435
2-15-78
LA-7072-MS

Informal Report

LA. 1842
UC-4, UC-25

Issued: January 1978

Preparation of Synthetic Standard Minerals

C. C. Herrick
S. J. Bustamante
R. W. Charles
R. E. Cowan
E. A. Hakkila
D. E. Hull
B. W. Olinger
R. B. Roof
H. Sheinberg
G. C. Herrick*

MASTER

*Short-term summer employee. Montana State University, Bozemann, MT 59715.

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87545

An Affirmative Action/Equal Opportunity Employer

UNITED STATES
DEPARTMENT OF ENERGY
CONTRACT W-7405-ENG. 36

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

CONTENTS

I. Introduction and Summary	1
II. Background	3
III. Experimental Techniques	3
IV. Experimental Apparatus	5
V. Experimental Procedures	15
VI. Mineral Characterization	18
VII. Experimental Results	21
VIII. Discussion	33
IX. Conclusions	33
References	34
Appendix A	37
Appendix B	43
Appendix C	47

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

PREPARATION OF SYNTHETIC STANDARD MINERALS

by

C. C. Herrick, S. J. Bustamante, R. W. Charles, R. E. Cowan,
E. A. Hakkila, D. E. Hull, B. W. Olinger, R. B. Roof,
H. Sheinberg, and G. C. Herrick

ABSTRACT

A number of techniques for synthetic mineral preparations have been examined. These techniques include hot-pressing in graphite dies at moderate pressures, high-pressure, high-temperature synthesis in a piston and cylinder apparatus, isostatic pressing under helium gas pressures, hydrous mineral preparations using water as the pressure medium, explosion-generated shock waves, and radio-frequency heating. Minerals suitable for equation-of-state studies (three-inch, high-density discs), for thermodynamic property determinations (low-density powders) and for microprobe standards (fusion-cast microbeads) have been prepared. Mechanical stress-strain calculations in the piston-cylinder apparatus have been initiated and their integration with thermal stress calculations is currently under investigation.

I. INTRODUCTION AND SUMMARY

The purpose of LASL's synthetic minerals program is to prepare pure, or at least well-characterized, minerals which can be used as standards for physiochemical measurements throughout the scientific community. This program has received support from LASL's New Research Initiatives Program, from the Division of Physical Research and from LASL programmatic activities.

The role of minerals in the development of many branches of physics and chemistry is well known, and their importance in technology and in the national economy widely appreciated. Although this program is drawn up in a developmental framework rather than in terms of specific applications, the chemical principles that pertain in preparing and characterizing the minerals, the types of physiochemical data for which they are needed, and the chemical, mechanical, and mathematical approaches that apply for accomplishing either task are largely the same.

The need for synthetic minerals originated with ERDA's responsibility in the areas of energy, mineral resources, and geodynamics. In each of these areas, practical difficulties appear because the number of materials and their

combinations is so vast it is impractical to make detailed measurements on all of them. Models, based on a relatively few "key measurements" of pure minerals, must be developed that can be used for predictions. Such models will require accurate experimental mineral data from at least two aspects. First, the data form the basis on which models are constructed; second, the data are necessary to test the validity of the assumed model.

Procedures for pure, fully reacted, surface-active mineral precursors have been developed. They are (1) a multiple calcining technique starting with weighable raw materials, (2) a sol-gel procedure using soluble nitrates with silicon tetrachloride, and (3) the combining of organometallic materials.

Apparatuses have been constructed and/or modified for experimental and fabrication purposes. These include (1) a Boyd-England piston and cylinder assembly for high-pressure, high-temperature mineral experiments, (2) a complete hydrothermal laboratory for hydrous mineral preparations, (3) special graphite dies tailored to specific mineral fabrication, and (4) innovative radio-frequency induction heating experiments for unconventional mineral experiments and production.

Three-inch discs (three each) of yttr garnet, spinel, and forsterite have been prepared for equation-of-state studies.

One-and-a-quarter-inch discs, used to obtain preliminary data for the three-inch discs, of periclase, quartz, and troilite have been fabricated. Preliminary results on wollastonite, enstatite, fluorriebeckite, fluortremolite, and anorthite have been obtained.

Anorthite and fluoreckermannite were prepared in pyrographite crucibles using radio-frequency heating. Other fluoramphibole experimental preparations, following suggestions found in the literature, were unsuccessful. A sealed platinum capsule technique was developed and used for fluoramphibole preparations.

A simple pipe bomb was used effectively to prepare a high-sulfur-bearing mineral.

Skull melting techniques are underdevelopment and these results are given in Los Alamos Scientific Laboratory report LA-7080-MS.

The plasma torch was used to melt small particles of forsterite and anorthite. Glass and crystalline microspheres for microprobe standards were manufactured. An analytical analysis of the spectral lines suggests a plasma temperature of 12 500°C. Recognition of such a high temperature has forced caution on the utility of this device for silicate compounds.

Alcalite, a zeolite-like material, was easily prepared starting with a gel. Additional zeolite preparations used reactive gels and organometallics.

Preparations of ferrous iron-bearing minerals have yet to be achieved. Special iron-plated dies have been constructed, and special procedures for precursor preparation are expected to aid in this problem.

A hydrothermal laboratory was constructed. The hydrous mineral richterite has been prepared, and experiments with pargasite, hastingsite, and holmquistite are under way.

Mineral preparations in the hot isostatic presses will require extensive modifications of the installed apparatuses and many preliminary experiments.

The use of shock waves as a mineral preparation technique has been attempted.

Analytical investigations of the mechanical stresses in both homogeneous and heterogeneous die assemblies have been fruitful although much remains to be done. Analysis of the equally important thermal stresses is a more difficult problem. Further probing of this problem will depend on the need for preparing large samples. The latter need will depend on the applicability of an oxide

calorimeter now under construction and the demand for mechanical properties of rocks and minerals.

II. BACKGROUND

A. Energy

In the recent past, numerous ideas have been advanced to moderate a predicted energy shortage. One idea is to extract heat from the earth's interior as conceived in the LASL hot dry rock program.¹ This approach uses water to extract heat at depth from 200 to 300°C granite. In such an underground situation, it is practically impossible to obtain all relevant information. Laboratory experiments on pure minerals are essential for interpretation of observations and guidance in exploration. In particular, thermodynamic data on minerals are needed to assess the reactions which result when a rock reacts with water. One of the objectives of the synthetic minerals program is to supply pure minerals for thermodynamic experiments.

B. Mineral Resources

Metal availability is also of concern in the U. S.² Future needs will require exploiting deposits considered uneconomical today. Solution mining has the potential, both in primary and secondary processing for beneficiation of low-grade materials to ores of economic value. Development of solution mining techniques will require far more knowledge of the basic chemical reactions of minerals than is currently available. Preparation of selected pure minerals constitutes the first step in determining the feasibility of solution mining techniques.

C. Geodynamics

Recent advances in shock-wave experiments suggest an approach that will permit simultaneous measurement of both longitudinal and bulk wave velocities and subsequent determination of the transverse velocity as shear moduli. By careful examination of the derived shear moduli at high pressure, various mantle candidates should be distinguishable. To test the validity of this approach, discs (75 to 130 mm in diameter) of pure, randomly oriented, very fine grained, isotropic, high-density minerals must be provided.

III. EXPERIMENTAL TECHNIQUES

A. Polycrystalline Techniques

1. Sintering. Sintering is the conventional method used to fabricate mixed oxides (minerals) with specific geometries. The term "sintering" refers to the process by which powders are consolidated into strong, dense, polycrystalline aggregates. The agglomeration is accompanied by a decrease in porosity and an increase in strength and density. Numerous studies have been made to provide understanding of these processes. A majority, however, are primarily concerned with empirically determining conditions for preparation of a useful product. The remaining studies have been made on model systems, generally simple metallic spheres, with the aim of understanding the elementary steps in the sintering process. The intention of these latter studies is to identify mechanisms by which atom movements occur and what effects the experimental parameters have on their rate of occurrence.

Since the early twenties surface tension^{3,4} has been accepted as the driving force in the sintering process, i.e., as the surface area decreases so must

the surface free energy and therefore the total free energy of the system. Such a process is analogous to formation of sedimentary and metamorphic rocks except time is measured in minutes or hours rather than centuries or aeons.

The lowest temperature at which sintering is detectable was investigated by Tammann.⁵ The ratio on the absolute temperature scale of this temperature to the temperature at which the material melts is referred to as the Tammann ratio. For many oxides the Tammann ratio is approximately one-half. With proper technique materials can be sintered to nearly theoretical density, in the absence of a liquid phase, at temperatures approximately two-thirds of their melting points.

Should a monolayer of eutectic liquid between multiple phases develop on one of the phases, "activated sintering" occurs. Presumably, the eutectic liquid provides a medium in which diffusion occurs more readily than it does across grain boundaries.

If more than a monolayer of liquid phase is formed, but not a sufficient quantity to separate the dominant phase particles during heating, the process is termed "liquid recrystallization sintering." With increasing amounts of the liquid phase (15 to 30 per cent by volume) densification is primarily the result of particle rearrangement. For still greater liquid contents, i.e., 30 to 50 per cent by volume, particles of the solid phase are separated by liquid during the firing process and no sintering is necessary for complete densification. This is the traditional method by which porcelains, electrical insulators, etc., are produced.

2. Hot-Pressing. Temperatures at which maximum densification is achieved are lowered by the application of pressure. This simultaneous application of temperature and pressure, hereafter termed "hot-pressing," is currently one of our principal methods of mineral fabrication.

3. Calcination. Before a material is hot-pressed, a heating or roasting operation, commonly called calcination, is employed to furnish improved raw materials in precursor form. Calcination is the most important operation in the preparation of synthetic minerals. For example, by heating at a suitable temperature, magnesite is converted to periclase ($\text{MgCO}_3 = \text{MgO} + \text{CO}_2\uparrow$) or a mixture of nitrates is converted to a mixture of oxides. Akin to calcining is the procedure of dissolving "old" $\text{Al}(\text{OH})_3$ and reprecipitating it as "fresh" $\text{Al}(\text{OH})_3$ in preparing gels for zeolite preparations.

4. Fusion - Casting. Fusion-casting is an important process in mineral synthesis. Electric arcs, induction heating, and resistance heating are used to prepare precursors, generally glasses, amenable to hot-pressing or conventional heat treating techniques.

B. Single-Crystal Techniques

Although single crystals are of secondary importance in the initial stages of this program, their value in many physical chemistry experiments cannot be overemphasized. Crystals have been grown from the vapor phase either by condensation or chemical reaction, by precipitation from aqueous or non-aqueous solutions, by pulling from a melt, by flame-fusion, and by application of very high pressure.

IV. EXPERIMENTAL APPARATUS

A. Conventional Presses

Considerable equipment is required for preparing polycrystalline synthetic minerals. With the equipment on hand for this program six fabrication processes are currently available. They are:

1. Ambient isostatic or die pressing;
2. Hot-pressing in graphite, carbide, or metal dies;
3. Hot isostatic pressing;
4. High-energy-rate forming at ambient temperature;
5. Explosive-pressing at ambient temperature;
6. Fusion-casting.

A list of the equipment necessary to implement these fabrication processes is given in Table I.

The ambient isostatic press is used to compact stoichiometric oxide material prior to calcining. Although the mechanism is abstruse the results with many materials are excellent.

Graphite dies are commonly employed in the hot pressing process. They are preferred to carbide or metal dies primarily because of cost and fabrication time. Their principal disadvantages are lack of strength and reactivity with the sample. A graphite die designed for 1-inch discs is detailed in Fig. 1 and an enlarged version, for the 3-in.-diam discs, is illustrated in Fig. 2. The internal surfaces of the graphite cylinder and punches are coated with a graphitic mold release and polished. Energy is supplied with an induction coil coupled to a 75-kW motor generator. Figure 3 is a schematic of the loaded assembly as positioned in an induction-heated hot press.

Experiments in the hot isostatic press require careful planning and execution. Each mineral precursor is individually sealed in a platinum capsule using an electron beam welder. Failure to provide total isolation of the sample will result in irreparable damage to the press components. Location of the samples, thermocouples, insulation, and baffles all affect the temperature gradients within the apparatus, and consequently, they affect the experimental results. Even the choice of pressure medium, helium or argon gas, has an observable effect. Nevertheless, the potential to prepare multiple small samples of pure minerals is sufficient incentive to continuously upgrade the equipment.

B. High-Temperature, High-Pressure Device

1. Single-Stage Piston and Cylinder. Boyd and England⁶ perfected a 1/2-in.-diam, single-stage piston and cylinder apparatus. Sketches for a 3/4-in.-diam, single-stage assembly were provided by H. Yoder, Jr.⁷ From these sketches, and with the help of people from the Geophysical Laboratory, a 3/4-in. single-stage piston and cylinder apparatus was designed (Figs. 4 and 5).

The entire assembly is locked in place with a 500-ton Rogers press (Fig. 6). An advancing carbide piston in the bore of a carbide cylinder compresses a sample furnace cell. The bore contains a lead-foil-covered talc sleeve that surrounds a sleeve of pyrex; the latter encloses a graphite sleeve. Inside the graphite are a ceramic (Alsimag 222) sleeve, the platinum sample holder, ceramic plugs, and the thermocouple. The latter is encased in a crushable ceramic

TABLE I
LIST OF EQUIPMENT

1. Isostatic and Die Pressing at Ambient Temperature
 - a. Isostatic presses (50 000 psi)
 - 4 in. by 12 in.
 - 12 in. by 24 in.
 - b. Hydraulic presses
 - 100 to 5000 tons capacity, pressures up to 2830 tons per square inch
 - 1.5-in.-diameter samples
 - c. Harwood Bridgeman apparatus
 - 200 000 psi on 1.25-in.-diameter samples
2. Hot-Pressing
 - a. Conventional presses
 - 20, 30, 100 and 400 tons capacity, 2250 tsi at 2400°C
 - b. Atmosphere or vacuum presses
 - 19 tons capacity, max. pressure 200 000 psi at 2700°C
 - 20 tons, 22000 psi at 1400°C
 - c. Hot-press
 - 200 tons capacity, max. pressure 220 000 psi
 - d. Harwood Bridgeman apparatus
 - 200 000 psi on 1.25-in.-diameter samples at 600°C
3. Hot Isostatic Pressing
 - a. 15 000 psi, 1600°C, 3 in. by 12 in.
 - b. 30 000 psi, 1600°C, 1.5 in. by 6 in.
4. High-Energy-Rate Forming
 - a. Vertical and horizontal Dynapak, 584 kilojoules
5. Explosive Pressing in Metal Dies
6. Belt Machine
7. Cubic Anvils

tube. A conical base plug of stainless steel (A.I.S.I. M-2) and a pyrophyllite insulator complete the experiment setup.

The talc sleeve transmits pressure to the sample. The graphite tube acts as a resistance heater and the crushable ceramic tube prevents extrusion of the thermocouple leads adjoining the platinum sample holder by swaging them into their original position.

a. Cylinder Design. As deduced from the principles of interference support, design of the single-stage cylinder requires that the tungsten carbide core be supported around its circumference by laminated steel rings. Following the sketches of Boyd and England, the design was modified to the extent that a tapered shim is wrapped around the core and both the core and shim are forced into the innermost of two hardened steel rings that have previously been pressed

Fig. 2. Three-inch high-pressure graphite die assembly.

Fig. 3. Graphite die assembly.

Fig. 4. High-pressure, high-temperature apparatus with 3/4-in. bore.

Fig. 5. Cavity assembly for 3/4-in.-bore apparatus.

Fig. 6. Experimental setup for 3/4-in.-bore piston-cylinder.

TABLE II
RESULTS OF FINITE ELEMENT CALCULATION

Gauge No.	Location (in.)	Strain (μm) ^a		
		Experiment	Computed	Difference
1	3.0	204	204	0
2	1.5	78	64	14
3	3.0	209	204	5
4	4.5	165	167	-2
5	1.125	35	32	3
6	2.250	152	142	10
7	3.0	212	204	8
8	3.750	210	215	-5
9	4.875	119	126	-7

^a24 950 psi load.

Miller, and Anderson,¹⁰ is sufficiently encouraging to warrant further investigation of the method. To this end a copy of the SAP-IV finite element code¹¹ has been obtained. This latter code is reputed to be more powerful than the TSAAS program of Browning et al., and if confirmed, will be employed for analysis of the Boyd-England assembly.

c. Applications. Although the single-stage piston and cylinder device was constructed primarily for the preparation of synthetic minerals, its utility is not confined to this task. With pressures up to 50 kbar and temperatures approaching 2000°C. synthetic chemical systems analogous to mineral systems anticipated deep in the Earth's crust can be studied.

PRELIMINARY

Fig. 7. Stress pattern in cylinder assembly at room temperature.

Fig. 8. Strain gauge placement on Bustamante and Sheinberg experiment.

Fig. 9. Cross section of six-anvil clamp intensifier.

Special applications of the single-stage apparatus have been made to studies of differential thermal analysis and to the measurement of nuclear magnetic resonance.¹² It has also been applied to DTA determinations of fast reactions and melting phenomena.¹³

Of particular interest is the comparison of measured to computed stresses. If a model can be developed that will accurately predict the mechanical and thermal stress patterns throughout the entire assembly, a realistic estimate of the funding necessary to operate LASL's 5 000-ton press for confining pressure experiments can be determined.

2. Cubic Press. A cubic press was located and moved in from an outlying site. A cross-sectional view of the six-anvil clamp intensifier compressing a sample is seen in Fig. 9. The original intent was to employ this apparatus for mineral preparation in the 50-to 100-kbar range.

Conversations with P. Bell at the Geophysical Laboratory have suggested using the cubic press as a back-up to the piston-cylinder device. The 100-kbar pressure limit given in the literature has been found to be optimistic. Values of about 70 kbar are more realistic and these pressures are similar to those anticipated from an improved version of the 3/4-in. piston and cylinder assembly using a WC(13% Co) cylinder and a WC(3% Co) piston. Because little, if any, pressure advantage is obtained with the cubic press, and because only milligram quantities can be synthesized, the cubic press will only be used if the piston-cylinder device is found lacking.

C. Fusion-Casting

Fusion-casting is an important industrial process for producing refractory materials. The chemical stability of the products is attributed to large crystal size, tight crystal bonding, interlocking crystals, high density, low permeability, and minimum porosity.

The properties of fused-cast materials can be varied by controlling factors such as composition, dissolved gases, degree of superheat, and rate of cooling.

Commercial fused-cast materials are melted in an electric arc furnace. The method is desirable because it permits materials to melt without container contamination. For the stoichiometric powder agglomerates required in this program, conventional arc melting is not practical. A tri-arc melter, designed by T. Reed at Lincoln Laboratories,¹⁴ has been constructed and awaits testing.

Closed and open crucibles of platinum, gold, iron, tantalum, graphite, boron nitride and glassy carbon have been used with either resistance or induction heating.

Fig. 10. Cage melter.

Cage Melting. Experiments with a "cage" furnace began at Los Alamos nearly a decade ago but were not considered for synthetic minerals until initial experiments using tungsten, molybdenum, tantalum, and boron nitride crucibles were found unsatisfactory for the fusion-casting technique.

Wenckus et al.¹⁵ developed a cage (skull) furnace for melting kilogram lots of ZrO_2 at temperatures up to $3000^\circ C$ in air. The method uses direct high-frequency induction heating of refractory materials contained inside a water-cooled cage. The stable melt is retained in a sintered shell (or skull) of its own composition. Fig. 10 shows the cage furnace constructed for the synthetic mineral project.

The technique assumes molten oxides are sufficiently conductive to couple with a radio-frequency field. This assumption is valid for alumina as illustrated in Fig. 11. Melting is initiated by RF coupling to metal chips embedded in the powder and is sustained by coupling with the molten mass. Kilogram lots of pure zirconia have been prepared by Wenckus for the Air Force Cambridge Research Laboratory with frequencies in the 3-7 megahertz range and power levels below 20 kW. The applicability of the technique has been confirmed at LASL and is the subject of a separate report.

D. Plasma Torch

A plasma torch is used to prepare microbeads. Figure 12 is a photograph of the plasma torch. A spectral analysis¹⁶ suggests a torch temperature of 12 500 K. In the version illustrated, approximately ten inches of helium plasma constitute the heating zone.

Fig. 11. Temperature dependence of electrical conductivity of Al_2O_3 .

assembly is pressed into a larger steel cylinder and placed atop a stack of flat steel plates. Both the outside cylinder and plates act as momentum carriers when the assembly is impacted by an explosion-driven steel plate. Samples subjected to pressures as high as 500 kbar can be recovered. Maximum temperatures attained during these experiments depend on the sample porosity.

A second technique utilizes sheet explosive wrapped around a steel jacket enclosing the material of interest. This assembly is embedded in a thick-walled steel cylinder and all voids filled with mercury. The last step is necessary to provide maximum coupling between the shock wave and the material under

Fig. 12. Plasma torch.

E. Explosive Synthesis

Shock compression of materials is of interest not only in the identification of new structures but also as a technique for mineral preparation.

Two basic techniques are currently available for mineral synthesis. The first involves placing a thin disc of material in a thick-walled steel cylinder and sealing the whole with a close-fitting steel rod. The latter is held in place with a pin. This starting

Fig. 13. Hydrothermal laboratory layout.

zeolites. Large (two-gallon capacity) surplus bombs have been received and are available for low-pressure (3000-psi), low-temperature (300°C) large quantity preparations.

Simple pipe bombs were fabricated from mild steel, gold plated, and sealed with platinum O-rings. Their principal utility is to prepare sulfur-bearing minerals.

investigation. A detonation wave initiated on the top of the explosive-cylinder assembly transverses the total sample length. Although the convergent pressures attained in this setup are less than those obtained in the first technique, the amount of material recovered is considerably greater.

F. Hydrothermal Bombs

An extensive hydrothermal laboratory now under construction is illustrated in Fig. 13. The apparatuses necessary for small quantity preparations of hydrous materials, 250-300 mg, are listed in Table III.

G. Miscellaneous Devices

Supplementary small general-purpose bombs (71-ml capacity, maximum pressures up to 10 000 psi, and upper temperature limit of 600°C) have been gold plated and used for investigating

TABLE III
APPARATUS IN HYDROTHERMAL LABORATORY

Vessel	Pressure (max) (psi)	Temperature (°C)	Medium	Remark
Rene 41, rod 12 in. by 1-1/4 in.	100 000	750	H ₂ O	partially completed
Rene 41, rod 12 in. by 1-1/4 in.	60 000	750	H ₂ O	initiated
Rene 41, tipping rod 24 in. by 1-1/4 in.	60 000	750	H ₂ O	initiated
Stellite 25, rod 12 in. by 1-1/4 in.	30 000	800	H ₂ O	complete
Stellite 25, rod 12 in. by 1-1/4 in.	30 000	800	CH ₄	complete

V. EXPERIMENTAL PROCEDURES

A. Raw Material Procurement

A major effort has been the procurement of raw materials suitable for mineral synthesis. The intent is to locate sources of materials that have a purity of at least 99.9 per cent, have a high surface activity, and are available at reasonable cost. Attempts to locate sources of pure simple compounds such as calcium, magnesium, aluminum or iron silicates, or sodium and potassium disilicates were unsuccessful and have been abandoned.

Sources of silica are (1) a fumed colloidal silica with an enormous surface area, (2) lumps of Brazilian quartz, (3) silicon tetrachloride, and (4) tetraethoxysilane.

Linde A, a polishing compound is the current choice for alumina; it is readily available in uniform particle sizes. Analytical reagent aluminum nitrate is used in sol-gel preparations.

Hydroxides, carbonates, or oxalates of magnesium, calcium, sodium, potassium, and lithium have been analyzed. Analytical grades of the above nitrates and oxides of magnesium and calcium have been purchased.

Other materials of interest, viz. iron, manganese, zinc, and chromium, have been obtained as oxides and nitrates. An effort to procure organometallic precursor raw materials has been made. Some methoxides, acetylacetonates and alcoholates have been purchased.

A thorough incoming inspection and inventory system has been initiated. Emission spectroscopy, chemical analysis, x-ray diffraction, and loss-on-ignition analysis are performed on all raw materials. Some raw materials were subjected to neutron activation analysis to test the potential of this analytical technique. The results (Table IV) were both satisfactory and quick.

B. Compound Preparation

The initial step in synthetic mineral preparation is obtaining a precursor of the desired stoichiometry from pure raw materials. If proper techniques are employed the resulting product is a fully reacted, single-phase material with the chemical purity of the starting materials and of sufficient surface activity to be amenable to hot-pressing.

In some cases, the starting materials are so finely divided that special procedures must be developed to handle them. In other cases, particularly with ferrous minerals, coarse particles, such as metallic iron, are added. Metal powders are rarely pure and their surface contamination increases with decreasing particle size. Coarse particles are prone to segregate from liquid slurries during the drying procedure. To overcome this purity-versus-size problem, a gel process has been developed for the initial blending step. The starting ingredients are combined with water, forming a slurry to which a deflocculating agent is added. This mixture is stirred in a household blender to promote homogenization and, following this blending operation, is quickly gelled by the addition of a polymeric gelling agent. The gel is dried in a vacuum oven. This procedure has proved successful in a number of preparations.

In many preparations, in particular the iron-bearing minerals, formation of an intimate mixture with a high surface activity does not occur following gel drying. Choosing a calcining temperature low enough to retain a high surface activity and high enough to ensure complete reaction is a time-consuming task. Furthermore, optimum temperatures may vary not only with each compound but with

TABLE IV
NEUTRON ACTIVATION ANALYSIS

Element	Compound					
	<u>SiO₂</u>	<u>CaO</u>	<u>MgO</u>	<u>K₂CO₃</u>	<u>Na₂CO₃</u>	<u>Al₂O₃</u>
Na	20 ± 3	< 10	92 ± 9	170 ± 12	M [*]	< 35
K	150 ± 18	8 ± 3	18 ± 4	M	- ^{**}	0.44 ± 0.22
Rb	< 20	< 20	< 20	< 20	< 20	< 20
Cs	< 2	< 2	< 2	< 2	< 2	< 2
Mg	2400 ± 200	< 120	M	< 60	< 4300	< 1100
Ca	50 ± 25	M	180 ± 50	< 10	< 1100	-
Sr	28 ± 4	180 ± 20	< 25	22 ± 10	210 ± 90	< 70
Ba	150 ± 30	< 4	16 ± 8	< 2	< 2	40 ± 20
Sc	0.62 ± 0.06	0.004 ± 0.001	0.008 ± 0.001	0.0004 ± 0.0001	0.039 ± 0.004	0.006 ± 0.001
Ti	50 ± 7	< 60	98 ± 10	< 9	< 200	-
V	2.8 ± 0.2	< 0.2	0.18 ± 0.07	< 0.04	< 0.6	-
Cr	6.2 ± 0.9	0.88 ± 0.13	2.0 ± 0.4	0.16 ± 0.05	0.08 ± 0.01	< 0.2
Mn	3.9 ± 0.2	2.0 ± 0.2	2.2 ± 0.6	0.4 ± 0.1	1.2	< 1.1
Fe	88 ± 10	< 14	36 ± 8	3.9 ± 0.9	14 ± 4	76 ± 9
Co	0.41 ± 0.07	0.56 ± 0.10	0.76 ± 0.12	0.38 ± 0.10	2.14 ± 0.6	0.44 ± 0.03
Ni	< 20	< 20	< 20	< 20	< 20	< 20
Cu	< 1.3	< 2.4	< 3.1	< 0.7	< 14	-
Zn	3.3 ± 1.2	2.7 ± 0.9	6.0 ± 2.1	0.62 ± 0.15	0.99 ± 0.16	2.2 ± 0.8
La	30 ± 3	0.13 ± 0.02	0.010 ± 0.003	-	-	0.009 ± 0.001

* Matrix element.

** Not reported due to interference from another element.

each combination of starting ingredients. Establishment of optimum calcining temperatures is aided by x-ray diffraction and "BET" surface area measurements. Fortunately, hot-pressing is a fairly forgiving process and maximal surface area is not always needed. In experiments to date, maximizing the extent of reaction was preferred to maximizing the surface area. This became apparent in trials in which non-homogeneous precursors inevitably yielded secondary phases.

It is our intent to avoid a grinding or ball-milling operation, where possible, following calcining, thereby eliminating an additional source of impurities. This can be accomplished using a multiple calcining method. In this technique, the precursor is isostatically pressed before calcining and jet milled afterwards. These steps are repeated as required, with periodic x-ray and surface area measurements, until a fully reacted material with a surface area greater than a square meter per gram is obtained. A flow diagram of the method is illustrated in Fig. 14. Although successful, this technique requires weeks or months of unexciting effort.

C. Sol-Gel Method

A sol-gel technique drastically reduces the number of calcining steps but is limited to gram-size rather than kilogram-size batches.

The sol-gel technique for silicates employs carefully standardized aqueous solutions of metal nitrates and silicon tetrachloride or other soluble materials.

Table V lists the source of the various oxides. Solutions of nitrates are prepared from metal carbonates by dropwise addition of nitric acid to the cooled salt.

The chosen concentrations of the individual solutions are governed by the solubility of the nitrate salt and factors peculiar to the particular investigation. Procedures for standardization of the solutions of the starting materials are suggested by Luth.¹⁷

SiO₂. React an aliquot of SiCl₄ with water, dry, ignite, and weigh.

CaO, MgO. Prepare nitrate solution from reagent grade carbonates by dissolving in nitric acid. Precipitate calcium oxalate in a suitable aliquot and ignite to CaO. Precipitate magnesium as ammonium phosphate and ignite to Mg₂P₂O₇.

Al₂O₃. Evaporate an aliquot of aqueous solution to dryness, ignite, and weigh.

K₂O, Na₂O. Carefully dry and weigh reagent grade carbonates, dissolve in nitric acid, and dilute to volume.

Preparation of mineral precursors requires combining calculated volumes of the standardized solutions in polyethylene containers. The requisite amount of silica is added to the aqueous mixture as silicon tetrachloride or the alcoholate. Depending on the composition of the mixture, a gel will form within a few hours on a steam bath. After the gel has formed, the drying process is completed with an infrared lamp. The powder is transferred to a crucible and ignited to decompose the nitrates. Grinding for two to four hours in an automated agate mortar and pestle under a water-free organic solvent completes the initial preparation prior to calcining the mixture of precursors.

TABLE V

SOURCE OF OXIDES FOR SOL-GELS

Oxide	Starting Material
SiO ₂	SiCl ₄ , fumed SiO ₂
Al ₂ O ₃	Al(NO ₃) ₃ · 9H ₂ O
CaO	CaCO ₃
MgO	MgCO ₃ or Mg metal
K ₂ O	K ₂ CO ₃ or KOH
Na ₂ O	Na ₂ CO ₃ or NaOH

VI. MINERAL CHARACTERIZATION

This program requires precise characterization of all initial, intermediate, and product materials. Our discussion is restricted to techniques currently employed in the synthetic minerals program.

A. Electron Microprobe

A finely focused, high-energy electron beam (5 to 25 kV) irradiates the sample, and x rays characteristic of the elements present are produced. Because wave length is characteristic of the element and intensity is related to the concentration, both qualitative and quantitative determinations can be made. All elements of nuclear charge greater than five (boron) are detectable with the 0.1- to 1- μ m-diam beam. Homogeneity of minerals can be determined with a precision of approximately one per cent when dealing with concentrations of one per cent or

Fig. 14. Multiple calcining method.

greater. There will be some variation about these numbers with the particular element and its matrix. Trace impurities generally have detection limits in the 100- to 1000-ppm range, again varying slightly with element and matrix. Quantitative analysis with this popular tool requires suitable standards. If proper standards are available, analyses with precisions of one to five per cent are routine.

B. Ion Microprobe

A monoenergetic primary ion beam on striking a sample surface produces secondary ions that are monitored with a mass spectrometer. The mass:charge

ratio identifies the isotope present and the secondary ion beam intensities measure its relative amount. All isotopes, including hydrogen, can be identified in the parts-per-million to parts-per-billion range using a primary beam of 2-to 500- μ m diameter. Some variation in detectability occurs with element and matrix changes. The price one pays for this increased sensitivity is the necessity of metallographic or petrographic preparation of the sample. Although the technique is extremely sensitive to contamination, satisfactory surfaces are prepared in situ by ion cleaning. Ion sputtering also provides the analyst with a means to explore samples in depth as well as on the surface. Neither the precision nor the accuracy is currently known. The technique is destructive but this aspect is mitigated by the smallness of sample required. Caution should be used in sputter-etching processes unless an independent method of determining the instantaneous depth is available to gauge the sputtering rate of individual species.

C. Neutron Activation

A sample is subjected to neutron bombardment, and the energies and intensities of induced gamma rays are measured. This method is extremely sensitive for many elements, with detection limits of a few nanograms for a 100-mg sample. Quantitative analyses are performed for several elements simultaneously with routine accuracies of 90% or better. This is probably the most sensitive, rapid analytical tool available for many trace elements. The method is non-destructive, however, the induced radioactivity may make the sample unacceptable for other applications. The following elements have been measured quantitatively in NBS-SRM-1633 (fly ash) with good precision and accuracy. Na, Mg, Al, Cl, K, Ca, Se, Ti, V, Cr, Mn, Fe, Cu, Zn, Ga, As, Br, Sr, Sb, Cs, Ba, La, W and U. Others, except carbon and lead, can be obtained with prompt neutron counting, i.e., simultaneous measurement during the bombardment process.

D. Atomic Absorption

A sample is dissolved and aspirated into a flame, from which absorption lines characteristic of a selected element are optically monitored. The method is generally not suitable for qualitative analysis. Quantitatively only one element at a time is determined but a number of elements can be sequentially analyzed from the same sample. This quantitative technique is very rapid and provides good accuracy with a precision of one per cent or better for concentrations in excess of a hundred parts per million. Sensitivity varies from the parts-per-billion to parts-per-million range depending on the element and its environment. The method is destructive; however, only a few milligrams of sample are needed for major constituents such as silicon. Flames and procedures have been developed for some sixty elements in a variety of matrices.

E. X-ray Fluorescence

Characteristic x rays, produced when a sample is irradiated with a high-energy (5-to 100-kV) photon beam, are measured. The wavelength of the induced x ray is characteristic of the element, and its intensity is related to the amount present. The technique will detect all elements of nuclear charge twenty-two (titanium) or greater. Recent instrument modifications permit extension of the method to elements with nuclear charges as low as sodium. Wavelength dispersive systems can do quantitative analysis with a precision of one per cent for major constituents and identify amounts greater than one microgram

for many elements following separation from the matrix. Attachment of energy dispersive systems enables quantitative analyses with a precision of one to five per cent for major constituents. As many as twelve elements can be simultaneously determined. Following development of software programs, this method should be applicable to mineral analysis, measuring all major constituents simultaneously with precisions approaching one per cent on a relative scale and detecting contaminants to limits approaching one hundred parts per million without special sample preparation.

F. Auger - ESCA

When the sample is irradiated with a monoenergetic electron beam and the emitted secondary electrons are monitored, the method is termed Auger Electron Spectroscopy (AES). Either technique is sensitive to the top few monolayers of surface, and less than a tenth of an atomic layer, or approximately 10^{-16} grams, is detectable. Bulk detection limits are in the half-to-ten per cent range, depending on the elements present. In the Auger mode, a fine (2- to 3- μ m) beam is used; in the ESCA mode the beam diameter is approximately 2 mm. These are highly sophisticated techniques requiring tedious sample preparation. The capability of differentiating between oxidation states in a particular element is, however, attractive. This apparatus has recently been installed at LASL.

G. Emission Spectroscopy

This old reliable method is routinely and constantly used. The sample is vaporized in an arc or spark discharge, and the wavelengths and intensities of emitted lines are measured and compared to previously determined standards. Most elements are detected, with limits for silicate systems varying from one to a thousand parts per million. With separations, detection limits can be improved into the parts per billion range (Table VI). Rapid quantitative analyses are made with a precision of ten to fifty per cent using visual or photometering to analyze the photographic film. The method is destructive but requires only milligram amounts of sample.

H. Thermogravimetric Analysis

A sample is heated at a controlled rate while its total weight loss is simultaneously and continuously monitored. This technique measures quantitatively the evaluation of H_2O , CO_2 , and/or other volatiles. A precision ranging from a tenth to one per cent has been found on runs with hydrates and carbonates. Because gas evolution is irreversible the method is destructive.

I. Wet Chemistry

Using classical gravimetric or volumetric methods, major constituents can be determined with a precision of a tenth of a per cent. The methods are generally slow, costly, require skilled analysts, and use grams of materials for optimum precision. These are the best and most reliable techniques for major constituent determinations and will be used before final certification of any standard mineral.

TABLE VI
SPECTROCHEMICAL ANALYSES

Element	Spinel	Yttrogarnet
Li	< 10	< 10
Be	< 1	< 3
B	300	200
Na	100	80
Mg	major	300
Al	major	major
Si	300	4000
P	< 300	-
K	< 100	< 200
Ca	50	300
Ti	< 10	60
V	< 10	< 10
Cr	3	10
Mn	< 3	6
Fe	30	< 200
Ce	< 3	< 10
Ni	10	< 10
Cu	15	20
Zn	< 30	< 100
Ga	5	< 10
Ge	< 10	< 30
Rb	-	< 100
Sr	1	4
Y	-	major
Zr	< 30	30
Nb	< 100	< 100
Mo	< 3	< 30
Ag	< 1	< 3
Cd	< 5	< 10
In	< 10	< 30
Sn	< 10	< 10
Sb	< 10	< 30
Ba	10	100
Ta	400	-
W	< 100	< 300
Tl	< 30	< 100
Pb	< 10	< 10
Bi	< 10	< 10

VII. EXPERIMENTAL RESULTS

A. Forsterite

The mineral forsterite (Mg_2SiO_4) was chosen as an appropriate starting

place. The mineral has utility as a standard for microprobe studies, in equation-of-state studies, and as an insulator in high-temperature micro-circuits.

The initial starting materials were colloidal silica and magnesium carbonate or magnesium oxide. A water slurry was prepared, dried, and calcined loose in a platinum crucible. An appropriate particle size distribution for hot-pressing, obtained by jet milling, is shown in Fig. 15 along with those used for mullite and wollastonite. The pressing parameters (time, temperature, and pressure) for forsterite can be seen in Fig. 16 for densifying a 3-in.-diam disc. Large inclusions were found in the final product prepared in this straightforward manner.

The procedure evolved to minimize sample inhomogeneity in forsterite was the multiple calcining method described previously and shown in Fig. 14. Both the extent of reaction and surface area were monitored as functions of temperature and calcining time. The extent of reaction was crudely determined by comparing the forsterite $hkl301$ reflection with the 200 reflection of

Fig. 15. Hot-pressing parameters for Forsterite.

Fig. 16. Hot-pressing parameters for forsterite.

periclase. A Quantasorb Surface Area apparatus, using a multi-point BET technique, measured the surface activity. Results of the extent-of-reaction and surface-activity monitoring experiments are given in Fig. 17. The periclase content and surface activity both decrease with increasing calcining temperature and number of cycles. Jet milling, in which collisions between streams of the precursor materials occur, enhances the surface activity without contaminating the product. Surface area results are also plotted in Fig. 17 as computed particle size. The relation employed was

$$d = 6/\rho s,$$

where

d = equivalent particle diameter in μm

ρ = material density in g/cm^3

s = specific surface area in m^2/g

It follows from Fig. 17 that a suitable precursor for hot-pressing forsterite requires repeated successive cold-pressing (30 000 psi), calcining ($> 1000^\circ\text{C}$), and jet milling. These operations are repeated three times in current forsterite preparations.

In the final product, microprobe analysis showed inhomogeneity only in the grain boundaries. Figure 18 shows microprobe analysis across a grain boundary. The intensities of the K_α x-ray lines for magnesium, silicon, and iron were measured at 2- μm intervals across the grain boundary, relative to the intensities of a Cal Tech forsterite standard. The forsterite standard has the composition 40.85% SiO_2 , 51.36% MgO , and 7.1% FeO . From this analysis the grain boundary phase is richer in silicon and poorer in magnesium than is the matrix. The boundaries are too narrow to identify the precipitate as SiO_2 .

Three 3-in.-diam discs are necessary for each experimental point in equation-of-state studies. Consequently, simultaneous pressing of three 3-in.-diam discs, separated by graphite spacers, is currently under review.

Small lots (1-2 g) can be successfully fusion-cast in pyrocarbon crucibles with induction heating. Fusion-casting of a kilogram lot in a conventional graphite crucible was unsuccessful. A crucible reaction and subsequent vaporization of magnesium metal occurred. X-ray analyses on forsterite lots, fusion-cast in pyrocarbon or glassy carbon crucibles, were performed. The x-ray diffraction powder pattern was taken with CuK_α radiation in a standard 114.6-mm powder camera. Forsterite is orthorhombic, space group pnma ; its structure is well known.¹⁸ From measurements on the powder film, corrected for film shrinkage, the lattice constants were refined by least squares techniques¹⁹ utilizing 313 lines, including the $K_{\alpha 1}$ - $K_{\alpha 2}$ splitting, to yield the following lattice constants:

Fig. 17. Extent of reaction and surface area with temperature.

$$a_o = 10.1974 \pm 7 \text{ \AA},$$

$$b_o = 5.9814 \pm 5 \text{ \AA}, \text{ and}$$

$$c_o = 4.7546 \pm 4 \text{ \AA}.$$

The values for K_{α_1} and K_{α_2} were taken as $1.54050 \text{ \AA}$ and $1.54434 \text{ \AA}$, respectively.

Table VII is a comparison lattice constants from this work with recent literature results.

Appendix A contains the observed and computed d spacings, their relative intensities, and assigned indices. The listed d spacings in the back-reflection region are the averages determined by comparing observed and measured K_{α_1} and K_{α_1} reflections. Neither thermal nor absorption corrections were applied to

Fig. 18. Ion spectroscopy of 3-in.-diam forsterite disc.

calculated relative intensities. The x-ray precession photographs of a single crystal of synthetic forsterite are also shown in Appendix A.

Forsterite as a Microprobe

Standard. Strong opinions have been expressed as to the best approach for microprobe standards. One school of investigators wants "exact copy" standards for specific mineral assemblages. To satisfy this demand, e.g., in the case of gallium containing minerals, would require an infinite variety of standards. Consequently, this approach was considered impractical. Chodas²⁵ suggests investigators use the Bence-Albee method based on pure oxides, simple silicates, or aluminates. Thus he suggests albite ($\text{Na}_2\text{Si}_2\text{O}_5$) for a sodium standard, wollastonite (CaSiO_3) for calcium and microcline ($\text{K}_2\text{Si}_2\text{O}_5$)

for potassium. Our approach is to consider those oxides, silicates, or aluminates which are compatible with the plasma torch. By placing emphasis on the most common elements, garnet and spinel structures can be utilized.

Figure 19 is a photograph of beads produced by passing 0.5-mm sintered forsterite particles through the plasma torch shown in Fig. 12. A majority of the beads are crystalline; the remainder are glass. With increasing purity of the sintered product the percentage of glass beads is increased. An electron microprobe investigation found aluminium and calcium in the grain boundaries of the crystalline beads. A similar analysis of the glass spheres did not detect these impurities. When the beads were subjected to ion microprobe analysis, Na, Al, K, and Ca were detected in the glass spheres but at significantly lower concentrations than found in a crystalline bead. The concentrations of Al, Na, and Ca in

TABLE VII

COMPARISON OF CELL CONSTANTS FOR FORSTERITE

Reference	a_o (Å)	b_o (Å)	c_o (Å)
This work	10.1974 ± 7	5.9814 ± 5	4.7546 ± 4
Yoder and Sahoma ²⁰	10.195 ± 5	5.9810 ± 10	4.7560 ± 5
Smyth and Hazen ²¹	10.207	5.980	4.756
Warner and Luth ²²	10.1984 ± 10	5.9821 ± 6	4.7547 ± 5
Fisher and Medaris ²³ (high pressure)	10.196 ± 2	5.979 ± 1	4.752 ± 1
Birle, Gibbs, ²⁴ Moore, and Smith (natural material)	10.225	5.994	4.762

Fig. 19. Forsterite microprobe beads.

at 12 500 K. Stoichiometry of three lots of beads, two glass and one crystalline, was determined by wet-chemical analysis. The results are presented in Table VIII. The agreement with theory (19.96 % Si and 34.56 % Mg) is satisfactory. Sufficient forsterite experience is now on hand to produce forsterite microprobe standards.

Scanning differential calorimetry up to 700°C was done on the three lots of beads before they were analyzed. Transformation from the glass to crystalline form did not occur.

B. Spinel

Because spinel (MgAl_2O_4) has many uses as a ceramic material at LASL it was the second synthetic mineral prepared. Previous experience with spinel preparation was used in its fabrication, with additional purity requirements imposed by the mineral program. Spinel was hot-pressed in the conventional manner and slices from a 3-in.-diam disc were examined using a microprobe. Large inclusions, sometimes as large as 40 to 50 μm in diameter, were present in the sample. The distributions of magnesium and aluminum throughout a particular inclusion are shown in Fig. 20. Predominantly MgO with little, if any, Al_2O_3 was found in the inclusions.

TABLE VIII

ANALYSES OF FORSTERITE BEADS

<u>Sample No.</u>	<u>Form</u>	<u>% Si</u>	<u>% Mg</u>
1	Glass	19.9	33.7
2	Glass	20.0	33.7
3	Crystalline	19.5	34.9

the glassy product were estimated to be in the 100 to 500 ppm range; that of potassium was estimated to be about 10 ppm. Whereas the impurities were concentrated in the crystalline spheres they appear to be random in the glass. Presumably, the lower impurity level enhances the formation of glass beads. The surfaces of the crystalline beads were less smooth than those of the glass beads. This minute difference in surface roughness permits the glass beads to roll slightly faster on a vibrating table than their crystalline counterparts and therefore provides a means of separation.

Volatilization of silica from the forsterite particles during passage through the plasma is a real possibility

Fig. 20. Ion probe of spinel inclusion.

Fig. 21. Ion probe of garnet inclusion.

C. Yttrogarnet

In yttrogarnet ($Y_3Al_5O_{12}$) small round inclusions generally less than 20 μm in diameter were present in the final product. The distributions of aluminum, yttrium, and silicon throughout a typical inclusion are shown in Fig. 21. Mainly Al_2O_3 with little, if any, yttrium or silicon was identified. Trace amounts of silicon, estimated to

be less than 1000 ppm, are distributed heterogeneously in the yttrogarnet phase. The silicon peak at 24 μm is approximately 1% of the intensity observed from SiO_2 and the peak at 47 μm has an intensity 5 to 10% that attributed to pure SiO_2 .

D. Diopside

When diopside ($CaMgSi_2O_6$) is prepared by fusion melting in a platinum crucible and then heat treated to induce crystallization, a crucible-contaminated product results. Isostatic pressing at 1300° and 16 000 psi produced a low-density product. When a tantalum container was used in the hot isostatic press, substantial crucible reaction occurred. Hot-pressing in a graphite die produced the two-phase precipitate shown in the photomicrograph in Fig. 22A.

Distributions of magnesium, calcium and silicon through a band of the precipitate containing only the dark phase are illustrated in Fig. 23B. This dark phase contains a higher calcium but lower silicon and magnesium content than the

Fig. 22A. Photomicrograph showing locations of one-dimensional analyses through precipitate in sample.

Fig. 22B. Distributions of Ca, Mg, and Si along scan B, Fig. 22A.

Fig. 22C. Distributions of Ca, Mg, and Si along scan A, Fig. 22A.

diopside matrix. Distributions of magnesium, calcium, and silicon through an area containing both light and dark areas (Fig. 22C) indicates the lighter phase, in the center, to be higher in magnesium and lower in calcium than either the darker phase or the diopside matrix. Based upon the diopside matrix containing 55.6% SiO_2 , the silicon content of the precipitates corresponds to the crysolite members, montreillite (CaMgSiO_4) and forsterite (Mg_2SiO_4).

Pure synthetic diopside was made by fusion-casting in a glassy carbon crucible. An x-ray diffraction powder pattern from recrystallized glass was obtained using $\text{CuK}\alpha$ radiation and a 114.6-mm powder camera. Diopside has the monoclinic space group C2/c as shown by Clark et al.²⁶ and Cameron et al.²⁷ From measurements on shrinkage-corrected film, followed by regression analysis using 83 lines, the following lattice constants were computed.

$$\begin{aligned} a_0 &= 9.7469 \pm 33 \text{ \AA}, \\ b_0 &= 8.9299 \pm 28 \text{ \AA}, \\ c_0 &= 5.2490 \pm 15 \text{ \AA}, \text{ and} \\ \beta &= 105.86^\circ \pm 0.02. \end{aligned}$$

Lattice constant comparisons of our results with previous investigations are given in Table IX.

Appendix B lists the observed and computed d spacings, relative intensities and assigned indices. Neither thermal nor absorption corrections were applied to the computed relative intensities.

Appendix B also shows precession photographs of single crystal diopside retrieved from the recrystallized glass.

E. Quartz

Quality Brazilian quartz was finely ground (iron mortar and pestle), leached with hydrochloric acid, and mixed with lithium fluoride (15 wt.%). Lithium fluoride was added as a flux for two reasons: (1) it has the capability to dissolve quartz, thereby producing a liquid layer on the surface of the particles; and (2) at high temperatures it volatilizes from the mixture during sintering. The highest density obtained using LiF as a fugative flux was seventy per cent relative to that computed from an x-ray analysis.

A striking difference was observed when water was used as a fluxing agent with colloidal silica. Hot-pressing the resulting silicic acid can lead to high-density discs of glass partially crystallized quartz, completely crystallized quartz or cristobalite depending on the pressing parameters (time, temperature, and pressure) chosen.

Hot-pressing fumed silica without a fluxing agent produced α -cristobalite. The product had a measured density of 2.14 g/cm^3 and crumbled when handled.

F. Fayalite

Fayalite (FeSiO_3) with no free iron is in demand for microprobe standards, equation-of-state studies, and as a source of fixed oxygen pressure in mineral synthesis.

A mixture of iron, hematite (Fe_2O_3), and silica was prepared using the gelling technique. The dried mix was calcined at 1000°C in an armco iron crucible for three days in a vacuum furnace. X-ray analysis of the sintered material showed high fluorescence indicating substantial amounts of free iron. Attempts to fusion-cast either the calcined or uncalcined mixture were unsuccessful. The casting experiments in both vacuum and helium environments were conducted using induction coupling to an armco iron crucible. Varying the heating rate or the soak time at 1400°C was not helpful.

TABLE IX
COMPARISON OF CELL CONSTANTS FOR DIOPSIDE

<u>Reference</u>	<u>a_o (Å)</u>	<u>b_o (Å)</u>	<u>c_o (Å)</u>	<u>β°</u>
This work	9.7469 ± 33	8.9299 ± 28	5.2490 ± 15	105.86 ± 0.02
Cameron, Sneno, ²⁷ Prewitt, Papike	9.746 ± 4	8.899 ± 5	5.251 ± 6	105.63 ± 0.06
Rutstein and Yund ²⁸	9.752 ± 2	8.926 ± 2	5.248 ± 2	105.83
Warner and Luth ²⁹	9.7506 ± 8	8.9294 ± 7	5.2518 ± 4	105.898 ± 0.003
Clark, Appleman ²⁶ and Papike	9.748	8.924	5.251	105.79

A second preparation looks very promising. Iron powder was fired in hydrogen at 700°C overnight. The freshly fired powder was intimately mixed with Fe_2O_3 and the mixture was slowly heated to 1000°C for twelve hours. X-ray analysis confirmed the sintered product as wustite (FeO). The product was jet-milled and blended with fumed silica in water. Roasting for four hours at 1100°C yielded a precursor material in which only fayalite x-ray lines were identifiable.

Graphite dies react with fayalite. Isolation of fayalite from the graphite is provided by plating iron on the inner circumference of the cylinder from an iron fluoroborate solution. The high-density graphite punches were not amenable to iron plating. Pure iron discs (.010-in. thick) are used between the sample and the punches. The lack of metal adherence to the punches suggested the iron coating of the graphite cylinder is mechanical rather than chemical. Because iron builds up on the axial portions of the cylinder, undercutting of the cylinder is necessary.

G. Hedenbergite

Attempts to prepare hedenbergite ($\text{CaFeSi}_2\text{O}_6$) or its stoichiometric glass from iron powder and hematite were also unsuccessful. During these melting trials some material vaporized from the mix and condensed on the cold concentrator. X-ray diffraction showed the water-soluble condensate to be sodium hydroxide. An organic-soluble material also effused from the crucible; it was assumed to be a decomposition product of the gelling agent.

Experiments are now in progress employing wustite as the precursor and the special iron-plated die constructed for the fayalite experiments.

H. Anorthite

Small lots of anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) were prepared using the metal nitrates-silicon tetrachloride technique. Care must be exercised in decomposing the nitrates to avoid spattering. The decomposed gel was fusion-cast in glassy carbon and pyrographite crucibles. The x-ray pattern contained only anorthite lines. Microprobe analysis of the precursor glass confirmed the material to be homogeneous within the capability of the instrument.

Fusion-casting and hot-pressing of anorthite prepared by conventional mixing of the powders produced a heterogeneous melt and a disc of poor crystalline quality with intermediate products.

I. Enstatite

In an attempt to prepare enstatite (MgSiO_3) calcining the precursor material at 1400°C for four hours in a platinum crucible yielded a sintered material consisting of 20-30% clinoenstatite and the remainder protoenstatite. Hot-pressing experiments are in progress.

J. Wollastonite

Commercial wollastonite (CaSiO_3) powder hot-pressed easily. Calcined pure precursor (pseudo-wollastonite) produced a low-density disc when the pressing parameters obtained from commercial powder runs were used.

K. Periclase

In attempts to prepare periclase (MgO) hot-pressing pure MgO or calcined MgCO_3 gave a low-density product. Magnesium hydroxide, prepared by refluxing MgO with water for twenty-four hours and pressing at 1240°C and 8000 psi, converted to periclase with a density 97.5% of theoretical.

L. Troilite

Hot-pressing a stoichiometric mixture of iron (hydrogen-reduced) and sulfur failed to produce troilite (FeS). Calcining isostatically pressed iron and sulfur in sealed quartz ampules was not successful. The ampules burst during the week-long heat treatment at 700°C . A gold-plated simple pipe bomb sealed with platinum O-rings and containing the stoichiometric mixture in a quartz boat yielded x-ray pure troilite after heating for a week at 700°C . When the calcined product was ground in a carbide mortar and pestle, hot-pressing was not successful. After switching to an iron mortar and pestle, hot-pressing was successful.

M. Amphiboles

A number of experiments to prepare the amphiboles listed in Table X have been performed.

In preparing amphiboles, either fluors or hydrous, care must be taken to avoid loss of the volatile components SiF_4 or H_2O . For these preparations the following starting materials were used:

1. calcium--freshly roasted (1000°C) CaO , or wollastonite,
2. silica--small particle SiO_2 obtained by drying silicic acid prepared by reacting water with colloidal silica,
3. alkali elements - disilicates prepared in the manner suggested by Schairer and Bowen,³⁰
4. magnesium--analytical grade MgF_2 ,
5. fluorine air-dried NaF or MgF_2 .

The stoichiometric amounts of the above starting materials were ground together, under petroleum ether, in an automated agate mortar and pestle and stored in sealed vessels or in a drying oven at 110°C .

Our initial experiments consisted of melting each fluoramphibole mixture in a graphite, pyrographite, or glassy carbon crucible. Only covered pyrographite crucibles withstood the melting (1400°C) and heat treatment (1000°C) processes. Fluoreckermannite was the only successful preparation, i.e., no loss of SiF_4 occurred. Previous investigators³⁴ have prepared fluortremolite and fluorendenite by this simple melting technique. They used large charges (30 cm^3) in a ventilated graphite crucible and a constant cooling rate of 100°C per hour. We, on the other hand, were only successful when the melt was quenched from 1400°C to 1000°C and held at this lower temperature overnight.

Considerable success in preparing fluoramphiboles was achieved by using sealed platinum crucibles. Platinum tubing (1/4-in. o.d., 0.01-in. wall) was cut with a razor blade into 1-in. lengths and annealed at 900°C .

TABLE X
AMPHIBOLES

	<u>A</u>	<u>X</u>	<u>Y</u>	<u>Z</u>	<u>Anions</u>	
Fluoranthophyllite		Mg ₂	Mg ₅	Si ₈	O ₂₂	F ₂
Holmquistite	Li	LiMg	Mg ₃ Al ₂	Si ₈	O ₂₂	(OH) ₂
Fluorcummingtonite		Mg ₂	fe ₅ ^a	Si ₈	O ₂₂	F ₂
Fluortremolite		Ca ₂	Mg ₅	Si ₈	O ₂₂	F ₂
Fluoredenite	Na	Ca ₂	Mg ₅	Si ₇ Al	O ₂₂	F ₂
Fluortschermakite		Ca ₂	Mg ₃ Al ₂	Si ₆ Al ₂	O ₂₂	F ₂
Fluorpargasite	Na	Ca ₂	Mg ₄ Al	Si ₆ Al ₂	O ₂₂	F ₂
Fluorferrohastingsite	Na	Ca ₂	fe ₄ Fe ^a	Si ₆ Al ₂	O ₂₂	F ₂
Fluorglaucophane		Na ₂	Mg ₃ Al ₂	Si ₈	O ₂₂	F ₂
Magnesiohastingsite		Na ₂	Mg ₃ Fe ₂	Si ₈	O ₂₂	(OH) ₂
Fluormagnesiohastingsite		Na ₂	Mg ₃ Fe ₂	Si ₈	O ₂₂	F ₂
Richterrite	Na	NaCa	Mg ₅	Si ₈	O ₂₂	(OH) ₂
Fluorrichterrite	Na	NaCa	Mg ₅	Si ₈	O ₂₂	F ₂
Fluoreckermannite	Na	Na ₂	Mg ₄ Al	Si ₈	O ₂₂	F ₂

^aThe symbol fe is used for divalent iron.

One end is pinched in, either manually or with a three jaw chuck, and the protruding seams fused shut. Approximately 150 mg of the amphibole starting mixture is inserted in the platinum tube and the whole assembly is clamped in a vise to expel occluded air before making the final seal. Fusing the remaining opening gas-tight requires care. Small quantities of powder adhering to the platinum results in a faulty seal. The sealed ampules were heated to 1450, 1400, 1350, or 1300°C for thirty minutes before holding at 1000°C for four hours. A slight weight loss (< 5 mg) was usually observed but in none of the experiments did the capsule burst and the weight loss become catastrophic.

Table XI lists some results obtained using the sealed platinum technique.

The technique is assumed viable. Ten fluoroamphibole mixes have been heated to 110°C under vacuum, pressed into platinum tubing (approximately 1-2 g) and welded shut with an electron beam. An outside contractor will isostatically press the samples to 1460°C under 30 000 psi to insure melting and heat treat the samples at 1000°C under 8000 psi. If, as anticipated, the results are satisfactory, the extensive modifications needed on LASL's hot isostatic press will be undertaken.

Mixtures of SiO₂ (glass), γ - Al₂O₃, MgO, Fe₂O₃, CaO, and the alkali metal disilicates were used to prepare hydroxide amphiboles. Stoichiometric proportions

TABLE XI
RESULTS OF AMPHIBOLE EXPERIMENTS

<u>Amphibole</u>	<u>Yield</u>	<u>Impurity</u>
Fluortremolite #4	95%	diopside
Fluoreckermannite #2	80-85%	unidentified
Fluorrichterite #1	85%	forsterite
Fluormagnesiohastingsite #2	90%	unidentified
Fluorpargastite #1	70%	20% forsterite
Fluoreckermannite #1	~ 100%	gas escapes on opening capsule
Fluoredenite #1	80%	possible diopside and/or forsterite
Fluormagnesiohastingsite #1	50%	unidentified

of the starting materials were sealed in precious metal capsules with an excess of water to ensure $P_{H_2O} = P_{total}$. This excess of water aids the diffusion process and lessens the homogeneity requirements of the starting materials. The sealed starting materials after insertion into rod vessels, are subjected to pressure and temperature. Under these experimental conditions the capsules are considered to be without strength.

For minerals containing elements of variable valence, particularly iron, additional precautions are necessary to define a specific oxidation state. The most popular methods are the use of solid "buffering" assemblages in nested capsules,³¹ hydrogen gas,³² and graphite-methane³³ mixtures to control the fugacity of oxygen and thereby the cation valence.

In this manner richterite was successfully prepared, the preparation of ferrohastingsite was partly successful (66% yield), but poor results were obtained in the riebeckite and holmquistite experiments.

N. Nepheline

Nepheline ($NaAlSi_3O_8$) was prepared as follows. $NaCO_3$, Al_2O_3 , and SiO_2 were sintered together in the proper proportions at a low temperature ($\sim 800^\circ C$). Sintering was repeated several times with intermediate grinding. The sintered product was melted into a glass sphere ($\sim 1300^\circ C$) in a glassy carbon crucible using induction heating. Heat treatment for one week at $1100^\circ C$ yielded nepheline.

O. Zeolites

The zeolites can be defined as hydrated aluminum silicates of the alkali and alkaline earth elements. The simplest zeolite-like mineral to prepare is analcite. It was prepared from a slurry of fused silica and finely divided aluminum hydroxide in sodium hydroxide solution. The reaction at $250^\circ C$ in a gold-plated Paar Bomb (71-ml capacity) was complete within a week and without stringent requirements on the total sodium ion present or temperature.

In our opinion, zeolites and clays constitute the biggest potential chemical problem associated with geothermal energy resources. It is clear from the literature that very little thermodynamic data are available for this class of substances. In numerous experiments other than the analcite preparation,

performed during this investigation the preparation of natural zeolites beginning with pure components (SiO_2 , $\text{Al}(\text{OH})_3$, etc.) is at best difficult. On the other hand, preparation of commercial zeolites is relatively straightforward. Many of the zeolites originally investigated by Milton and his colleagues at Union Carbide³⁵ have been prepared in this investigation.

From this experience we have concluded that synthetic zeolites are probably metastable species. The final product is sensitive to pH, temperature, time, and amount of solvent (water) present.

We are now preparing large batches (30 to 50 grams) of sodium and potassium zeolites for shipment to Argonne National Laboratory and the USGS. These preparations contain secondary zeolite phases but will be extensively characterized and the thermodynamic properties determined calorimetrically. By varying the number of silica molecules and the type and amount of alkali metal attached to a single alumina for a given geometrical configuration,³⁶ an energy contribution can be assigned to each component. The sum of these component parts³⁷ will then be used to extrapolate to the thermodynamic properties of identified natural zeolites.

P. Stishovite

Attempts to prepare this high-density modification of SiO_2 were made using shock waves. Twenty-five grams of the shocked material were carefully dissolved in hydrofluoric acid after the extraneous mercury was leached with nitric acid. The last few undissolved milligrams were subjected to x-ray analysis. No x-ray lines indicating the presence of stishovite were observed. Further experiments using the shock-wave technique are anticipated.

VIII. DISCUSSION

Each mineral has its own peculiar factors of preparation and therefore becomes an experimental or developmental problem. Hot-pressing is the most convenient technique but is highly dependent on time, pressure, temperature, and impurity content. Although the technique is somewhat forgiving with respect to particle size, it is most unforgiving when an inhomogeneous precursor is used.

The sol-gel method eliminated the tedious jet milling necessary when blending powdered oxides but is limited by the solubility of the metal nitrates to small (< 25 g) batches. Substitution of silicon tetrachloride for the more conventional Ludox has so far proved satisfactory.

Sealed platinum capsules are a convenient technique for substituting fluorine atoms for the hydroxyl groupings in amphiboles.

Pressures available in this program are up to 700 000 psi (calculated) in the piston and cylinder apparatus, 7000 psi in large graphite dies, 8000 psi in smaller (1-1/4-in.) graphite dies, 60 000 psi in the hot isostatic press, and in the megabar range using explosive techniques.

IX. CONCLUSIONS

A capability to prepare synthetic mineral standards at Los Alamos Scientific Laboratory has been developed. Although much remains to be done for specific applications the support for this program has provided the opportunity to focus laboratory equipment on an increasingly important field. A number of current LASL projects such as neutron activation analysis, fate of trace elements in coal, determination of geothermal brine compositions, the use of forsterite in high-temperature electronics and shock-wave investigations have received input

from this project. In addition, the utilization of LASL's 5000-ton press, the thermodynamics of minerals, the preparation of samples for mechanical testing, and the burial of radioactive wastes are programs to which LASL's synthetic minerals program can contribute.

REFERENCES

1. A. G. Blair, J. W. Tester, and J. J. Mortensen, "LASL Hot Dry Rock Geothermal Project," Los Alamos Scientific Laboratory report LA-6525-PP. (October 1976).
2. D. A. Brobst and W. P. Pratt, "U. S. Mineral Resources," Geol. Survey Prof. Pop. 820, (1973).
3. R. L. Coble and J. E. Burke, "Sintering in Ceramics," in Progress in Ceramic Science, Vol. B, J. E. Burke, Ed. (Macmillan Pub. Co., New York, 1963) p. 197.
4. J. White, "Basic Phenomena in Sintering," in Science of Ceramics, Vol. 1, G. H. Stewart, Ed. (Academic Press, London and New York, 1962) p. 1.
5. G. Tammann, "Metallography," The Chemical Catalog Co., New York, 1925 translation, p. 26.
6. F. R. Boyd and J. L. England, "Apparatus for Phase-Equilibrium Measurements at Pressures up to 50 Kilobars and Temperatures up to 1750°C," J. Geophysical Research 65, 741-748 (1960).
7. H. S. Yoder, Jr., Geophysical Laboratory, personal communication, October 1975.
8. A. E. Macrae, Overstrain of Metals (His Majesty's Printing Office, London, 1930).
9. S. J. Bustamante and H. Sheinberg, "Determination of Hoop Stresses in a Cylindrical Steel Die By Compacting Metal Powders," Powder Met. 6, 36-51 (1960).
10. R. V. Browning, D. G. Miller, and C. A. Anderson, "TSAAS: Finite Element Thermal and Stress Analysis of Axisymmetric Solids with Orthotropic Temperature-Dependent Material Properties," Los Alamos Scientific Laboratory report LA-5599-MS, 1974.
11. G. C. Herrick, University of California at San Diego, personal communication.
12. G. Kennedy and R. Newton in Solids Under Pressure, W. Paul and D. Warshaw, Eds. (McGraw Hill Book Co., New York, 1963) p. 163.
13. P. M. Bell and J. L. England, "High-Pressure Experimental Techniques," in Researches in Geochemistry, Vol. 2, P. H. Abelson, Ed. (John Wiley and Sons, NY, 1967), p. 619
14. T. B. Read, "Arc Techniques for Material Preparation and Czochralski Crystal Growth," Proc. Third Intern. Symp., Asilomar, California, 1967 (Butterworths, London, 1969) p. 655.

15. J. F. Wenckus, M. L. Cohen, A. G. Emslie, W. P. Wenaski, and P. F. Strong, Air Force Cambridge Research Laboratory report AFCRL-TR-75-0213 (February 1975).
16. T. Bieniewski, Los Alamos Scientific Laboratory, personal communication (February 1977).
17. W. C. Luth and C. O. Ingamells, "Gel Preparation of Starting Materials for Hydrogeothermal Experiments," *Am. Mineral* 50, pp. 255-258, 1965.
18. R. W. G. Wyckoff, *Crystal Structures*, 2nd Ed. (Interscience Publishers, New York, 1968) Vol. 4, p. 160.
19. R. E. Vogel and C. P. Kempter, "A Mathematical Technique for the Precision Determination of Lattice Parameters," *Acta Crystal* 41, pp. 1130-1134 (1961).
20. H. S. Yoder, Jr., and T. G. Sahoma, "Olivine X-ray Determinative Curve," *Am. Mineral* 42, pp. 475-491 (1957).
21. J. R. Smyth and R. M. Hazen, "The Crystal Structures of Forsterite and Hertonolite at Several Temperatures Up to 900°C," *Am. Mineral* 58, pp. 588-593 (1973).
22. R. D. Warner and W. C. Luth, "Two-Phase Data for the Join Monticellite (CaMgSiO_4)-Forsterite (Mg_2SiO_4): Experimental Results and Numerical Analysis," *Am. Mineral* 58, pp. 1009-1015 (1973).
23. G. W. Fisher and L. G. Medaeks, Jr., "Cell Dimensions and X-Ray Determinative Curve for Synthetic Mg-Fe Olivines," *Am. Mineral* 54, pp. 741-753 (1969).
24. J. P. Birtle, G. V. Gibbs, P. B. Moore, and J. V. Smith, "Crystal Structures of Natural Olivines," *Am. Mineral* 53, pp. 807-824 (1968).
25. A. Chodas, Calif. Inst. Tech., private communication (October 1976).
26. J. R. Clark, D. E. Appleman, and J. J. Papike, "Crystal-Chemical Characterization of Clinopyroxenes Based on Eight New Structure Refinements," *Mineral Soc. Amer. Spec. Pap.* 2, pp. 31-50 (1969).
27. M. Cameron, S. Senero, C. T. Prewitt, and J. J. Papike, "High-Temperature Crystal Chemistry of Acmite, Diopside, Hedenbergite, Jadeite, Spodumene and Areyite," *Am. Mineral* 58, pp. 594-618 (1973).
28. M. S. Rutstein and R. A. Yund, "Unit-Cell Parameters of Synthetic Diopside-Hedenbergite Solid Solutions," *Am. Mineral* 54, pp. 238-245 (1969).
29. R. D. Warner and W. C. Luth, "The Diopside-Orthoenstatite Two-Phase Region in the System $\text{Ca MgSi}_2\text{O}_6$ - $\text{Mg}_2\text{Si}_2\text{O}_6$," *Am. Mineral* 59, pp. 98-109 (1974).
30. J. F. Schairer and N. L. Bowen, "The System $\text{K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$," *Am. Jour. Sci.* 253, pp. 681-746 (1955).

31. H. P. Eugster, "Heterogeneous Reactions Involving Oxidation and Reduction at High Pressure and Temperature," J. Chem. Phys. 26, pp. 1760-1761 (1957).
32. H. R. Shaw, "Hydrogen Osmosis in Hydrothermal Experiments," in Researches in Geochemistry, Vol. 2, P. H. Abelson, Ed. (John Wiley and Sons, NY, 1967) pp. 521-541.
33. H. P. Eugster and G. B. Skippin, "Igneous and Metamorphic Reactions Involving Gas Equilibria," in Researches in Geochemistry, Vol. 2, P. H. Abelson, Ed. (John Wiley and Sons, NY, 1967) p. 492.
34. H. R. Shell, J. E. Comefors and W. Eitel, Bur. Mines Rept. p. 5417 (1958).
35. D. W. Breck, Zeolite Molecular Sieves (John Wiley and Sons, NY, 1974).
36. R. M. Barrer and W. Sieber, "Hydrothermal Chemistry of Silicates. Part 21. Zeolites from Reaction of Lithium and Caesium Ions with Tetramethyammonium Aluminosilicate Solutions," J. C. S. Dalton, pp. 1020-1026 (1977).
37. Y. Tardy and R. M. Garrels, "Prediction of Gibbs Energies of Formation of Compounds from the Elements - II. Monovalent and Divalent Metal Silicates," Geochim. et Cosmochim. Acta 41, pp. 87-92 (1977).

APPENDIX A

X-ray precession photographs of
Ultrapure forsterite

Taken with

Mo K_α radiation

From x-ray powder patterns taken with
Cu K_α radiation the lattice constants
of the orthorhombic unit cell were
determined to be

$$a_o = 10.1974 \pm 7$$

$$b_o = 5.9814 \pm 5$$

$$c_o = 4.7546 \pm 4 \text{ \AA.}$$

a) c* axis
b* axis

b) c* axis
110* direction

c) c* axis
a* axis

TABLE A-I

CRYSTAL DATA FOR ULTRAPURE FORSTERITE, Mg_2SiO_4

<u>d_{obs}</u>	Rel. Obs. <u>Int.</u>	<u>d_{calc}</u>	Rel. Calc. <u>Int.</u>	<u>Indices</u>
5.0847	ms-	5.0987	22	200
4.3134	w	4.3093	3	101
3.8783	vvs-	3.8803	69	210
3.7185	ms	3.7220	23	011
3.4822	ms+	{3.4964}	14	111
		{3.4773}	15	201
		{3.0062}	6	211
2.9901	ms-	{2.9907}	18	020
		2.7652	62	301
2.7615	vvs-	2.5100	78	311
2.5101	vvs-	2.4570	100	121
2.4538	vvs	2.3452	12	410
2.3400	ms	2.3153	10	102
2.3117	ms	2.2675	43	221
2.2697	st	2.2468	31	401
2.2453	ms	2.1592	21	112
2.1556	ms	2.0303	5	321
2.0290	w	{1.9481}	3	302
1.9446	wt	{1.9401}	3	420
		1.8743	7	501
1.8733	wt	1.8610	2	022
1.8607	vvwt	1.8308	1	122
1.8309	vvw	1.8095	4	131
1.8072	vvwt	1.7886	4	511
1.7874	vw+	1.7482	69	222
1.7476	vvs+	1.7387	20	402
1.7353	vw+	1.6696	15	412
1.6681	ms-	1.6349	15	610
1.6329	ms-	1.6173	20	331
1.6159	ms	1.6004	1	601
1.5979	vvw	1.5882	4	521
1.5853	vv+	{1.5705}	11	430
1.5682	mv+	{1.5661}	4	103
		{1.5479}	> 1	502
		{1.5460}	> 1	611
1.5490	vvw-	1.5320	2	013
1.5305	vw	{1.5150}	3	113
1.5124	mw	{1.5135}	3	203
		{1.5108}	4	132
		{1.5031}	6	422
1.4937	s	{1.4986}	6	512
		{1.4954}	30	040
1.4756	s	1.4776	43	620
1.4642	vw+	{1.4672}	1	213
		{1.4634}	2	232

TABLE A-I (Cont.)

<u>d_{obs}</u>	Rel. Obs. Int.	<u>d_{calc}</u>	Rel. Calc. Int.	<u>Indices</u>
1.4351	w	{1.4364}	3	303
		{1.4349}	2	240
1.3943	m	{1.3967}	8	313
		{1.3929}	11	701
1.3870	m-	1.3874	8	123
		{1.3504}	22	223
1.3486	ms+	{1.3471}	1	612
		{1.3460}	8	403
1.3134	m-	{1.3153}	10	341
		{1.3132}	5	413
1.2927	w	1.2934	5	630
1.2639	vw	{1.2658}	2	042
		{1.2626}	1	721
1.2554	vw	{1.2561}	2	142
		{1.2550}	1	622
		{1.2481}	2	631
1.2463	vw+	{1.2467}	1	810
		{1.2449}	3	441
		{1.2421}	1	702
1.2415	vw	{1.2401}	3	033
1.2280	vw-	1.2274	2	423
1.2227	vw+	1.2227	4	532
1.2066	vvw-	1.2059	> 1	811
1.1886	w+	1.1887	6	004
1.1868	vvw-	1.1862	1	342
1.1696	vvw	1.1689	3	541
1.1656	mw-	{1.1655}	4	333
		{1.1647}	3	250
1.1616	vvw	1.1601	2	051
1.1542	w-	1.1545	5	523
1.1470	vw	1.1471	3	722
1.1442	vvw-	1.1418	1	731
1.1382	mw-	{1.1385}	3	821
		{1.1379}	4	613
1.1345	mw-	1.1337	6	442
1.1234	w-	1.1234	3	802
1.1157	w-	1.1156	5	433
1.1042	vvw-	1.1041	1	812
1.0975	m-	{1.0982}	3	124
		{1.0979}	6	351
1.0796	w-	1.0796	3	224
1.0721	w	1.0725	4	703
1.0632	w	{1.0637}	3	243
		{1.0628}	2	152
1.0505	vw	1.0505	2	324
1.0337	m	1.0342	11	921

TABLE A-I (Cont.)

<u>d_{obs}</u>	Rel. Obs. <u>Int.</u>	<u>d_{calc}</u>	Rel. Calc. <u>Int.</u>	<u>Indices</u>
1.0187	mw	{1.0194}	> 1	352
		{1.0192}	9	741
1.0115	vw	1.0122	2	514
1.0048	vw	1.0052	2	1010
0.9997	w+	1.0004	5	443
0.9928	w	0.9933	4	803
0.9851	w	0.9855	5	452
		{0.9787}	3	832
0.9776	w+	{0.9784}	1	260
		{0.9783}	3	650
0.9707	w	0.9713	6	161
0.9640	vvw	0.9646	1	931
0.9610	vw	0.9614	2	614
0.9551	vvw	0.9555	1	742
0.9498	vvw	0.9507	1	153
		{0.9468}	1	105
0.9468	w	{0.9466}	2	552
		{0.9459}	1	1021
0.9422	vvw	0.9427	1	823
0.9369	w	0.9372	4	1002
		{0.9352}	3	115
0.9346	w	{0.9348}	1	205
0.9304	w	0.9305	5	044
0.9259	mw-	0.9262	7	624
0.9212	vvw	0.9210	1	704
0.9186	vw	0.9192	3	353
0.9155	vw	0.9158	2	305
0.9127	vvw	0.9130	1	534
		{0.9079}	1	1030
0.9072	vvw	{0.9075}	> 1	751
0.9048	mw-	0.9048	7	262
0.8982	w	0.8982	4	842
0.8976	vvw	0.8975	1	344
0.8941	vvw	0.8942	1	453
0.8915	vvw-	0.8910	> 1	405
		{0.8875}	1	362
0.8872	vvw-	{0.8872}	> 1	941
0.8805	w	0.8808	5	923
		{0.8756}	3	325
0.8755	w	{0.8752}	2	634
0.8734	vw	0.8741	3	444
		{0.8715}	6	743
0.8712	w+	{0.8705}	1	1121
0.8643	vvw	0.8648	1	462
		0.9619}	1	505
0.8617	vvw	{0.8617}	> 1	752
0.8595	mw	0.8599	8	660

TABLE A-I (Cont.)

<u>d_{obs}</u>	<u>Rel. Obs. Int.</u>	<u>d_{calc}</u>	<u>Rel. Calc. Int.</u>	<u>Indices</u>
0.8549	mw	{0.8553}	6	135
		{0.8548}	2	1112
0.8528	w	0.8530	3	515
0.8506	vvw	0.8498	2	1200
0.8485	mw	{0.8489}	6	1013
		{0.8481}	3	1032
		{0.8466}	1	544
0.8463	vvw	{0.8464}	1	235
		{0.8462}	> 1	661
0.8442	vvw	0.8442	1	942
0.8408	w+	{0.8413}	4	1210
		{0.8410}	3	071,163
0.8347	vvw	0.8348	1	824
0.8325	m-	{0.8325}	6	263
		{0.8324}	7	653
0.8280	w+	0.8282	10	525
0.8271	w	0.8274	8	843
0.8220	vvw	0.8243	2	1023
		{0.8174}	2	1220
0.8162	mw	{0.8164}	6	371
		{0.8162}	1	644
0.8122	vvw	0.8125	1	914
		{0.8107}	1	761
0.8101	mw	{0.8106}	2	951
		{0.8102}	5	470
0.8084	vw+	0.8086	4	662
0.8017	w	{0.8016}	2	172
		{0.8011}	4	463
		{0.8002}	1	1103
0.8003	w-	{0.8002}	1	1202
		{0.8000}	3	145
0.7980	vvw	0.7987	1	471
0.7940	m	{0.7943}	3	272
		{0.7941}	12	1042
0.7928	vw	{0.7931}	1	1113
		{0.7931}	1	1212
0.7921	w	{0.7927}	2	245
		{0.7925}	3	1132
0.7901	vw	0.7901	2	106
0.7894	vw	0.7893	3	715
0.7876	mw-	0.7878	7	1033
0.7843	vw+	{0.7846}	2	943
		{0.7842}	3	744
0.7831	w	0.7833	4	116
0.7816	mw	0.7817	11	1230
0.7810	mw-	0.7810	7	345
0.7797	mw-	0.7797	7	563

TABLE A-I (Cont.)

<u>d_{obs}</u>	Rel. Obs. Int.	<u>d_{calc}</u>	Rel. Calc. Int.	<u>Indices</u>
0.7792	mw-	0.7792	8	554
		{0.7775}	3	571
0.7777	mw	{0.7775}	3	762
		{0.7773}	3	1141
0.7764	mw+	0.7764	15	216
0.7760	mw	0.7761	12	1050
0.7747	vw	0.7748	2	861
0.7729	w	0.7730	5	1123,1222

APPENDIX B

X-ray precession photographs of
Ultrapure Diopside

Taken with

MoK_α radiation

From x-ray powder patterns taken with
 CuK_α radiation the lattice constants of
the monoclinic unit cell were determined
to be

$$a_0 = 9.745 \pm 3$$

$$b_0 = 8.923 \pm 3$$

$$c_0 = 5.249 \pm 2 \text{ \AA}$$

$$\beta = 105.86^\circ \pm 0.02$$

b) $\rightarrow c^*$ axis
 $\downarrow hh0^*$ direction

a) $\rightarrow c^*$ axis
 $\downarrow a^*$ axis

c) $\rightarrow c^*$ axis
 $\downarrow b^*$ axis

d)

TABLE B-I

CRYSTAL DATA FOR ULTRAPURE DIOPSIDE, $\text{CaMgSi}_2\text{O}_6$

<u>d_{obs}</u>	Rel. Obs. <u>Int.</u>	<u>d_{calc}</u>	Rel. Calc. <u>Int.</u>	<u>Indices</u>
3.3350	m-	3.3448	10	021,02 $\bar{1}$
3.2313	m	3.2332	25	220
2.9878	vvs	2.9908	100	22 $\bar{1}$
2.9327	ms-	2.9499	27	310
2.8774	ms+	2.8927	37	31 $\bar{1}$
2.5586	m	2.5656	25	13 $\bar{1}$
		{ 2.5246 }	42	002
2.5136	vvs-	{ 2.5180 }	<1	112
		{ 2.5159 }	42	221
2.2969	w+	2.3015	18	311
		{ 2.2145 }	10	112
2.2002	w+	{ 2.2012 }	1	22 $\bar{2}$
		{ 2.1976 }	10	022,02 $\bar{2}$
2.1477	w	2.1554	10	330
2.1236	mw	2.1328	19	33 $\bar{1}$
2.1001	vw+	2.1072	9	42 $\bar{1}$
2.0394	m	2.0418	20	041,04 $\bar{1}$
2.0119	mw	2.0140	12	40 $\bar{2}$
1.9993	w	2.0057	8	202
1.9645	w	1.9686	8	13 $\bar{2}$
1.8550	vvw	1.8598	2	331
		{ 1.8352 }	7	510
1.8289	w	{ 1.8296 }	3	222
1.8085	vvw	1.8130	4	132

TABLE B-I (Cont.)

<u>d_{obs}</u>	Rel. Obs. Int.	<u>d_{calc}</u>	Rel. Calc. Int.	<u>Indices</u>
1.7488	w+	1.7544	15	150
1.7154	vw	1.7191	2	512
1.6706	vw	1.6724	5	042,042
1.6567	vw	1.6574	7	313
1.6218	s+	{1.6249}	15	531
		{1.6235}	18	223
1.5851	vw	1.5866	2	530
1.5631	vw+	1.5626	4	600
1.5488	vw+	1.5506	5	350
		{1.5288}	6	602
1.5245	w	{1.5256}	3	621
		{1.5227}	7	402
1.5033	mw	1.5031	14	133
1.4860	vw	1.4883	5	060
1.4608	vw	1.4617	2	441
1.4437	vw	1.4463	3	622
1.4212	m	1.4225	20	531
1.4069	mw-	{1.4093}	10	352
		{1.4074}	5	152
1.3894	vw	1.3895	5	223
1.3733	vw	{1.3757}	1	711
		{1.3737}	1	243
		{1.3301}	7	712
1.3285	w	{1.3266}	5	621
1.3164	vw-	1.3164	4	533
1.2826	mw-	{1.2828}	4	262
		{1.2821}	7	062,062
		{1.2634}	1	461
1.2629	w	{1.2623}	4	004
1.2467	w	1.2480	9	352
1.1722	vw	1.1720	2	800
1.1473	vw	{1.1473}	1	172
		{1.1471}	4	604
		{1.0757}	6	281
1.0741	mw-	{1.0745}	5	752
		{1.0664}	2	662
1.0665	w-	{1.0658}	5	571
		{1.0654}	1	314
1.0508	vw	1.0512	4	354
1.0395	vw+	{1.0412}	1	315
		{1.0406}	4	533
1.0283	vw	1.0291	3	173
1.0167	vw	1.0156	3	661,931
		{1.0028}	2	404
1.0011	w-	{1.0027}	<1	554
		{1.0021}	2	571
		1.0007	2	154

TABLE B-I (Cont.)

<u>d_{obs}</u>	Rel. Obs. <u>Int.</u>	<u>d_{Calc}</u>	Rel. Calc. <u>Int.</u>	<u>Indices</u>
0.9768	vw+	0.9772	5	135
0.9637	w-	{0.9642}	4	933
		{0.9639}	1	464
0.9225	2-	{0.9224}	6	754
		{0.9216}	1	931
0.9158	w-	{0.9169}	2	752
		{0.9160}	4	225

APPENDIX C

Fig. C1. Plate increment.

Consider the equilibrium of a small element abcd cut out from the plate by the two radial sections OC and OB perpendicular to the plate, and two cylindrical surfaces ad and bc, with radii r and $r + dr$, normal to the plate. The normal stress components in the radial direction are denoted by σ_r and the normal stress component in the tangential direction by σ_θ . For the shearing stress component $\tau_{r\theta}$ is the symbol used. The positive directions of the stress components are indicated in Fig. C1.

Assuming the stresses are uniformly distributed over the sides of a small element, the normal force in the radial direction acting on the side ad of the element is $\sigma_r r d\theta$ (the thickness

of the plate is taken to be unity). The normal force on the side bc of the element, taking into account the variation of the stress component σ_r is

$$\left(\sigma_r + \frac{\partial \sigma_r}{\partial r} dr \right) (r + dr) d\theta.$$

The normal forces acting on the sides ab and cd are $\sigma_\theta dr$ and $\left(\sigma_\theta + \frac{\partial \sigma_\theta}{\partial \theta} d\theta \right) dr$, respectively, giving a resultant in the radial direction equal to $\sigma_\theta dr d\theta$ if a small quantity of a higher order is neglected. The shearing forces acting on the sides ab and cd of the element give a force in the radial direction equal to

$$\frac{\partial \tau_{r\theta}}{\partial \theta} d\theta dr.$$

It is also assumed that a body force R per unit volume is acting in the radial direction. The body force acting on the element abcd is then $R r dr d\theta$. Summing up all forces in the radial direction, we obtain the following equation of equilibrium:

$$\left(\sigma_r + \frac{\partial \sigma_r}{\partial r} dr \right) (r + dr) d\theta - \sigma_r r d\theta - \sigma_\theta dr d\theta + \frac{\partial \tau_{r\theta}}{\partial \theta} dr d\theta + R r dr d\theta = 0.$$

In the same manner the equation of equilibrium of the element in the tangential direction can be written. Neglecting small quantities of higher order and canceling the factor $dr d\theta$, the two equations reduce to

$$\left. \begin{aligned} \sigma_r + \frac{1}{r} \frac{\partial \tau_{r\theta}}{\partial \theta} + \frac{\sigma_r - \sigma_\theta}{r} + R &= 0 \\ \frac{1}{r} \frac{\partial \sigma_\theta}{\partial \theta} + \frac{\partial \tau_{r\theta}}{\partial r} + \frac{2 \tau_{r\theta}}{r} &= 0 \end{aligned} \right\} \quad (1)$$

If there is no body force R , the stress function $\phi(r, \theta)$ * will be used in the solution of Eq. (1); by substitution it can be proved that these equations are satisfied by taking

$$\left. \begin{aligned} \sigma_r &= \frac{1}{r} \frac{\partial \phi}{\partial r} + \frac{1}{r^2} \frac{\partial^2 \phi}{\partial \theta^2} \\ \sigma_\theta &= \frac{\partial^2 \phi}{\partial r^2} \\ \tau_{r\theta} &= \frac{1}{r^2} \frac{\partial \phi}{\partial \theta} - \frac{1}{r} \frac{\partial^2 \phi}{\partial r \partial \theta} = - \frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial \phi}{\partial \theta} \right) \end{aligned} \right\} \quad (2)$$

Any component ϕ , of r and θ , substituted into equation (2), gives stress components satisfying the equations of equilibrium (1), when $R = 0$.

To get a stress distribution in an elastic body, the condition of compatibility must also be satisfied. [The equations derived by application of the equations of statics for absolutely rigid bodies and containing the three stress components σ_r , σ_θ , $\tau_{r\theta}$ are not sufficient for the determination of these components. The problem is a statistically indeterminate one, and in order to obtain the solution the elastic deformation of the body must also be considered.] In the case of cartesian coordinates this condition requires that the stress function satisfy the equation

$$\frac{\partial^4 \phi}{\partial x^4} + 2 \frac{\partial^4 \phi}{\partial x^2 \partial y^2} + \frac{\partial^4 \phi}{\partial y^4} = 0$$

Or on transformation to polar coordinates the relation between polar and cartesian coordinates is given by

$$r^2 = x^2 + y^2 \quad \theta = \arctan \frac{y}{x},$$

which, after some manipulation, give the compatibility equation in polar coordinates;

$$\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} \right) \left(\frac{\partial^2 \phi}{\partial r^2} + \frac{1}{r} \frac{\partial \phi}{\partial r} + \frac{1}{r^2} \frac{\partial^2 \phi}{\partial \theta^2} \right) = 0. \quad (3)$$

If the stress distribution is symmetrical with respect to the axis through O perpendicular to the xy plane (Fig.C1), the stress components do not depend on θ and are functions of r only. From symmetry it follows also that the shearing stress $\tau_{r\theta}$ must vanish. Then only the first of the two equations of equilibrium, Eq. (1) remains and we have

$$\frac{\partial \phi}{\partial r} + \frac{\sigma_r - \sigma_\theta}{r} + R = 0 \quad (4)$$

If the body force R is zero, we may use the stress function ϕ . Because of the symmetry this function depends only on r , and the equation of compatibility Eq. (3) becomes

*This function was introduced in the solution of two-dimensional problems by C. B. Airy, British Assoc. Adv. Sci. Rept., 1962 and is sometimes called the Airy stress function.

$$\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r}\right)\left(\frac{\partial^2 \phi}{\partial r^2} + \frac{1}{r} \frac{\partial \phi}{\partial r}\right) = \frac{\partial^4 \phi}{\partial r^4} + \frac{2}{r} \frac{\partial^3 \phi}{\partial r^3} - \frac{1}{r^2} \frac{\partial^2 \phi}{\partial r^2} + \frac{1}{r^3} \frac{\partial \phi}{\partial r} = 0. \quad (5)$$

This is an ordinary differential equation that can be reduced to a linear differential equation with constant coefficients by introducing a new variable t such that $r = e^t$. In this manner the general solution of Eq. (5) can be obtained. This solution has four constants of integration, which must be determined from the boundary conditions. By substitution it can be checked that

$$\phi = A \log r + Br^2 \log r + Cr^2 + D \quad (6)$$

is the general solution. The corresponding stress components from Eq. (2) are

$$\begin{aligned} \sigma_r &= \frac{1}{r} \frac{\partial \phi}{\partial r} = \frac{A}{r^2} + B(1 + 2 \log r) + 2C \\ \sigma_\theta &= \frac{\partial^2 \phi}{\partial r^2} = -\frac{A}{r^2} + B(3 + 2 \log r) + 2C \\ \tau_{r\theta} &= 0 \end{aligned} \quad (7)$$

If there is a hole at the origin of coordinates the solution may be adapted to represent the stress distribution in a hollow cylinder submitted to uniform pressure on the inner and outer surfaces by taking $B = 0$ (Fig.C2).

Taking B as zero, Eq. (7) becomes

$$\left. \begin{aligned} \sigma_r &= \frac{A}{r^2} + 2C \\ \sigma_\theta &= -\frac{A}{r^2} + 2C \end{aligned} \right\} \quad (8)$$

Fig. C2. Hollow cylinder.

The boundary conditions are:

$$(\sigma_r)_{r=a} = -p_i, \quad (\sigma_r)_{r=b} = -p_o$$

Substituting in the first of Eq. (8), we obtain the following equations to determine A and C :

$$\begin{aligned} \frac{A}{a^2} + 2C &= -p_i \\ \frac{A}{b^2} + 2C &= -p_o \end{aligned}$$

from which

$$A = a^2 b^2 (p_o - p_i) / (b^2 - a^2)$$

and

$$2C = \frac{p_i a^2 - p_o b^2}{b^2 - a^2}$$

Substituting these in Eq. (8) the following expressions for the stress components are obtained as

$$\left. \begin{aligned} \sigma_r &= \frac{a^2 b^2 (p_o - p_i)}{b^2 - a^2} \cdot \frac{1}{r^2} + \frac{p_i a^2 - p_o b^2}{b^2 - a^2} \\ \text{and for the angular direction} \\ \sigma_\theta &= \frac{a^2 b^2 (p_o - p_i)}{b^2 - a^2} \cdot \frac{1}{r^2} + \frac{p_i a^2 - p_o b^2}{b^2 - a^2} \end{aligned} \right\} \quad (9)$$

In the particular case where $p_o = 0$ and the cylinder is submitted to internal pressure only, Eq. (9) gives

$$\left. \begin{aligned} \sigma_r &= \frac{a^2 p_i}{b^2 - a^2} \left(1 - \frac{b^2}{r^2} \right) \\ \sigma_\theta &= \frac{a^2 p_i}{b^2 - a^2} \left(1 + \frac{b^2}{r^2} \right) \end{aligned} \right\} \quad (10)$$

These equations show that σ_r is always a compressive stress and σ_θ a tensile stress. The latter is greatest at the inner surface of the cylinder where

$$(\sigma_\theta)_{\max} = \frac{p_i (a^2 + b^2)}{b^2 - a^2} \quad (11)$$

This quantity, $(\sigma_\theta)_{\max}$ is always numerically greater than the internal pressure p_i and approaches it as b increases, so that it can never be reduced below p_i , however much material is added on the outside.