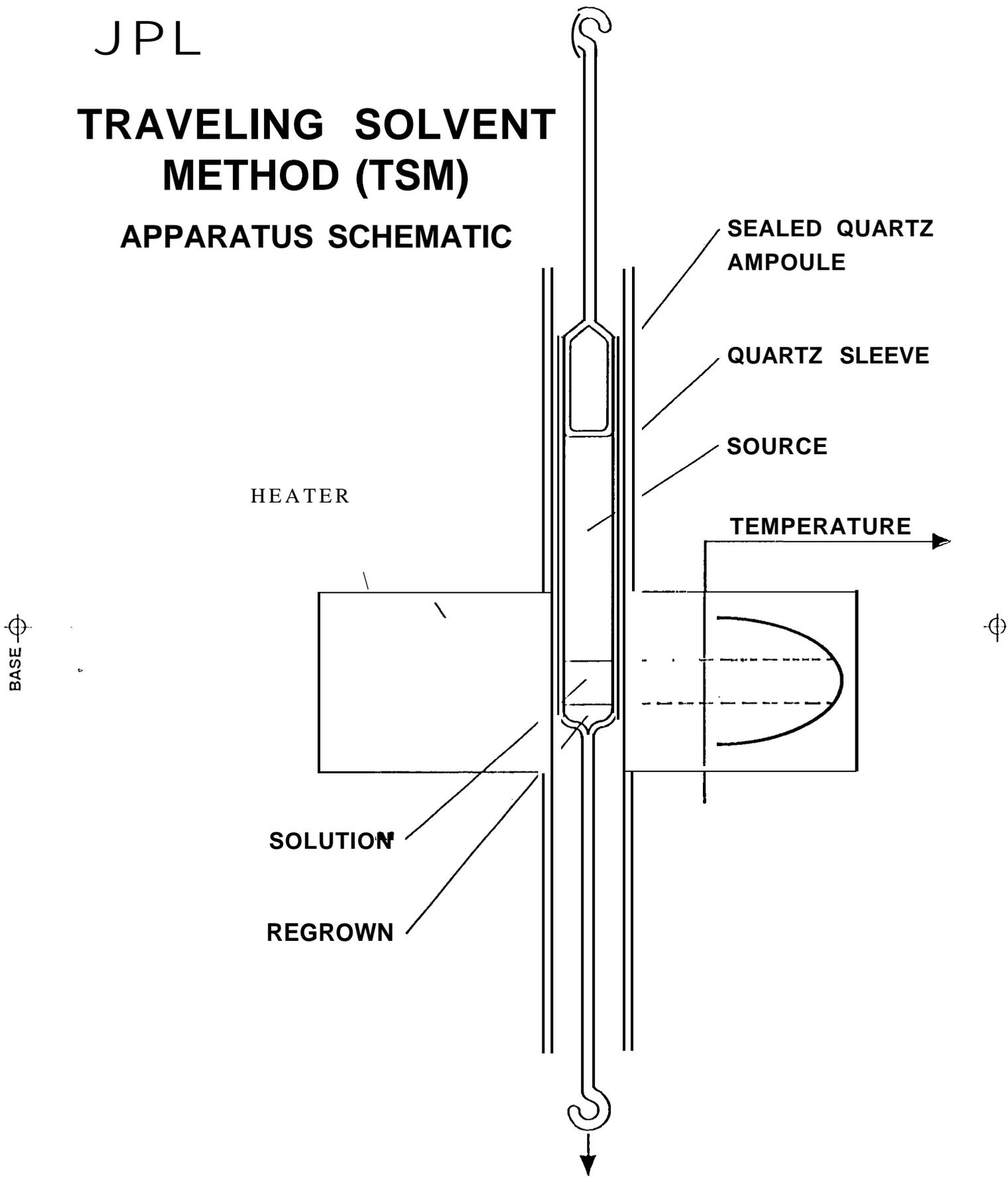


Figure 15