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PHYSICAL CHARACTERIZATION OF ELECTRONIC MATERIALS, DEVICES AND THIN FILMS

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ManLabs, Inc.
21 Erie Street
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Contract No. F19(628)-67-C-0173

Project No. 5620
Task No. 562003
Work Unit No. 56200301

FINAL REPORT

1 December 1967 - 1 December 1969

January 1970

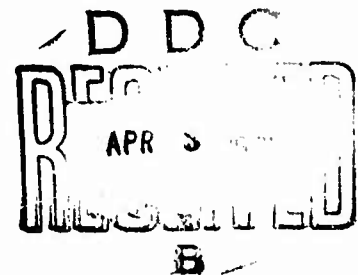
Contract Monitor: Jane A. Bruce
Solid State Sciences Laboratory

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OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
BEDFORD, MASSACHUSETTS 01730

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ABSTRACT

Part I - In support of research being conducted by the Properties and Phenomena Branch, Solid State Science Laboratory, Air Force Cambridge Research Laboratory, a service effort is being conducted by ManLabs, Inc., that is directed toward the characterization of specified physical, chemical and structural properties of submitted specimens. Experimental methods include chemical analysis, reflection electron diffraction, X-ray diffraction and fluorescence analysis, light microscopy and electron probe microanalysis, in addition to the determination of specific properties, such as density, hardness and thermal conductivity. Special services, such as crystal orientation, cutting, grinding and polishing, are also being performed. Specific materials submitted for characterization include spinel, cobalt silicide, lithium germanate, silicon, mercury sulfide, cadmium sulfide, silicon carbide, quartz, ruby, calcite, magnesium oxide, cesium copper chloride, gallium arsenide, boron, potassium tantalum niobate, alundum, yttrium-iron garnet, yttrium-aluminum garnet, germanium and lithium niobate. In addition, a variety of specimens have been submitted for specific studies such as phase identification, crystallinity and chemical analysis.

Part II - High pressure experiments were carried out on Al-S and Al-Se alloys to produce tetrahedral, unsymmetrical Group IV analogs, as suggested by Compton and Hall¹. Two new compounds, $\delta\text{Al}_2\text{S}_3$ and $\delta\text{Al}_2\text{Se}_3$, were synthesized at pressures of 7 to 50 Kb at temperatures of 800° to 875°C. Both compounds have the cubic defect spinel structure of $\alpha\text{Al}_2\text{O}_3$. The synthesis experiments have pointed out the presence of tetrahedral-to-octahedral coordination densification transformations which compete with the high pressure synthesis of new tetrahedral Group IV analog compounds.

FOREWORD

This report was prepared by ManLabs, Inc., 21 Erie Street, Cambridge, Massachusetts, under Air Force Contract No. F19628-67-0173-P001. The work was administered by the Office of Aerospace Research, Air Force Cambridge Research Laboratories, United States Air Force, Bedford, Massachusetts, with Miss Jane Bruce acting as contract monitor and Mr. Norman Pickering providing technical liaison.

ManLabs' personnel that have participated in this program are Dr. Edward T. Peters, Dr. S. Andrew Kulin, Dr. Edward V. Clougherty, Harvey Nesor, Raymond Yeaton, James Elling, Robert Russell, Konstantin Kredor, Irita Grierson, Joseph Davis, Vernon Kousky, George Martin and John Ross.

This is a technical report and describes studies which were initiated 1 December 1967 and were concluded 1 December 1969.

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PART I - SERVICE STUDIES

I. INTRODUCTION

A continuing investigation of the formation and characterization of high purity crystalline materials is being carried out by the Properties and Phenomena Branch, Solid State Science Laboratory, Air Force Cambridge Research Laboratory. In general, studies have been concerned with preparing materials that have desirable electronic and/or optical properties and with developing and evaluating new methods of crystal preparation. ManLabs, Inc. has conducted a service effort directed toward the characterization of selected chemical, physical and structural properties of specimen materials submitted by workers at AFCRL; in addition, ManLabs, Inc. has provided specific services such as crystal orientation and cutting. Summaries of previous studies carried out by ManLabs, Inc. have been reported in "Physical Evaluation of Thin Films of Solid State Materials," E. T. Peters, et al., AFCRL-66-132, February 1966, "Physical Evaluation of Thin Films of Solid State Materials," Edward T. Peters, AFCRL-67-0081, January 1967 and "Physical Evaluation of Electronic Materials, Devices and Thin Films," Edward T. Peters, AFCRL-67-C-0173, January 1968.

A wide variety of specimens have been submitted for characterization; the results of ensuing analyses have been reported individually for each specimen (or group of specimens) in the form of a letter report. Additional sections of this report, therefore, will describe the various experimental methods and procedures that have been employed and will summarize the results of analytical services. The presentation of results will be subdivided into sections concerned with the method of analysis as applied to a variety of materials.

A complete listing of all analyses and services is presented in Appendix A.

II. EXPERIMENTAL METHODS

The following experimental methods and procedures have been employed in the course of the program.

A. Electron Diffraction

The crystallinity and orientation of several thin film deposits have been examined by reflection electron diffraction in which the specimen is placed almost parallel to an electron beam. Electrons diffract from surface asperities and are recorded on a film placed below the specimen. Amorphous materials yield very broad, diffuse ring or halo patterns, polycrystalline materials yield concentric ring patterns and single crystal materials yield spot patterns. The ring patterns can be utilized to determine interplanar spacings of the reflecting planes, allowing specimen identification. Single crystal spot patterns can be analyzed to determine both the structural identification and orientation of the specimen.

Particular orientations are achieved by rotations about two orthogonal axes normal to the electron beam and by a lateral translation. The camera constant (i. e., the relation between ring radius or spot distance from film center to interplanar spacing) is determined by means of a known standard. This constant is strongly dependent on electron beam voltage, but is rather insensitive to other microscope adjustments. All examinations reported herein have been carried out on a Hitachi HU-11 Electron Microscope, operated at 100 kv.

B. X-ray Diffraction

Powder sample identification and lattice parameter measurements have been carried out by X-ray diffraction methods. When large samples are available, one utilizes a diffractometer which yields a strip chart recording of peak intensity versus Bragg angle. Small quantities of material are examined by the Debye-Scherrer camera technique. The specimen is placed in a small diameter capillary tube, which is positioned at the center of the camera. Diffraction lines are recorded on a film located on the circumference of the camera. In either case, measurements of the diffraction line positions allow calculation of the interplanar spacings of the lines and identification of the specimen material.

Precise lattice constants have been determined by a least square extrapolation of the lattice constant computed for each reflection versus the Nelson-Riley function. The required calculations have been programmed and are carried out on an IBM 1130 computer.

Back reflection X-ray patterns have been utilized to determine the crystallinity of a specimen. Polycrystalline materials yield ring (pinhole) patterns which can be used for qualitative measures of grain size, lattice parameter and preferred orientation. Single crystal materials yield spot (Laue) patterns which are utilized to confirm crystallinity, to provide

specimen orientation and to give a qualitative estimate of crystal strain. The latter is based upon observed spot distortion, diffuseness or fragmentation. Single crystal orientation is carried out by conventional back reflection Laue methods. The specimen holder is transferred from the X-ray unit directly to the grinding machine where specific specimen configurations are prepared by appropriate cutting and grinding. When required, the specimen faces are polished to about a 1 micron surface finish by hand lapping with diamond or alumina grit.

Quantitative crystal perfection measurements have been carried out by means of a double crystal spectrometer. In operation, a high perfection analysing crystal is used to produce a monochromatic, parallel ray beam. This radiation impinges upon the second (specimen) crystal, which is slowly rotated through an angle ω about a rocking axis which is included in the surface of the specimen and is perpendicular to the X-ray plane. The resulting rocking curve (X-ray intensity versus ω) that is obtained from reflection planes parallel to the specimen surface has an angular breadth at half maximum intensity which is directly related to small angle tilt boundaries and dislocation strain distributions within the specimen. After correcting for geometrical and natural (Darwin-Princ) broadening, the half breadth values can be utilized in calculating dislocation densities.

C. X-ray Emission Analysis

Qualitative and trace element analyses have been carried out on several materials by X-ray emission methods. In this technique, an intense X-ray source illuminates the specimen causing the formation of secondary X-rays characteristic of the specimen elements, i.e., X-ray "fluorescence". Dispersive analysis of these X-rays by an analyzing crystal allows calculation of the fluorescent X-ray wavelengths and identification of the elements within the specimen. By employing a helium path, X-ray emission analysis is applicable for all elements from aluminum ($Z = 13$) to uranium ($Z = 92$). Quantitative analyses can be made if known chemistry standards are available for producing a correction curve of X-ray intensity versus concentration.

D. Electron Probe Microanalysis

The electron probe microanalyser is utilized to determine the chemical composition of a specimen volume about 1 micron in diameter. In principle, a finely focussed electron beam impinges on the specimen and converts its energy to X-rays which are characteristic of the specimen elements. These X-rays are dispersively analyzed by means of an analyzing crystal to yield identification of the X-rays and thus, the specimen elements.

The instrument at ManLabs is capable of analyzing for all elements from boron ($Z = 5$) to uranium ($Z = 92$). Analyses can be qualitative or quantitative. The method is nondestructive and can be used for chemical identification and for chemical distributions as a function of distance.

In addition to chemical analyses, the electron probe can be utilized for a microdiffraction method which leads to very precise lattice parameters. For this method, a point source of a divergent beam X-rays is generated within a thin single crystal specimen by means of the incident electron beam of the microanalyzer. The divergent X-rays which fulfill the Bragg law for various sets of planes are diffracted by the planes resulting in diffraction (and absorption) cones characteristic of the specimen. The resulting information collected on a film placed below the specimen is called a Kossell pattern and consists of numerous curved lines. Judicious measurement of specific line (or conic) intersections can lead to lattice parameters accurate to 1 part in 100,000. In cases where the characteristic X-rays associated with the specimen are not suitable for diffraction, a very thin ($\sim 5\mu$) foil of a selected metal can be placed directly above the specimen to produce a known divergent source of X-rays. A Kossell camera has been built at ManLabs, Inc. for evaluating the effectiveness of measuring very small changes in lattice parameter caused by irradiation damage.

E. Chemical Analyses

A fully equipped analytical laboratory is available for wet chemical, emission spectrographic and spectrochemical analyses.

F. Density

The specific density of bulk specimens has been determined by the water displacement method (at room temperature), utilizing a 10 ml calibrated volumetric flask and a precision balance. At least three independent measurements were made for each specimen.

G. Hardness

Specimens are mounted in epoxy and are polished to about a 1 micron surface finish to provide a uniform surface topography. Hardness measurements are made on a Leitz Durimet Microhardness Tester, utilizing either Knoop or Vickers pyramid indentors. Hardness values are reported in kg/mm^2 .

H. Light Microscopy

Specimens are polished by conventional methods to produce a smooth and uniform surface condition. In some cases, etchants are utilized to delineate structural features. Photographs up to 2000 magnifications are obtained on either Zeiss or Leitz metallographs.

I. Electron Microscopy

Various surface replication techniques can be applied to a variety of specimen surfaces to provide high magnification (2000X to 50,000X) electron micrographs of surface features. Hitachi HU-11 and RCA-EMU electron microscopes are available for high magnification metallography.

J. Thermal Conductivity

A liquid helium cryostat and associated electronic circuitry are available for making thermal conductivity measurements by the series comparison method. A complete description of the equipment is available in "Study of the Thermal Conductivity of Lithium Germanate by the Series-Comparison Method," Scientific Report No. 1, AFCRL Contract No. F19628-67-C-0173, May 1967.

III. ANALYTICAL RESULTS

A. X-ray Diffraction

1. Phase Analysis

A number of specimens have been submitted for phase analysis by means of X-ray diffraction techniques. Diffractometer traces are employed in most cases; Debye-Scherrer film patterns are employed when only small amounts of specimen material are available and for comparison with diffractometer methods.

All diffraction scans are accompanied by a data sheet listing all diffraction lines and various identified phases. The groups of specimens analyzed are summarized in Table 1.

2. Lattice Parameter Determination

Several specimens were submitted for phase analysis and precise lattice parameter measurements. Lattice parameters were determined by a least square extrapolation of the lattice constant computed for each reflection versus the Nelson-Riley function. The results obtained are summarized below:

<u>AFCRL No.</u>	<u>Specimen No.</u>	<u>Chemistry</u>	<u>$a_o, \text{\AA}$</u>	<u>$b_o, \text{\AA}$</u>	<u>$c_o, \text{\AA}$</u>
01450	1	MgO: Al ₂ O ₃ (1:1)	8.0494	---	---
	2	MgO: Al ₂ O ₃ (1:2)	8.0087	---	---
	3	MgO: Al ₂ O ₃ (1:3)	7.9732	---	---
	4	MgO: Al ₂ O ₃ (1:6)	7.9617	---	---
00981	11:22:1-67	Lithium Germanate	7.376	16.735	9.711
02777	YAG-1	Y ₃ Fe ₄ Al ₄ O ₁₂	12.3125	---	---
	YAG-2	Y ₃ Fe ₃ Al ₃ O ₁₂	12.2458	---	---
	YAG-3	Y ₃ Fe ₂ Al ₂ O ₁₂	12.1766	---	---
	YAG-4	Y ₃ FeAlO ₁₂	12.0915	---	---

3. Studies of Crystal Perfection by Means of X-ray Laue Method and Double Crystal Spectrometer

(a) Several gel-grown calcite crystals (AFCRL No. 01415) were submitted for characterization of crystallinity. Transmission Laue patterns were obtained from crystals which were $\sim 1/16''$ on edge. The Laue spots were sharp and clear with no evidence of any distortion; the crystals were thus confirmed to be free of gross strains.

(b) A piece of boron (AFCRL No. 01833) was examined by X-ray Laue methods. On the basis of spot splitting and fragmentation it could be confirmed that the crystal had a highly mosaic structure. The cylinder axis was found to be $\sim 12^\circ$ from the $[111]$ rhombohedral or $[0001]$ hexagonal axis.

(c) A ruby boule, No. 4-23-68-III-2, AFCRL No. 01622, was submitted for various characterization studies. X-ray Laue patterns showed no evidence of gross imperfections. The boule was oriented and cut to yield $(2\bar{1}\bar{1}0)$ and (0001) slices. These were polished and etched to yield dislocation densities. Preparation process of the (0001) -plane included chemical polishing in 85% H_3PO_4 at $425^\circ C$ for 3 minutes, and then at 320° for 5 minutes. The $(2\bar{1}\bar{1}0)$ plane preparation included polishing in potassium aluminum fluoride at $900^\circ C$ for 1 minute. Both specimens were etched in potassium bisulfate at $675^\circ C$ for ~ 30 seconds. The following densities were counted:

Plane	Typical Area	Area Containing Numerous Subgrains
(0001)	$8.7 \times 10^5 \text{ per cm}^2$	13.8×10^5
$(2\bar{1}\bar{1}0)$	4.7×10^5	8.6×10^5

(d) A specially prepared 0.005 w/o Cr, 60° ruby boule, AFCRL No. 01480, was submitted for characterization of crystal perfection by means of double crystal spectrometer rocking curve measurements. Approximately 1" lengths of boule were grown at rates of $1/8"$, $1/4"$ and $1/2"$ per hour.

The boule was oriented, sliced, ground and polished to yield slices about $1/16"$ thick and having a $(1\bar{2}13)$ surface plane. Using Cu radiation and a (220) silicon analyzing crystal, rocking curves were obtained from 3 positions - near the bottom, center and top of each crystal. Sets of curves were taken with the $[10\bar{1}0]$ first normal and then parallel to the axis of the spectrometer.

Analysis of the rocking curve data yields the following conclusions:

On the average, the $[10\bar{1}0]$ perpendicular position yields more narrow, intense and uniform peak shapes than does the $[10\bar{1}0]$ parallel position. For the $[10\bar{1}0]$ perpendicular geometry, the center position yields narrower peaks than does the top and bottom portions. It can be inferred that the central core zone of the boule is of greater perfection than is the outer peripheral zone.

There is no sharp difference in rocking curves obtained for the various growth rates. In general, a very slight increase in broadening is observed as the growth rate increases.

(e) A section of a spinel boule, AFCRL No. 02549, was metallographically polished and etched. A very high density of both random and low angle boundary etch pits were revealed. Side reflection X-ray photographs suggested a highly mosaic crystal. Double crystal spectrometer curves exhibited multiple peaks with a mosaic spread of 5 to 9 minutes.

B. Chemical Analyses

Several different techniques, including emission spectroscopy, X-ray fluorescence, etc., were utilized to determine the chemical composition of given specimens in a qualitative or quantitative manner, as required. The results of a number of emission spectroscopy analyses are summarized in Table 2.

Chemical analysis of a stoichiometric spinel crystal (DJEVA, AFCRL No. 02549) gave the following results:

$$\begin{array}{l} 80.32 \pm 0.35 \text{ Al} \\ 19.02 \pm 0.20 \text{ Mg} \end{array}$$

Several ruby and sapphire crystals were submitted for determination of trace metal impurities by emission spectrographic analysis (AFCRL No. 01781, Specimen Nos. RA, RS, SA, AFCRL No. 01643, Specimen No. 5-15-68-II-1). Specimens were crushed in a "diamond mill". The powder was acid leached to remove impurities introduced during crushing. Spectrographic analysis yielded the following results:

<u>Specimen No.</u>	<u>Results</u>
Ra, RS	Reduction in Cr and Si contents
SA	Reduction in Cr, Mg, Mn and Si content
5-15-68-II-1	Trace amounts of Cr (100-1000 ppm)
	Fe and Si (10-100 ppm)
	Cu and Mg (1-10 ppm)
	Ca (0.1-1.0 ppm)

Six specimens of natural quartz, including unirradiated natural, dark citrine, mixed citrine and smoky, medium smoky and dark smoky, were analyzed for impurities using X-ray fluorescence methods (AFCRL No. 02143). A General Electric perma quartz standard was employed for a blank of background intensities.

A small amount of Ni (0.15% or less) was found in the dark smoky specimen and a small amount of Zn (0.20% or less) in the clear quartz; detectability limits are 0.10% or less.

C. Electron Probe Microanalysis

A number of specimens have been submitted for electron probe microanalysis with specific analytical requirements. Table 3 will briefly describe the results obtained.

D. Crystal Orientation and Cutting

A number of ruby boules, as well as $\text{Li}_2\text{Ge}_7\text{O}_{15}$, MgO , RbMnF_3 , CdS , spinel, KTN and quartz crystals have been oriented, cut and polished according to stated size specifications and specimen orientations. The experimental procedures are generally as follows. The crystals were mounted onto steel blocks with "quartz" cement and were oriented to plane by back-reflection X-ray Laue methods. The required pieces were fabricated by cutting and grinding with diamond wheels and polished to obtain the desired surface finish. The final orientations were checked by X-ray Laue patterns.

A summary of the various crystal chemistries and specimen dimensions is given in Table 4.

E. Miscellaneous Analyses

1. Density Determination

Bulk and powder densities have been determined for a number of different specimens by means of the water displacement method. The results are summarized in Table 5.

2. Thermal Expansion Coefficient of Cobalt Silicide

The thermal expansion coefficient of a single crystal CoSi rod was measured over the range of room temperature to 1000°C by means of a AUC grade graphite dilatometer. Heating was carried out in a graphite muffle tube furnace with an argon atmosphere. The temperature at each 100° interval was allowed to stabilize prior to taking measurements.

The average thermal expansion coefficient for CoSi in a $[111]$ direction was determined to be:

$$\alpha [28^\circ - 1000^\circ\text{C}] = 12.0 \pm 0.2 \times 10^{-6} \text{ in/in/}^\circ\text{C}$$

3. Determination of Crystallinity of Ge Thin Film Deposits

A number of germanium thin film deposits were submitted for analysis by reflection electron diffraction methods in order to

define the crystallinity of the deposit. The results obtained can be summarized as follows:

<u>AFCRL No.</u>	<u>Ge, Specimen No.</u>	
01869	40	Some lattice strain, evidence for polycrystalline Ge
01869	41	Polycrystalline
01869	42	Some lattice strain
01869	43	Some lattice strain
01869	44	Considerable imperfection
01869	45	Very imperfect; poor patterns

TABLE 1
X-RAY DIFFRACTION ANALYSIS

<u>Quantity</u>	<u>Specimen Material</u>	<u>ARCRL No.</u>
4	MgO: Al ₂ O ₃	01450
1	HgS on CdS	01657
1	Bi ₂ O ₃ : GeO ₂	01790
1	NaBiO ₃	02353
1	KF	02353
4	Ce ₂ V ₂ O ₈	02353
1	CeB ₂ O ₅	02353
1	CeBi ₂ O ₅	02353
1	Na ₂ TiO ₃	02353
1	Na ₂ SiO ₃	02353
1	NaF	02353
1	BaF ₂	02353
1	La ₂ (MoO ₄) ₃	02353
1	Y ₂ V ₂ O ₈	02353
1	Y ₂ Cr ₂ O ₈	02353
9	GeO ₂ + BeO	02036
4	Y ₃ Fe _{5-x} Al _x O ₁₂	02777
1	Nd ₂ (SO ₄) ₃ · xH ₂ O	02718

TABLE 2
RESULTS OF EMISSION SPECTROSCOPY ANALYSIS

AFCL No.	Spec. No.	Material	10-100	3-30	1-10	0.1-1.0	0.03-0.3	0.01-0.1	* .003-.03	* .001-.01	* .003-.003	* .0001-.001	* .00003-.0003	* .00001-.0001
01644	57-A	-	Ag, Mg	-	-	Mn	-	-	Cr	-	-	Ca, Fe, Si	-	-
01768	CB-2	HgS	Hg	-	-	-	-	Si	Cd, Fe, Na, Cu	-	-	Sn, Mg	-	Ag, Ca
01897	HgS-X	HgS	Hg	-	-	-	-	Si	Cd	-	-	Cu, Mg	-	Ag
02085	#1	Ruby	Al	-	-	Cr	-	Si	Fe, Na	Ca, Ga, Mg	Cu	Ba, Ni, Ti	Ag, B	Mn
02085	#2	Ruby	Al	-	-	Cr	-	Si	Fe	Ca, Ga, Mg, Na	Cu	Ni, Ti	Ag	Mn
02085	-	AlNH ₄ (SO ₄) ₂ · H ₂ O	-	-	-	-	-	-	-	Si	Ca, Fe, Na	Cu, Ga, Mg	Ag, Ni	Ba
02085	-	CrNH ₄ (SO ₄) ₂	-	Cr	-	-	-	-	-	-	Ca	Al, Fe, Mg	Cu, Ni, Ti	-
02360	#1	Ruby	Al	-	-	-	Cr	Si	Mg	Fe, Ca	Zr	Na, Ba	Ga, Cu, Ni, Ti	Mn, Ag
02360	#2	Ruby	Al	-	-	-	Cr	Si	Mg	Fe, Ca	Zr	Na, Ba	Ga, Cu, Ni, Ag	Mn
02587	-	Alundum	Al	-	-	Ca	-	Si	Fe	Mg, Na	Ba, Zr	Ga, Mn, Ti	Cr, Cu, Sr, V	Ag, B, Ni, Pb, Sn
02549	-	Spinel	Mg, Al	-	-	-	-	Si	-	Cu, Fe, Cr	-	B, Zr, Ti	-	Ag, Ni, In

* Range - Weight %

TABLE 3

SUMMARY OF RESULTS USING ELECTRON PROBE MICROANALYSIS

<u>AFCRL No.</u>	<u>Material</u>	<u>Analyze for:</u>	<u>Results Obtained</u>
01513-18	Germanium	As	Detected traces of As on surface of all specimens
01559	KTN crystals (2)	Uniformity in chemistry	a) Uniform crystal chemistry b) Slightly higher Ta/Nb ratio (3-5%) in golden crystal c) Higher Ta content (few %) at the center of the face (both crystals)
01415	Calcite	Si	Observed Si at growth steps and within inclusions of the crystal
01868	SiC	Ni	Random distribution of Ni particles with mean diameter of $\sim 5\mu$.
01835	Spinel	Nd, Cr	a) Stringers of Nd, $\sim 10\mu \times \sim 200\mu$, at periphery of specimen b) No Cr observed
02007	CeIO ₃	Si	No Si observed
02069	Spinel	Nd, Cr	a) Stringers contain $\sim 25\%$ Nd (compared to 86% Nd in Nd ₂ O ₃) b) Cap and center cross-sections contain about equivalent amounts of Cr; center slice has somewhat higher Nd content than cap section
02079	Lithium germanate	Chemistry of black inclusions	"Black inclusions" were found to be pits in the surface of the crystal
02099	SiC	Metal distribution	a) Spec. 3-53-1 consists solely of SiC b) Spec. 3-63-1 has a continuous film of Co
02136	CsCuCl ₃	Qualitative distribution of elements	Found that Cs, Cr and Cl intensities were uniform; no additional elements detected
02149	GaAs	Chemistry of surface film	Presence of C and probably N

TABLE 3(CONT)

SUMMARY OF RESULTS USING ELECTRON PROBE MICROANALYSIS

<u>AFCRL No.</u>	<u>Material</u>	<u>Analyze for:</u>	<u>Results Obtained</u>
02548	YiG	Ca, V and In	Uniform intensity of Ca, V and In
02411	Ruby	Cr in band	Inside of band - $140-180 \pm 50$ ppm Band - $200-300 \pm 50$ ppm Outside - no Cr
02739	Ge	Chemistry of anomalies	Only Ge detected
02409	α SiC	Ni, Cr, Cs or Fe	
	Spec. #3-69-1		No metallic element detected
	3-86-1		No metallic element detected
	3-86-16		No metallic element detected
	3-113-1		No metallic element detected
	3-95-2		Random distribution of Ni globules (2-6 μ diameter)
02413	SiC, #3-109	Ni, Cr, Cs or Fe	
	- face		Particles of Ni(10-25 μ in extent)
	- cross section		No Ni detected
	3-112-1		Fe globules (5-10 μ in extent), random distribution
02750	SiC	Metal deposits	
	Spec. #3-114-16		Layer of Cr
	3-118-1		Cs(1-3 μ dia.), at $\sim 10\mu$ intervals
	3-118-2		Diffuse spots of Cs ($\sim 5\mu$)
	3-118-3		Ni (1-2 μ dia.), at $\sim 10\mu$ intervals
	3-118-4		No Ni detected
	4-121-1		No Ni detected
02850	Ge	Chemistry of anomalies	
	Sample - Oct. 6		a) Spherical particles-Ni, Cu, Ge-traces of Si, Fe, Mn b) Mottled region-Ge, trace of Cu c) Dark region-Ge, Ni, Cu, Si d) Matrix-Ge, traces of Si, W
	Sample - Oct. 7		a) Dark pit-Gi, Cu, Ni, trace of Fe, Si, Ca b) Mottled region-Ge, Cu, trace of Ni c) Elongated region-Ni, Ge, Cu, trace of Fe d) Matrix - pure Ge
02935	Ge	Chemistry of protrusion	Only Ge detected

TABLE 4
CRYSTAL CUTTING: CRYSTAL IDENTIFICATION AND
SPECIMEN REQUIREMENTS

<u>Job No.</u>	<u>Specimen No.</u>	<u>Chemistry</u>	<u>Plane</u>	<u>Dimensions</u>
01079	11:22:1-67	Lithium Germanate	(100), (010), (001)	15/16x3/16x3/16
01523	12:21:67-III-1	Ruby	(0001), (2110), (0110)	5mm on edge
01523	55-B	Ruby	(0001), (2110), (0110)	1/32x3/4x1/32 5/16x5/16x3/4
01556		MgO	(100)	5/8x1/8x1/8
01698	83	BaMgF_3	(100), (010), (001)	Maximum
01700	3:7:1-68	$\text{Bi}_{12}\text{GeO}_{20}$	[111] = 1, [112] = 2	1/8x1/8x1/8
01702	3:14:1-68	$\text{Li}_7\text{Ge}_7\text{O}_{15}$	[100] - 3, [110] - 1, 3, [001] - 3	1/8x1/8x1/8
01600	2-6-68-III-1	Ruby	(1010)	6-1/16" thick 6-1/8" thick
00741	4-15-68-III-1	Ruby	[0001] [1123] [1120]	1/4x1/4x3/4
01635		RbMnF_3	(100), (011), (011)	2x2x4.3 mm
00742		Al_2O_3	Random	1/4x1/4x1/8
01636	No. 1 No. 3	Ruby	(0001) (1010)	1/4x1/4x1/8 1/4x1/4x1/8
01637	No. 2	Ruby	(1010)	1/4x1/4x1/8
01759	275-24	Quartz	(0001), (2110), (0110)	1 cm cube
01641		$\text{Ba}_{0.4}\text{Na}_{0.2}\text{NbO}_3$	[001]	3x3x18 mm
01646	Sawyer-Swept	Quartz	X, Y, Z	0.575x0.450x 0.120 in.
01829	6-7-68-III-1 6-13-68-III-1 6-17-68-III-1	Ruby	[1010] [1012] [1011]	1.063x.313x.313
01524	1700-6	Quartz	X, Y, Z	0.997x0.894x 0.595

TABLE 4 (CONT)

CRYSTAL CUTTING: CRYSTAL IDENTIFICATION AND
SPECIMEN REQUIREMENTS

<u>Job No.</u>	<u>Specimen No.</u>	<u>Chemistry</u>	<u>Plane</u>	<u>Dimensions</u>
02009		Quartz	X, Y, Z	2.3x1.5x1.5 cm
02069	11-1-68-II-1	Sapphire-Ruby	Random	0.375 x length
02017	261-22	Quartz	X, Y, Z	0.75 x 1.78 x 0.45
02083	261-22	Quartz	X, Y, Z	Maximum
01903		3-CdS	(0001)	Maximum
02011				
02083	261-22	Quartz	X, Y, Z	Maximum
02125	6 Spec.	Quartz	X, Y, Z	10x14, 3 mm
01993	12-17-68-II-1A	Ruby	Boule Axis	1/8" thick slices
01995	60°CZ	Ruby	(0001)	Maximum
01994	12-17-68-III-1B	Ruby	(0001)	Maximum
02150	64B, C & D	Spinel	(100)	0.25, 0.02, 0.13" thick
02434		Ruby	(0001)	15x1x1 mm (2)
02357	A6-17	Quartz	X-axis	15x1x1 mm (2)
		Quartz	Z-axis	15x1x1 mm (2)
	1700-6	Quartz	X-axis	15x1x1 mm (2)
		Quartz	Z-axis	15x1x1 mm (2)
	261-22	Quartz	X-axis	15x1x1 mm (1)
		Quartz	Z-axis	15x1x1 mm (2)
02501	C7-6	Quartz	11 pieces as specified	
02505	N-3	Quartz	X-face	120x575x450 mils
			Y-face	
			Z-face	
02504	261-22	Quartz	X-face (2)	120x450x575 mils
			Y-face (2)	450x120x575 mils
			Y-bar (2)	100x120x575 mils
			Y-face	575x350x120 mils
02503	261-225	Quartz	Z	575x220x120 mils
02502	A6-17	Quartz		100x100x750 mils (3)
02506	N-2	Quartz	ES	~ 500 mils
			X-face	120x575x450 mils
			Y-face	575x120x450 mils
			Z-face	450x575x120 mils
			2 pieces	100x704x100 mils

TABLE 4 (CONT)

CRYSTAL CUTTING: CRYSTAL IDENTIFICATION AND
SPECIMEN REQUIREMENTS

<u>Job No.</u>	<u>Specimen No.</u>	<u>Chemistry</u>	<u>Plane</u>	<u>Dimensions</u>
02552	X371-9	Quartz		Oscillator piece Sweeping piece X, Y, Z, as specified
02825	3 crystals	CuCl		Maximum
02827	1 crystal	KTN		1 cm x 1 cm (12)
00605		LiNbO ₃		Submitted for polishing

TABLE 5
DENSITY DETERMINATION BY WATER DISPLACEMENT

<u>AFCRL No.</u>	<u>Specimen No.</u>	<u>Chemistry</u>	<u>Density-g /cc</u>
01667	J58 (bulk)	SiC	2.875
	J58 (200 lbs)	SiC	2.954
	J59 (bulk)	SiC	2.140
01905	10:25:1-66	$\text{Na}_4\text{Ge}_9\text{O}_{20}$	3.85
	1:27:1-67	$\text{Na}_4\text{Ge}_9\text{O}_{20}$	3.15
	Aolux 1720	$\text{Na}_4\text{Ge}_9\text{O}_{20}$	2.86
02448	12:12:1:68	Li Germanate	
	1.2 g sample		4.04
	2.0 g sample		4.01

APPENDIX A
LIST OF ANALYTICAL SERVICES

<u>Index</u>	<u>AFCRL No.</u>	<u>Requestor</u>	<u>Specimen No.</u>	<u>Material</u>	<u>Analytical Methods</u>
1	01406	Posen	10:26:67-III-1	Ruby	Crystal orientation and cutting double crystal spectrometer rocking curves
2	01539	Marshall	124	Cobalt Silicon	Thermal expansion coefficient
3	01450	Lipson	397-1 to 4	Spinel	X-ray diffraction ID, precise lattice parameters
4	01079	Powell	11:22:1-67	Lithium Germanate	Crystal orientation and cutting
5	01529	Bruce	11:22:1-67	Lithium Germanate	Crystal orientation and cutting, precise lattice parameters
6	01533	Powell	12:21:67-III-1	Ruby/Sapphire	Crystal orientation and cutting
7	01523	Pitha	55B	Ruby	Crystal orientation and cutting
8	01513	Kennedy	78	Germanium	Electron probe microanalysis
9	01514	Kennedy	79	Germanium	Electron probe microanalysis
10	01515	Kennedy	87	Germanium	Electron probe microanalysis
11	01516	Kennedy	88	Germanium	Electron probe microanalysis
12	01517	Kennedy	89	Germanium	Electron probe microanalysis
13	01518	Kennedy	90	Germanium	Electron probe microanalysis
14	01480	Posen	1:24:68-III-1	Ruby	Crystal orientation and cutting, double crystal spectrometer rocking curves
15	01554	Lipson	1:27:1-67 10:25:1-67	Nd-doped sodium Germanate	Index of refraction

APPENDIX A (CONT)
LIST OF ANALYTICAL SERVICES

<u>Index</u>	<u>AFCRL No.</u>	<u>Requestor</u>	<u>Specimen No.</u>	<u>Material</u>	<u>Analytical Methods</u>
16	01415	Armington	C-1	Calcite	X-ray Laue, electron probe microanalysis
17	01657	Armington	C-1	HgS on CdS	X-ray diffraction ID
18	01556	Sahagian		MgO	Crystal orientation and cutting
19	01698	Powell	83	RbMnF ₃	Crystal orientation and cutting
20	01667	Smiltens	8J _s , 9J _s	Silicon Carbide	Bulk density, metallographic analysis
21	01702	Dugger	3:14:1-68	Lithium Germanate	Crystal orientation and cutting
22	01559	Capone		KTN crystals	Electron probe microanalysis
23	00741	Sampson	4:15:68-III-1	Ruby	Crystal orientation and cutting
24	01600	Sampson	21-6:68-III-1	Ruby	Crystal orientation and cutting
25	01722	Posen	7N43, JN48, B ⁺	Si(irradiated)	Precise lattice constants via Kossel patterns
26	01635	Seavey		RbMnF ₃	Crystal orientation and cutting
27	00742	Sampson		Ruby, Sapphire	Crystal orientation and cutting
28	01781	Ryan	RA, RS, SA	Ruby, Sapphire	Emission spectroscopy
29	01636	Adamski	R1, R3	Ruby	Crystal orientation and cutting
30	01637	Adamski	R2	Ruby	Crystal orientation and cutting
31	01622	Sahagian	4:23:68-III-2	Ruby	X-ray Laue, dislocation density measurement
32	01790	Dugger	4:26:1-68	Bi ₂ O ₃ :GeO ₂	X-ray diffraction ID
33	01759	Capone	275-24	Quartz	Crystal orientation and cutting
34	00981	Dugger	4:16:1-68	Lithium Germanate	Precise lattice parameters

APPENDIX A (CONT)

LIST OF ANALYTICAL SERVICES

<u>Index</u>	<u>AFCRL No.</u>	<u>Requestor</u>	<u>Specimen No.</u>	<u>Material</u>	<u>Analytical Methods</u>
35	01641	Sahagian		Ba _{0.4} Na _{0.2} NbO ₃	Crystal orientation and cutting
36	01769	Armington	CB-2	HgS on Substrate	Electron probe microanalysis, metallographic analysis
37	01643	Goodrum	5:15:68-II-1	Ruby	Emission spectroscopy
38	01646	Brown	Sawyer-Swept	Quartz	Crystal orientation and cutting
39	01644	Pitha	57-A		Emission spectroscopy
40	01869	Kennedy	#40-45	Germanium	Reflection electron diffraction
41	01905	Lipson	10:25:1-66 1:27:1-67, Aolux 1720	Na ₄ Ge ₉ O ₂₀	Bulk density
42	01868	Comer	3-23A&B	Silicon Carbide	Electron probe microanalysis
43	01768	Armington	CB-2	HgS	Emission spectroscopy
44	01897	Armington	HgS-X	HgS	Emission spectroscopy
45	01829	Sampson	6-7-68-III-1, 6-13-68-III-1, 6-17-68-III-1	Ruby	Crystal orientation and cutting
46	01906	Slobodnik		LiNbO ₃	X-ray Laue orientation
47	01524	Brown	1700-6	Quartz	Crystal orientation and cutting
48	01835	Adamski	9-15-68-II-1	Spinel	Metallography, electron probe microanalysis
49	01833	Armington		Boron	X-ray Laue orientation, metallography
50	01903	Armington		CdS	Crystal orientation and cutting
51	02007	Armington	CIO-3	CeIO ₃	Metallography, electron probe microanalysis
52	02009	Capone		Quartz	Crystal orientation and cutting

APPENDIX A (CONT)

LIST OF ANALYTICAL SERVICES

Index	AFCRL No.	Requestor	Specimen No.	Material	Analytical Methods
53	02011	Armington	CS-2, CS-3	CdS	Crystal orientation and cutting
54	02069	Adamski	9-16-68- II-1	Spinel	Electron probe microanalysis
55	01990	Adamski	11-1-68- II-1	Sapphire, Ruby	Crystal orientation and cutting
56	01999	Slobodnik		LiNbO ₃	X-ray Laue orientation
57	02018	Armington	C-2	Calcite	Metallography, electron probe microanalysis
58	02017	Capone	261-22	Quartz	Crystal orientation and cutting
59	02083	Capone	261-22	Quartz	Crystal orientation and cutting
60	02069	Adamski	1 Spec.	Spinel	Electron probe microanalysis
61	02079	Comer	9-19-I- 68	Li Germanate	Electron probe microanalysis
62	02099	Comer	3-51-113- 63-1	SiC	Electron probe microanalysis
63	02085	Dickinson	Ruby(2) + Sulfates(2)	Al ₂ O ₃ + 0.2 Cr ₂ O ₃	Emission spectroscopy
			Al NH ₄ (SO ₄) ₂ · H ₂ O		
64	02143	Brown	6 Spec.	Quartz	X-ray fluorescence
65	02125	Brown	6 Spec.	Quartz	Crystal orientation and cutting
66	01993	Weiner	12-17-68- III-1A	Ruby	Crystal orientation and cutting
67	01995	Weiner	60° CZ	Ruby	Crystal orientation and cutting
68	01994	Weiner	12-17-68- III-1B	Ruby	Crystal orientation and cutting
69	02136	Armington	CS-3	CsCuCl ₃	Electron probe microanalysis
70	02149	Bouthillette	Lis C 22-1	GaAs	Electron probe microanalysis

APPENDIX A (CONT)

LIST OF ANALYTICAL SERVICES

<u>Index</u>	<u>AFCRL No.</u>	<u>Requestor</u>	<u>Specimen No.</u>	<u>Material</u>	<u>Analytical Methods</u>
71	02150	Pitha	64B, C & D	Spinel	Crystal orientation and cutting
72	02353	Dugger	15 Spec.	Several	X-ray diffraction ID
73	02036	Dugger	30 Spec.	BeO-GeO ₂	Debye-Scherrer ID
74	02434	Dickinson		Ruby	Crystal orientation and cutting
75	02360	Dickinson	No. 1 & 2	Ruby	Emission spectroscopy
76	02392	Capone	C 2-1, L-5	Quartz	Crystal orientation and cutting
77	02357	Capone	A 6-17, 261-22, 1700-6	Quartz	Crystal orientation and cutting
78	02501	Brown	C 7-6	Quartz	Crystal orientation and cutting
79	02448	Lipson	12:12:1:68	Li Germanate	Bulk density
80	02416	Sahagian	I, II, III	KTN	Emission spectroscopy, electron probe micro-analysis, hardness, bulk density, electrical resistivity
81	02599	Sahagian		Spinel	Chemical analysis, emission spectroscopy, crystal perfection studies
82	02505	Brown	N-3	Quartz	Crystal orientation and cutting
83	02504	Brown	26-12	Quartz	Crystal orientation and cutting
84	02503	Brown	261-22S	Quartz	Crystal orientation and cutting
85	02502	Brown	A6. 17	Quartz	Crystal orientation and cutting
86	02506	Brown	N-2	Quartz	Crystal orientation and cutting
87	02587	Dickinson		Alundum	Emission spectroscopy
88	02545	Dickinson	#1	Ruby	Chemical analysis
89	02548	Euler	1-5, incl.	YIG	Electron probe microanalysis

APPENDIX A (CONT)

LIST OF ANALYTICAL SERVICES

<u>Index</u>	<u>AFCRL No.</u>	<u>Requestor</u>	<u>Specimen No.</u>	<u>Material</u>	<u>Analytical Methods</u>
90	02411	Dickinson	10 Ap	Ruby	Electron probe microanalysis
91	02409	Comer	5 Spec.	SiC	Electron probe microanalysis
92	02550	Dickinson	#1	Ruby	Chemical analysis
93	02738	Brown		Quartz	Crystal orientation and cutting
94	02552	Brown	X371-9	Quartz	Crystal orientation and cutting
95	02739	Kennedy		Ge	Electron probe microanalysis
96	02413	Comer		SiC	Electron probe microanalysis
97	02825	Armington	3 Spec.	CuCl	Crystal cutting
98	02750	Comer	6 Spec.	SiC	Electron probe microanalysis
99	02827	Pickering	1 Spec.	KTN	Emission spectroscopy, electron probe microanalysis, hardness, density, crystal cutting
100	02850	Kennedy	2 Spec.	Ge	Electron probe microanalysis
101	00605	Carr	1 Spec.	Li NbO ₃	Crystal polishing
102	02935	Kennedy	Ge 115 RF	Ge	Electron probe microanalysis
103	02777	Czerlensky	4 Spec.	YAG	X-ray diffraction ID, precise lattice parameters
104	02718	Gordon	1 Spec.	Nd ₂ (SO ₄) ₃ · H ₂ O	X-ray diffraction ID

PART II - HIGH PRESSURE SYNTHESIS

I. INTRODUCTION

Considerable high pressure research has been directed toward the synthesis of elemental diamond and structurally analogous tetrahedral zinc blende, B-3, and wurtzite, B-4, compounds. However, these structures are not close-packed and it has been established that the equiatomic III-V compounds, which are stable at one atmosphere in the zinc blende structure, themselves undergo pressure induced phase transformations to denser structures, specifically to either cubic sodium chloride, B-1, or the beta tin¹. High pressure synthesis studies designed to produce compounds with tetrahedral coordination should consider the relative stability of structures with higher coordination; stoichiometric factors relating to relative phase stability should also be considered. Several phase stability controlling parameters for tetrahedrally coordinated materials are discussed in a previous report of high pressure synthesis studies².

Hall and Compton³ suggest the Al_2S stoichiometry for high pressure synthesis and predict a tetrahedral structure for the compound. This stoichiometry provides an isoelectronic, two-atom analog of silicon with an average of four bonding electrons per atom.

High pressure synthesis studies were initiated for the Al-S binary system at stoichiometries corresponding to Al_2S and Al_2S_3 to provide experimental data for this system. Defect zinc blende and defect wurtzite structures are stable at one atmosphere for Al_2X_3 and Ga_2X_3 compounds, where X = S, Se or Te⁴. Shafer, et al.⁵ report an arsenic stabilized Al_2S_3 compound with a defect spinel structure isomorphous with γAl_2O_3 .

II. EXPERIMENTAL

The mixed solid reactants, Tables 6, 9 and 10 were placed in a boron nitride encapsulation tube 0.50 inch o. d. by 0.40 inch i. d. by 1.00 inch long, and the modified internal anvil high pressure apparatus² was assembled. The load on the system was adjusted to produce the desired pressure on the reactants, then the temperature was raised to the reaction level and maintained for a set time, usually 10 minutes. Next, the temperature was quenched to ambient at the high pressure and finally the pressure was slowly returned to one atmosphere. The reaction product was removed from the high pressure system and stored in a desiccator.

X-ray diffraction was the principal method employed to identify reaction products; metallographic procedures were also employed when feasible to complement X-ray phase identification. Precise lattice parameter values were obtained for selected reaction products using the Nelson Riley extrapolation function⁶.

III. RESULTS AND DISCUSSION

The results of a series of a high pressure synthesis reaction performed for the Al-S system provided in Table 6 demonstrate that stabilization of $\delta\text{Al}_2\text{S}_3$, a new compound, is the dominating pressure effect in this system. The $\delta\text{Al}_2\text{S}_3$ is isomorphous with $\gamma\text{Al}_2\text{O}_3$. The metastability of the high pressure polymorph, $\delta\text{Al}_2\text{S}_3$ is evidenced by the reversion to $\alpha\text{Al}_2\text{S}_3$ ⁴ under vacuum at 875°C for 10 minutes. The observed d-spacings for $\delta\text{Al}_2\text{S}_3$ obtained by elemental synthesis are compared with values reported by Shafer, et al. for the isostructural, as stabilized Al_2S_3 in Table 7. Separate lattice parameter calculations were performed, employing the data obtained from several of the $\delta\text{Al}_2\text{S}_3$ reaction products and from original data reported for the as-stabilized Al_2S_3 ; these results are also provided in Table 7. The synthesis of a tetrahedral compound at the Al_2S composition is thus complicated by, and apparently made more difficult by the pressure stabilization of the new phase, $\delta\text{Al}_2\text{S}_3$.

An examination of the underlying hypothesis for predicting tetrahedral coordination for stoichiometries which are isoelectronic with a Group IV element reveals that "counting bonding electrons" is a necessary but not complete criterion for predicting bonding and coordination characteristics. In order to consider the requirements for sp^3 hybridization and the consequent tetrahedral coordination for the Al_2S and Al_2S_3 stoichiometries, it is convenient to write the fraction formulas $\text{Al}_{2/2}\text{S}_{1/2}$ and $\text{Al}_{2/3}\text{S}_{3/3}$, respectively. Since the defect wurtzite structure is stable at one atmosphere for $\beta\text{Al}_2\text{S}_3$, 1/3 of the metal sites are vacant and a total of 8 bonding electrons are available and required for metal-nonmetal and vacancy-nonmetal bonding. The former comprise 2/3 and the latter 1/3 of the bonds. In contrast, the fractional formula for Al_2S requires that 1/2 of the S sites are vacant and thus only 6 of the required 8 bonding electrons are available for metal-nonmetal and metal-vacancy bonding. According to this analysis, tetrahedral coordination is not predicted for the Al_2S stoichiometry as suggested by Hall and Compton³.

Several of the binary stoichiometries suggested by these authors, however, are found in ternary compounds stable at one atmosphere with tetrahedral coordination. Structural data for three systems provided in Table 8 show an effective stabilization of the tetrahedral structure by the introduction of the Group IV element. By rewriting the ternary compounds with fractional formulas as $\text{Mg}_{1/2}\text{Ge}_{1/2}\text{P}_{2/2}$, $\text{Be}_{1/2}\text{Si}_{1/2}\text{N}_{2/2}$ and $\text{Al}_{2/2}\text{C}_{1/2}\text{O}_{1/2}$ it is seen that each ternary stoichiometry provides the required 8 bonding electrons for each two atom unit or 4 electrons per atom. Thus, such stoichiometries provide the requisite number of bonds and bonding electrons for tetrahedral coordination; however, these compounds do not have defect structures.

The results of a series of high pressure synthesis experiments designed to produce a tetrahedral structure for Al_2S Si provided in Table 9 demonstrate the pressure stabilization of $\delta\text{Al}_2\text{S}_3$ in the presence of silicon and excess

aluminum. Metallographic procedures employed to analyze the reaction products showed the excess aluminum and free silicon as a eutectic mixture in agreement with the one atmosphere binary phase diagram⁴. Electron microprobe analyses showed no evidence of Si diffusion into the Al_2S_3 phase. Lattice parameter calculations⁶ performed for the reaction product obtained at 800°C afforded $a_0 = 9.93(8)\text{\AA}$ in reasonable agreement with the values obtained for the reaction products in the Al-S binary system.

High pressure synthesis experiments were performed in the Al-Se system to explore pressure stabilization of a structure isomorphous with $\gamma\text{Al}_2\text{O}_3$ for Al_2Se_3 which is stable at one atmosphere in a defect wurtzite structure. High pressure syntheses at 800°C for 10 minutes at 35 kilobars produced a structural change in wurtzite Al_2Se_3 to cubic phase analogous to $\delta\text{Al}_2\text{S}_3$; similar treatment of elemental reactants ($2\text{Al} + 3\text{Se}$) produced a product with the same d-spacings. Precise lattice parameter calculations⁶ employed for these data afforded identification of a cubic defect spinel structure isomorphous with $\gamma\text{Al}_2\text{O}_3$ with $a_0 = 10.47(7)\text{\AA}$. The high pressure polymorph appears to undergo a hydrolytic decomposition at ambient conditions but the material is easily retained in a desiccator at room temperature.

The synthesis of high pressure polymorphs with a defect spinel structure isomorphous with $\gamma\text{Al}_2\text{O}_3$ from compounds stable at one atmosphere in a defect tetrahedral structure for Al_2S_3 and Al_2Se_3 suggested the extension of synthesis studies to Ga_2S_3 and Ga_2Se_3 , which are also stable at one atmosphere in a defect zinc blende structure³. The results of high pressure syntheses in the Ga-S and Ga-Se systems provided in Table 5 show that the dominating pressure effect is stabilization of hexagonal GaS and GaSe which are produced with a preferred (0001) orientation. This structure is stable at one atmosphere in both systems. Metallographic examination revealed a plate-like structure for both materials.

IV. CONCLUSIONS

The successful preparation and retention of two new high pressure polymorphs, $\delta\text{Al}_2\text{S}_3$ and $\delta\text{Al}_2\text{Se}_3$, with defect spinel ($\gamma\text{Al}_2\text{O}_3$) structures from the Al_2S_3 and Al_2Se_3 compounds stable at one atmosphere in defect tetrahedral structures (zinc blende or wurtzite) contrasts the pressure induced transformation of the III-V zinc blende compounds to denser cubic or tetragonal structures which can only be retained with difficulty at very low temperatures. The utilization of high pressure to effect stabilization of new tetrahedral structures requires a more fundamental description of stability controlling parameters than has been developed as yet. The selection of stoichiometries appropriate for tetrahedral structures can be predicted with some confidence for ternary systems which contains a binary Group IV element analog and a tetrahedral promoting Group IV element. Successful synthesis of new solid state materials from such compositions may be accomplished at ambient pressures. High pressure could produce stabilization of denser phases at other stoichiometries and thus destabilize the desired product.

REFERENCES

1. W. Klement, Jr. and A. Jayaraman, Progress in Chemistry of The Solid State, 3, (1966).
2. E. V. Clougherty and L. Kaufman, "Thermodynamic Study of Synthesis of New Compound Phases under High Pressure," AFCRL-68-0109, February 1968.
3. H. T. Hall and L. Compton, *Inorg. Chem.*, 4, 1213 (1965).
4. W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals*, Pergamon Press, New York, Volume I (1958) and Volume II (1967).
5. H. Schafer, G. Schafer and A. Weiss, *Z. Anorg. Chem.* 325, 77 (1963).
6. J. B. Nelson, D. P. Riley, *Proc. Phys. Soc.*, 57, 160 (1945).

TABLE 6
REACTION CONDITIONS FOR SYNTHESIS IN THE Al-S SYSTEM

<u>Reactants</u> ¹	<u>Temperature</u> °C	<u>Pressure</u> kilobars	<u>Products Identified By</u> <u>X-ray Diffraction</u>
2Al+S	875	50	Al, δ Al ₂ S ₃
2Al+S	875	30	Al, δ Al ₂ S ₃
2Al+S	875	7	Al, δ Al ₂ S ₃
4Al+ α Al ₂ S ₃	875	30	Al, δ Al ₂ S ₃
α - Al ₂ S ₃	875	30	δ Al ₂ S ₃
2Al+3S	875	30	δ Al ₂ S ₃

THERMAL DECOMPOSITION CONDITIONS

δ Al ₂ S ₃	875	vacuum	α Al ₂ S ₃
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1. All reactants are spectroscopically free of arsenic; reactants were mixed in the indicated molar amounts

TABLE 7
X-RAY DATA AND LATTICE PARAMETERS OF δ Al_2S_3

<u>hkl</u>	<u>Measured</u>		<u>Literature⁵</u>	
	<u>I/I₀</u>	<u>d(Å)</u>	<u>I/I₀</u>	<u>d(Å)</u>
111	30	5.764		5.712
220	10	3.520		3.504
311	40	2.9995		2.986
222	80	2.8733		2.859
400	100	2.4859		2.474
224	5	2.0316		2.021
511	20	1.9148		1.909
440	80	1.7584		1.754
531	5	1.6800		1.679
260	-	--		1.569
622	20	1.4990		1.496
444	--	--		1.434
711	--	--		1.392
264	--	--		1.326
Extrapolated ⁶		$a_0 = 9.932 \pm 0.007 \text{ Å}$		$a_0 = 9.933 \pm 0.014 \text{ Å}$
Literature ⁵		-		$a_0 = 9.93 \pm 0.01 \text{ Å}$

<u>Lattice Parameters</u>		
<u>Reactants</u>	<u>Products</u>	<u>a₀(Å)</u>
2Al+S	Al+ δ Al_2S_3	9.971 ± 0.007
4Al+2 α Al_2S_3	Al+ δ Al_2S_3	9.979
α Al_2S_3	δ Al_2S_3	9.946
2Al+3S	δ Al_2S_3	9.938

TABLE 8
STRUCTURAL FEATURES OF TERNARY GROUP IV ELEMENT ANALOGS

<u>Binary Analog</u>	<u>Ternary Analog</u>	<u>Ternary Compound Structure</u>
MgP ₂	MgGeP ₂	Zinc Blende
BeN ₂	BeSiN ₂	Wurtzite
Al ₂ O	Al ₂ CO	Wurtzite

TABLE 9
REACTION CONDITIONS AND RESULTS OF SYNTHESSES IN THE
Al-Si-S SYSTEM AT 30 KILOBARS
(REACTANTS*: 2Al+Si+S)

<u>Temperature</u> °C	<u>Time</u> min	<u>Product Characterization</u>
490	10	X-ray Diffraction Identified Al, Si and δ Al ₂ S ₃ for all products. Metallic, x-ray Analyses showed a eutectic structure and discrete light grey and dark grey phases for all products.
800	10	
1100	10	
1300	10	
1300	30	
1360	60	

*High purity elemental reactants were mixed in the indicated molar amounts

TABLE 10
REACTION CONDITIONS FOR SYNTHESIS
IN THE Ga-S AND Ga-Se SYSTEMS

<u>Reactants</u> *	<u>Temperature</u> °C	<u>Pressure</u> kilobars	<u>Time</u> min	<u>Remarks</u>
Ga_2S_3	800	30	10	Increase in relative amount of GaS over Ga_2S_3
Ga_2S_3	1200	30	10	No change
Ga_2S_3	1200	50	10	Increase in relative amount of GaS over Ga_2S_3
$\text{Ga}_2\text{S}_3 + \text{Ga}$	1200	50	10	Complete conversion to GaS
Ga_2Se_3	800	30	10	No change
Ga_2Se_3	1200	30	10	No change
$\text{Ga}_2\text{Se}_3 + \text{Ga}$	1200	50	10	Complete conversion to GaSe

*High purity reactant powders were mixed in the indicated molar amounts. The Ga_2S_3 contained an identifiable amount of hexagonal GaS; no identifiable impurity phases were found in Ga_2Se_3 .

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13. ABSTRACT		
Part I- In support of research being conducted by the Properties and Phenomena Branch, Solid State Science Laboratory, Air Force Cambridge Research Laboratory, a service effort is being conducted by ManLabs, Inc., that is directed toward the characterization of specified physical, chemical and structural properties of submitted specimens. Experimental methods include chemical analysis, reflection electron diffraction, X-ray diffraction and fluorescence analysis, light microscopy and electron probe microanalysis, in addition to the determination of specific properties, such as density, hardness and thermal conductivity. Special services such as crystal orientation, cutting, grinding and polishing, are also being performed. Specific materials submitted for characterization include spinel, cobalt, silicide, lithium germanate, silicon, mercury sulfide, cadmium sulfide, silicon carbide, quartz, ruby, calcite, magnesium oxide, cesium copper chloride, gallium arsenide, boron, potassium tantalum niobate, alundum, yttrium-iron garnet, yttrium-aluminum gasket, germanium and lithium niobate. In addition, a variety of specimens have been submitted for specific studies such as phase identification, crystallinity and chemical analysis. Part II- High pressure experiments were carried out on Al-S and Al-Se alloys to produce tetrahedral, unsymmetrical Group IV analogs, as suggested by Compton and Hall¹. Two new compounds, $\delta\text{Al}_2\text{S}_3$ and $\delta\text{Al}_2\text{Se}_3$, were synthesized at pressures of 7 to 50 Kb at temperatures of 800^o to 875^oC. Both compounds have the cubic defect spinel structure of $\alpha\text{Al}_2\text{O}_3$. The synthesis experiments have pointed out the presence of tetrahedral-to-octahedral coordination densification transformations which compete with the high pressure synthesis of new tetrahedral Group IV analog compounds.		

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