HYDROTHERMAL GARNET CRYSTALS

FINAL SUMMARY REPORT

December 27, 1966

Contract NONr-4657(00)
ARPA Order No. 306-62, Code 4730

UNION
CARBIDE

UNION CARBIDE CORPORATION
LINDE DIVISION

Contract Nonr-4657(00)
Program Code Number 4730
Authorization ARPA Order 306-62
Task Number NR017-718

HYDROTHERMAL GARNET CRYSTALS

Hydrothermal Crystal Growth of Calcium Aluminosilicate Garnet Containing Divalent Rare Earth Ions

FINAL TECHNICAL SUMMARY REPORT

December 27, 1966

Contract Period: July 16, 1964-July 15, 1965
Contract Cost: $76,140

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This research is part of Project DEFENDER under the joint sponsorship of the Advanced Research Projects Agency, the Office of Naval Research and the Department of Defense.

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ABSTRACT

The aim of this research was the hydrothermal growth of single crystals of grossular garnet, $Ca_3Al_2Si_3O_{12}$, containing divalent activator ions such as Eu, Sm, Gd, Ce and Mn. Such crystals were desired as possible new laser materials with efficient pumping and high fluorescent yield characteristics. Hydrothermal processes were successfully developed for growth of synthetic grossular on seeds and have yielded good quality fully synthetic crystals up to 3 mm x 5 mm x 9 mm. Incorporation of the rare earth ions Eu, Sm and Yb into the lattice under reducing conditions was achieved, but excitation and fluorescence spectra indicated the presence of only trivalent rare earth ions in the grossular crystals.

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FOREWARD

This report constitutes the Final Summary Report on all of the work performed by the Silicate Research Group of the Tonawanda Laboratory under Contract Nonr-4657(00). It also includes some additional work carried out after the close of the contract period with Union Carbide Corporation funds. The program was directed by Miss E. M. Flanigen, the principal investigator, and monitored by Dr. Van O. Nicolai of the Physics Branch of the Office of Naval Research, the Project Scientific Officer. Project scientists were Dr. A. M. Taylor and Mr. N. R. Mumbach who carried out all of the experimental work. Dr. D. W. Breck of Union Carbide Research Institute served as consultant throughout the program. The Final Report was prepared and written by Miss Flanigen.

At the request of Dr. Nicolai the grossular crystals grown under this contract were submitted to Dr. R. C. Ohlmann of Westinghouse Research Laboratories, Pittsburgh, Pennsylvania, for measurement of the excitation and fluorescence spectra under contract with the Office of Naval Research. The results obtained by Dr. Ohlmann are reported in detail in the Final Technical Summary Report for Contract Nonr-4658(00), dated November 15, 1965.

I. SUMMARY AND CONCLUSIONS

Crystals of grossular garnet, $Ca_3Al_2Si_3O_{12}$, containing divalent activator ions such as Eu, Sm, Gd, Ce and Mn, were desired as possible new laser crystals with efficient pumping and high fluorescent yield characteristics. Two successful methods have been developed for the growth of single crystal grossular in hydrothermal systems. Growth on a seed was achieved (1) by ΔT transport from grossular nutrient and (2) by diffusion of oxide components from separate oxide nutrient sources to the grossular seed under ΔT conditions. Optimum growth parameters are: growth temperature = 540-660°C., ΔT = 10-100°C., and mineralizers calcium chloride and ammonium chloride.

Two distinct pressure ranges for growth have been established, low-pressure (~ 500 bars or < 40% fill) in a region of retrograde solubility or negative slope for the solubility-temperature curve, and high-pressure (~ 2000 bars or >60% fill) where normal solubility or a positive slope for the solubility-temperature curve is observed. Linear growth rates averaged from 0.02 to 0.05 mm. per day at low pressures and 0.1 to 0.4 mm. per day at high pressures. Fully synthetic grossular crystals of good quality have been grown in sizes up to 3 mm. x 5 mm. x 9 mm.

The activator ions Eu, Sm and Yb were successfully incorporated into the grossular lattice under reducing conditions at concentration levels of 0.1 to 1 wt. %. Reducing conditions were maintained in the growth system by two techniques. In the first of these the rare earth ion was added as the trivalent chloride combined with Al metal, and in the second the rare earth metal was added to the hydrothermal system. The metal reacts with water to generate a hydrogen over-pressure and to maintain reducing conditions throughout the growth period. Crystals of the gallium analogue of grossular, $Ca_3Ga_2Si_3O_{12}$, doped with Eu and Sm were grown under reducing conditions.

The valency of the dopant activator ion was investigated in a preliminary way in this laboratory. All attempts to establish positive evidence for the presence of divalent activator ions in the doped grossular crystals by qualitative spectroscopic techniques, either absorption or fluorescence in the visible or ultraviolet region, were unsuccessful. In most cases fluorescence typical of the trivalent ions was observed. However, there was indirect evidence for the presence of Eu^{2+} in at least one doped crystal where duplicate analyses showed 0.1 wt. % Eu present but no trace of the bright pink-orange fluorescence observed in Eu^{3+}-doped crystals of grossular at 0.01% concentration. Similarly, a deep pink-red fluorescence observed visually for a 0.1 wt. % Sm-doped grossular crystal indicated the presence of divalent ion, but was not confirmed spectroscopically. Impurities of Fe and Mn incorporated during growth, the presence of trivalent activator ions, or concentration effects, may cause quenching of the fluorescence of the divalent rare earth ion in grossular. Fluorescence characteristics of the gallium analogue of grossular, $Ca_3Ga_2Si_3O_{12}$, containing Eu and Sm appear to be similar to those of grossular. The Yb-doped grossular was royal blue in color and showed no visible fluorescence based on visual observation; no attempt was made to establish the valence state.

After the close of the contract period a more detailed examination of the emission and fluorescence characteristics of several of the Eu and Sm-doped grossular crystals grown under this contract was made by Dr. R. C. Ohlmann of Westinghouse Research Laboratories at the request of

Dr. Nicolai of ONR. Dr. Ohlmann reported that the emisson and fluorescence spectra of the Eu and Sm grossular crystals were characteristic of the trivalent ion. He did not examine the fluorescence spectrum below 4000 Å and therefore would not have detected the presence of Eu^{2+} if it fluoresced in the near-ultraviolet. His data are conflicting in the case of two Sm-doped grossular crystals. He interprets their fluorescence spectrum as that due to Eu^{3+} in one crystal and Sm^{3+} + Eu^{3+} in another, and suggests the crystals were mislabeled with respect to dopant ion. Since the fluorescence spectrum of Eu^{3+} and Sm^{2+} are nearly identical, such a conclusion seems unwarranted unless the chemical identity of the dopant in the crystals is verified by analysis. His results could also be interpreted as Sm^{2+} in one case and a mixture of Sm^{3+} and Sm^{2+} in the other.

Spontaneously nucleated micro-crystals of grossular of high chemical purity and containing Sm and Eu activator ions were grown hydrothermally under reducing conditions to elucidate the effect of foreign ion impurities on fluorescence, but time did not allow any spectroscopic examination of these crystals before the close of the contract period.

Synthetic micro-crystals of the feldspar anorthite, $CaAl_2Si_2O_8$, were grown as by-products in the hydrothrermal grossular process. Incorporation of Eu under reducing conditions yielded a Eu-doped anorthite which showed a strong blue-white fluorescence attributed to Eu^{2+}.

Satisfactory methods for the hydrothermal growth of macro single crystals of grossular and Eu, Sm and Yb-doped grossular have been developed. Control of valency to yield divalent activator ions appears to be difficult but technically feasible with additional research effort.

Incorporation of Mn^{2+} in grossular should offer no technical problems. Continuation of the work seems justified if there is sufficient interest in grossular as a host lattice for laser crystal application.

II. INTRODUCTION

The objective of the contract research program was the hydrothermal growth of macro single crystals of the garnet grossular, $Ca_3Al_2Si_3O_{12}$, containing divalent activator ions such as Eu, Sm, Gd, Ce and Mn. Grossular has a typical garnet structure, is cubic, space group Ia3d, a = 11.874 Å, with 8 formula units in the cubic unit cell. All of the metal ions are in the special positions 16a, 24c, and 24d.[1,2] Each oxygen is at the corner of four polyhedra in 96h, one tetrahedron surrounding the Si^{4+}, one octahedron surrounding the Al^{3+} and two dodecahedra surrounding the Ca^{2+} ions. The many different varieties of garnet are due to the large variety of ions which can occupy these three sites in the garnet structure.[3] The general formula for one unit is written as $A_3B_2C_3O_{12}$ where A represents a dodecahedral ion or a c site, B an octahedral ion or a site, and C a tetrahedral ion or d site. It is easier to consider the A ion as occupying the center of a distorted cube in eight-fold coordination. A model of the framework structure and the coordination polyhedra in grossular is shown in Figure 1.

The dodecahedral A or c sites are the ones of interest for the substitution of divalent rare earth ions and must be considered from the ionic radii point of view. In pyrope garnet, ($Mg_3Al_2Si_3O_{12}$), the Mg-O distances are 2.202 and 2.335 Å.[4] Based on crystal radii, coorected for eight-fold coordination, the expected distance is 2.14 Å. Similarly, in grossular the reported Ca-O distances are 2.33 and 2.49 Å, compared to a calculated distance of 2.49 Å.[2] It is reported that Sr^{2+} (corrected ionic radius = 1.175 Å) occupies c sites but does not fill them. This is based upon results obtained on garnet synthesized at atmospheric pressure. It should be pointed out that under hydrothermal conditions, the formation of a $Sr_3Al_2Si_3O_{12}$ phase may be possible. But the partial substitution for Sr^{2+} (up to 33%) in a synthetic garnet of composition $(SrY_2)(SnFe)Fe_3O_{12}$ strongly suggests that limited substitution of Sr^{2+} for Ca^{2+} to the extent necessary is likely.[5]

The crystal chemistry of the divalent rare earths is similar to that of the alkaline earths. Europium II is much like the alkaline earth ion strontium II.[6,7] This is due to the close correspondence of ionic radii.

Some Ionic Radii

Ion	Ionic Radius, Å
Ca^{++}	0.99
Sr^{++}	1.13
Sm^{++}	1.11
Eu^{++}	1.09
Tm^{++}	0.94
Yb^{++}	0.93
La^{+++}	1.04
Mn^{++}	0.80
Mg^{++}	0.65

Geochemically, europium follows strontium in many minerals and rocks and is concentrated in those which are rich in strontium. Similarly, minerals which contain lead (radiu of lead II is 1.20 Å) contain noteworthy amounts of europium. Strontianite ($SrCO_3$) and pyromorphite [$Pb_5Cl(PO_4)_3$] contain up to 860 g. of europium per ton. It is logical to conclude that a crystal which accommodates strontium II will also accommodate a divalent rare earth. Substitution of the larger gallium or indium ion for Al in silicate garnet should expand the lattice slightly to facilitate substitution of the larger divalent rare earth ion. For example, the silicate garnet, $Ca_3In_2Si_3O_{12}$, synthesized hydrothermally by Mill,[12] has a unit cell size of 12.35 Å compared to 11.87 Å for grossular.

Europium II is the most stable of the divalent lanthanides. It is quite stable in weakly acidic solutions in the absence of atmospheric oxygen or other oxidizing agents. In 6 M hydrochloric acid it oxidizes very slowly in the absence of oxygen by the reaction

$$\text{Eu II} + H^+ \rightarrow \text{Eu III} + 1/2\ H_2$$

This reaction is catalyzed by the presence of platinum black. In the presence of oxygen the fast reaction

$$\text{Eu II} + H^+ + 1/2\ O_2 \rightarrow \text{Eu III} + 1/2\ H_2O$$

occurs.[8] Europium II is prepared from aqueous europium III solutions by reduction with magnesium, aluminum, iron or zinc. The solid divalent halides are usually made by reduction of the anhydrous trihalides by hydrogen. Other compounds, such as $EuCO_3$, can be made by metathetical reactions in aqueous solution.[9] This suggests several ways of producing and maintaining europium II in a hydrothermal medium.

Samarium II is less stable toward oxidation than europium II or ytterbium II. It is a powerful reducing agent and is unstable in aqueous solution. Thulium II is even less stable in water. The ytterbium II ion is also a powerful reducing agent and is oxidized rapidly in aqueous solution. It is more stable than samarium II but considerably less than europium II. A number of compounds have been prepared, however. It is apparent, therefore, that direct substitution of the divalent ion from the hydrothermal medium is more probable with europium II, so initial efforts were confined to this ion. In the case of samarium, ytterbium and thulium, it may be possible to produce the divalent species by a secondary reaction, i.e., substitution of the trivalent ion followed by γ-irradiation.

The garnet spessartine, $Mn_3Al_2Si_3O_{12}$, was reported to have been synthesized by Gorgeu in 1883[10] by the fusion of a mixture of white clay with manganous chloride in water vapor-saturated hydrogen. It has been extensively investigated by others.[1] Mme. Christophe-Michel-Levy[13] reported the hydrothermal synthesis of spessartine and an iron-substituted spessartine, $(Fe, Mn)_3Al_2Si_3O_{12}$, although she was unsuccessful in synthesizing the iron end number in the series, almadine, $Fe_3Al_2Si_3O_{12}$. Coes[14] and Yoder[15] effected the synthesis of almadine hydrothermally. The magnesium garnet pyrope ($Mg_3Al_2Si_3O_{12}$), was synthesized by Coes at 900°C. and 30,000 atm.[14] The hydrothermal synthesis of garnets containing V^{3+}, In^{3+} and Sc^{3+} has been reported by Mill.[12] Laudise and co-workers[16] crystallized yttrium iron garnet and yttrium gallium garnet under hydrothermal conditions and achieved single crystal growth on seeds. Mill[17] also synthesized yttrium iron garnet hydrothermally.

There is an extensive literature on the phase relations of grossular and hydrogrossular.[1] Anhydrous grossular was first synthesized hydrothermally by Yoder[18] in 1954 from a calcium aluminosilicate glass at 800°C. and water vapor pressures as low as 2000 atm. Roy and Roy[11] have reported that essentially pure grossular, a = 11.86 Å, and n = 1.736, or negligible water content, was formed between 550 to 860°C. and 2000 atm. of water vapor pressure. They claim that grossular is the stable phase at least as low as 600°C. and does not require pressure to reach equilibrium. The water pressure is simply the catalyst for formation.[11] They used gels or glasses of the proper composition. No additional base, such as OH^-, was employed.

No previous reports are known of attempted single crystal growth of grossular. Three techniques are commonly used for growing large single crystals of high melting oxides: melt, flux and hydrothermal. Melt pulling or flame fusion methods cannot be readily applied to grossular because of its incongruent melting behavior. Flux techniques, although probably applicable, usually lead to flux inclusions and unsatisfactory optical quality. Hydrothermal growth was chosen for grossular crystals. The disadvantages of slow growth rates and high temperature-high pressure techniques are compensated for by the high degree of crystal perfection achieved. The prior art in hydrothermal crystal growth of large single crystals has been limited for the most part to single component oxide crystals such as silica (quartz), alumina (sapphire, ruby) and zinc oxide. The application of hydrothermal crystal growth to three and four component oxide systems such as doped grossular, presented a difficult technical problem because of the complexity of the phase assemblages. The oxidative instability of divalent rare earth ions in aqueous systems and the large size of the $R.E.^{2+}$ ions (1.1 Å) compared to the Ca^{2+} ion (0.99 Å) also presented formidable problems in doping with the rare earth activator ion.

The two major technical problems to be solved were to first establish conditions for hydrothermal growth of single crystal grossular on a seed, and second, define conditions suitable for doping with divalent rare earth ions. The major portion of the contract period was spent solving the first of these. As a result effort devoted to doping with divalent rare earth ions was limited in scope and not completed under the contract period.

III. EXPERIMENTAL

A. Hydrothermal Equipment

A detailed description of hydrothermal equipment is given by Laudise and Nielson.[19] Hydrothermal vessels or bombs used in this work are shown in Figure 2 and described below.

1. Morey Bomb: A small vessel of 15 to 20 cc capacity with a usable volume 2 cm. I.D. and 5 cm. I.L., sealed by flat plate closure employing a gold or platinum disc gasket 2 to 5 mils thick, constructed of stainless steel, Inconel X or René metal, equipped with noble metal liners of platinum or gold. In a few cases the flat plate closure was backed up with modified Bridgman seal. Maximum operating p,t conditions 500°C., 20,000 psi, or 600°C., 12,000-14,000. Purchased from Tem-Pres, Inc., State College, Pennsylvania.

2. Tapered Lens Ring-Sealed Bomb: Vessel of Linde design and construction, 50-70 cc capacity, usable volume 2 cm. I.D. x 16 cm. I.L., constructed of Incomel X, seal effected by means of tapered lens ring of Incomel X fitted between the taper on the neck of the bomb and a matching taper on the bomb head. The design does not allow for complete noble metal lining but was used in conjunction with a thick walled gold crucible fit inside the bomb and sealed loosely with a screw-on gold cap. Pressure balancing

is achieved by matching the per cent fill inside and outside the crucible. Maximum operating p,t conditions 700°C., 15,000 psi.

3. Microreactors or Test Tube Bombs: Long, narrow vessel, 2.5 cm. O.D. x 23 cm. O.L., 6 cc volume, 6 mm. I.D. x 15 cm. I.L., cone seat type "cold" seal closure, constructed of Stellite, Hastelloy-C, René or Inconel X. Used in conjunction with sealed gold tubes with pressure balancing as above. Maximum operating p,t conditions 900°C., 10,000 psi for short periods, 750°C., 30,000 psi for long periods. Purchased from Tem-Pres, Inc., State College, Pennsylvania.

4. Kennedy Bomb: Design and construction by Prof. G. C. Kennedy,[20] UCLA, 145 cc capacity, usable volume 2.5 cm. I.D. x 25 cm. I.L., modified Bridgman seal effected by deforming copper seal ring between tapered head and bomb, tapered thread on nut for ease of opening. Used with gold crucibles as above in 2.

The operating pressure in the bomb was in most cases that pressure developed by the hydrothermal medium at the operating temperature and was controlled by the per cent fill of the bomb. To avoid unnecessary sources of leakage the bombs were not equipped with pressure gauges. In the case of pure water and dilute solutions of mineralizers the P-V-T curves of Kennedy[21] for pure water were used to calculate the pressure from per cent fill. The pressure-temperature relations for 5N NH_4Cl were measured at several degrees of fill and these curves used to estimate pressures of the concentrated mineralizer solutions. It should be emphasized therefore that the only known pressure parameter is per cent fill and that pressure estimates for concentrated mineralizer systems are only approximate values. In the case of the microreactors the pressure in some cases was generated externally as a transmitted hydrostatic pressure and here the pressure was known accurately. The latter, in particular, applies to the determination of phase stability for grossular.

The temperature was controlled with standard resistance type tube furnaces and Pyrovane controllers. Temperature gradients were imposed by varying the position of the bomb in the furnace and in some cases where a high ΔT was desired, a small circular auxiliary heater was attached to the bottom of the bomb. In all cases the temperature was measured with thermocouples strapped to the outside of the hydrothermal vessel and it is probable that the internal temperature and ΔT differ somewhat from the measured values.

To avoid the frustrating problem of undetected leaks during long hydrothermal growth runs, a simple bomb balance was devised. The loaded bomb was suspended within the furnace on one end of a pivoted arm counterbalanced on the other end with a container filled with lead shot. A pointer indicator showed changes in balance and could detect loss of as small as 10% of the hydrothermal fluid during a run. The majority of the mineralizing systems used for grossular growth were slightly acidic or basic halide solutions which are highly corrosive toward even the most corrosion resistant alloys. It was therefore necessary throughout the work to use noble metal lined vessels (Morey), sealed gold or platinum tubes (microreactors), or gold crucibles (lens ring and Kennedy). The crucibles did not afford complete isolation of the mineralizer fluid or protection of the bomb from corrosion. Short runs were carried out successfully in unlined bombs but such use drastically reduced the useful bomb life and led to extensive contamination of the crystals with ions dissolved from the bomb (e.g., Co, Ni).

B. Reagents

Four nutrient sources were used for grossular growth: meshed natural pink grossular from Lake Jaco, Chihuahua, Mexico; synthetic micro-crystals of grossular grown hydrothermally; mixed oxide components; and glasses of grossular composition. The natural grossular nutrient contained significant concentrations of Fe and probably Mn (see analysis in Table 1) which were sources of impurity ions incorporated into the grossular crystal during growth. In fact it appeared that the growing grossular often served as a scavenger for traces of transition metal ions in the system. The source of the mixed oxide components were $Ca(OH)_2$, $CaCO_3$ or $CaCl_2$, $Al(OH)_3$ or α-Al_2O_3 powder, and crushed and meshed natural rock crystal quartz. The salts used as mineralizers and the other chemicals were all C.P. grade. The glasses were prepared by melting and remelting appropriate oxide components.

Sources of rare earth (R.E.) ions were the chlorides (in a few cases oxides) of the trivalent R.E., or the R.E. metal. All reagents were 99.5+% purity. Growth under reducing conditions was achieved by using mixtures of the $R.E.^{3+}$ chloride (or oxide) in conjunction with metallic Al or Ca which generated H_2 and a reducing atmosphere, or preferably the R.E. metal itself.

C. Seeds

Seed plates were cut from natural dodecahedral crystals of pink grossular from Lake Jaco, Chihuahua, Mexico for most growth experiments. Rare high optical quality pink grossular dodecahedra from Asbestos, Quebec were used as source of seed plates near the end of the contract period to grow the final crystals. In addition grossular growth on almadine garnet and synthetic yttrium aluminum garnet seed plates was investigated. Characteristics of the seed materials are included in Table 1. Unit cell measurements on the Mexican grossular indicated a close to anhydrous composition.

D. Growth Process

When a thermal gradient method at high pressures with normal solubility was used for growth of grossular or doped grossular as a seed with natural grossular mesh as nutrient, the following reaction geometry was employed. The nutrient was positioned in the bottom of the reactant container and the seed suspended near the top usually by means of a platinum wire or frame. The maximum temperature was maintained at the bottom of the bomb. For the ΔT transport method at low pressures in the region of retrograde solubility the reverse geometry was employed with the nutrient in a platinum basket in the top cooler portion and the seed in the bottom hotter portion. For most of this work the micro-reactors with sealed gold tubes were used since their geometry was best suited to control of ΔT. However, the Morey and Lens Ring bombs were occasionally used for the thermal gradient method, often in conjunction with a gold or platinum baffle just above the nutrient to increase the ΔT. Other nutrient sources successfully substituted for natural grossular mesh in both thermal gradient processes were glasses, synthetic microcrystals of grossular, and mixed oxide components.

In the process based on diffusion of single oxide components to a seed under slight ΔT conditions, several different geometries for the nutrient components were used. In some cases the seed was suspended between separated oxide components positioned in the bottom and top of the bomb. The final optimum process for the oxide diffusion method had mixed oxide components positioned in one end of the hydrothermal vessel, a baffle in between, and the seed in the other. The maximum temperature was at the bottom of the vessel. In normal solubility P-T regions the nutrient was in the bottom and seed in the top. In regions of retrograde solubility, the seed was in the bottom and pellets of nutrient oxides stacked on top of the baffle. Platinum or gold lined Morey vessels were used almost exclusively for the oxide diffusion method. Although external thermal gradients as high as 100°C. were imposed the maximum possible separation of seed and nutrient is about 4 cm. with a 2 cm. diameter volume. Even with a baffle system there is some doubt if significant thermal gradients are present in the reaction system.

The hydrothermal medium was added as an aqueous solution of the appropriate mineralizing salt. The salt concentrations were such that the solution did not exceed saturation under ambient conditions. If $R.E.Cl_3$ was used it was completely dissolved in the hydrothermal medium before adding the solution to the bomb. When reducing conditions were desired, metals (Al, Ca, Eu, Sm or Yb) were used which reacted with H_2O and generated H_2 to provide the reducing atmosphere. The metals were added as nuggets to the system immediately before closure of the bomb. There was little loss of hydrogen. As an additional precaution in the last part of the contract period the loaded bomb was purged with nitrogen to remove O_2 from the system before adding the metal. The hydrogen overpressure was readily detected as a residual ambient pressure after termination of the run and verified the persistance of reducing conditions throughout the run. A further check was made by testing the hydrothermal fluid with $KMnO_4$ solution immediately after opening the bomb. Reducing conditions were accepted only if both ambient hydrogen pressure and decolorization of several drops of 0.1N $KMnO_4$ by the hydrothermal fluid were observed after the growth experiment.

IV. RESULTS AND DISCUSSION

Initially, phase equilibria studies in the $CaO \cdot Al_2O_3 \cdot SiO_2$ system in several mineralizing systems were carried out to establish the P-T limits for grossular stability. The published data[1] in pure water on grossular phase relations indicated that single crystal growth of anhydrous grossular should be favorable within the temperature range 550° to 850°C. and at pressures at least as low as 1000 bars. The stability field for grossular varied appreciably with mineralizer. The mineralizer systems investigation are listed in Table 2. Grossular crystallized from 10-20% $CaCl_2$, ammoniacal 10-20% $CaCl_2$ (pH ~ 10), 5N NH_4Cl, NH_4Br, NH_4F-NH_4OH, and concentrated NH_4OH. In general, grossular did not crystallize from K_2CO_3, $(NH_4)_2CO_3$, 5%, 30% $CaCl_2$, H_3BO_3 and $AlCl_3$ and several other salt solutions. Instead phases such as anorthite, $CaAl_2Si_2O_8$, wollastonite, $CaSiO_3$, idocrase, $Ca_6Al(AlOH)(SiO_4)_5$, or epidote, $Ca_2Al_2OHSi_3AlO_2$, were formed. Screening studies of seeded growth on grossular as a function of mineralizer were next carried out with the results shown in Table 2. Based on these initial investigations, parameters chosen for the development of a hydrothermal process to grow single crystal grossular on a seed were: T = 525°-700°C., p = 9000-50,000 psi, mineralizing systems $CaCl_2$ and NH_4Cl.

The formation of hydrogrossular,[22] [$Ca_3Al_2Si_{3-x}O_{12-4x}(OH)_{4x}$], with isomorphous substitution of $2H_2O$ for SiO_2, or intermediate compositions of hydrated grossular, did not seem to be a problem. Unit cell measurements on a hydrothermal grossular grown at 600°C. and 15,000 psi showed $a_0 = 11.863 \pm 0.003$, indicating an anhydrous grossular composition (less than 1 wt.-% H_2O). The unit cell constant varies with water content from 11.85 Å for anhydrous grossular to 12.56 Å for the fully hydrated garnet $Ca_3Al_2(OH)_{12}$.[11] Unit cell measurements can be used therefore to determine the water content. At growth temperatures above 550°C. anhydrous compositions are stable; between 400°-500°C. some hydration does occur.[11]

The hydrothermal processes developed for single crystal growth of grossular and doped grossular on a seed can be divided conveniently into 1) thermal gradient and 2) oxide diffusion methods. In the first, ΔT transport from grossular nutrient to seed through a temperature gradient and long diffusion zone occurs. The mechanism of transport appears to be one of convective overturn where the driving force is a density-concentration gradient resulting from temperature difference in the system. Growth occurs at both high pressure under conditions of normal solubility and at low pressures under retrograde solubility conditions. In the oxide diffusion method the individual oxide components are dissolved and transported through a concentration gradient generated by the higher solubility of the single component oxides compared to the less soluble grossular. The diffusion path is relatively short and although a high external ΔT is imposed the gradient conditions in the reaction system in the diffusion zone a[illegible] believed to be small and must play a minor role in the process. However, no growth occurred under isothermal conditions. There is a slow conversion of the nutrient oxides to microcrystalline grossular in situ and thus the mechanism probably changes with time, approaching a thermal gradient one. However, for some period self-nucleation is minimal and solution, transport and growth on the seed predominates. The mineralizing system seems to play the critical role in suppressing spontaneous nucleation. Growth at both higher pressure-normal solubility and lower pressure-retrograde solubility was observed with the oxide diffusion method. However, the difference between the two pressure regions (~ 14,000 psi vs. < 10,000 psi) is significantly less than with the thermal gradient method, and there is some doubt that the solubility temperature characteristics are distinctly different between the two.

Details of the preferred processes developed for hydrothermal growth of grossular are shown in Table 3. In the thermal gradient method, optimum growth occurred in the high pressure-normal solubility region at nutrient temperature 660°C., seed temperature 590°C., temperature gradient ~ 10°/cm., 70% fill, external pressure 45,000 psi, with 20% $CaCl_2$ mineralizer. In the low pressure-retrograde solubility region, optimum growth parameters were temperature 540°-640°C., gradient 5-10°/cm., 35% fill (estimated pressure < 10,000 psi), 10% $CaCl_2$ mineralizer. Linear growth rates up to 0.4 mm/day and 0.15 mm/day were observed at high and low pressures, respectively, with sustained growth rates of 0.25 mm/day and 0.05 mm/day, respectively. Crystal quality was generally poor due mainly to Fe impurities derived from the natural grossular nutrient. Microscopically these appeared as a high density of wisps of brown or black inclusions of unknown composition. Crystal inclusions of anorthite and wollastonite were also observed. Substitution of a high purity glass of grossular composition as nutrient markedly improved the quality. The resulting grossular growth was exceptionally transparent, and contained fewer anorthite and wollastonite inclusions. Thus, using the thermal gradient method at high pressure and glass as nutrient, good quality fully synthetic grossular crystals can be produced at reasonable growth rates (0.2-0.4 mm/day).

In the oxide diffusion method optimum growth parameters are: higher pressure-normal solubility, 550°C., ΔT 20°C., 50% fill (~ 14,000 psi), 6% NH_4Cl mineralizer; lower pressure-retrograde solubility, seed temperature 640°C., nutrient temperature 530°C., ΔT ~100°C., 40% fill (~10,000 psi), 10% $CaCl_2$ mineralizer. As mentioned above the presence of a distinct difference in solubility characteristics between the two pressure regions is questionable. A brief study of growth rate as a function of % fill was made for the oxide diffusion method. In the higher pressure process observable growth began at 30% fill, increased regularly to a maximum at 50% fill, then dropped abruptly to 0 above 50% fill. In the lower pressure region there also was a regular increase in growth rate from 30% fill to a maximum at 42% fill above which the rate again dropped abruptly to 0. The sharp drop to 0 growth rate in both cases seemed to be related to the conversion of the bulk of the nutrient to anorthite. Sustained linear growth rates of 0.04 mm/day and 0.02 mm/day were observed at the higher and lower pressure, respectively. The crystal quality was consistently high probably because of the absence of impurity ions in the system. Imperfections were concentrated at the natural grossular seed-new growth interface and grew out with distance from the seed plate. As expected seed quality played an important role and the highest quality new growth was obtained using the optically clear Asbestos, Quebec grossular seed plate. Although there is a significant sacrifice in growth rate compared to the thermal gradient method, the lower pressures and short diffusion path used in the oxide diffusion method offers a significant advantages with respect to hydrothermal equipment, in that relatively simple and trobule-free noble metal lined Morey vessels can be used.

In addition to growth on natural grossular seed, grossular grew on almadine garnet, $Fe_3^{2+}Al_2Si_3O_{12}$, even though there is an appreciable mismatch in unit cell size, 11.52 Å for almadine and 11.85 Å for grossular. No growth occurred on yttrium aluminum garnet seed, a_o = 12.02 Å. Brown andradite garnet, $Ca_3Fe_2^{3+}Si_3O_{12}$, a_o = 12.04 Å, almadine garnet, and a Co-garnet, probably $(Co^{2+}, Ca)_3Al_2Si_3O_{12}$, were grown inadvertently on natural grossular seed plates. The Fe and Co were derived from the bomb material and natural grossular nutrient. As indicated above the best seed material was the high quality pink grossular dodecahedra from Asbestos, Quebec. However, even this was not of completely satisfactory purity since it contained 0.5% Mn and 0.5% Fe impurities. There was some evidence that the impurity ions diffused into the new grossular growth. Ideal seed material would be third or fourth generation synthetic hydrothermal grossular grown from a high purity system. Growth rate was a function of seed orientation with the maximum growth rate in the [100]direction.

The specificity of mineralizer appears to be complex but seems related to control of congruency of solubility and relative rate of transport of the several oxide components. As stated above in the oxide diffusion method in particular, it also serves to suppress self nucleation of the oxide components. Slightly basice halides (pH 7.5-10) of NH_4 and Ca were the most effective mineralizers, although growth was also achieved in slightly acidic halide solutions (pH ~ 5.5). There appears to be a pH limitation for grossular growth related to the instability of grossular in more strongly acid or basic solutions. The pH is controlled by the mineralizing solution and is measured only at ambient conditions before and after the hydrothermal run. At reaction P-T conditions the pH is not known. In general the ionization constant of aqueous salt solutions decreases with increasing temperature at high pressure and therefore the acidity or alkalinity may be much weaker under crystal growth conditions.

Grossular was successfully doped with 0.1 to 1 wt.-% Eu, Yb and Sm under varying oxidizing and reducing conditions using both thermal gradient and oxide diffusion growth methods. A slightly acidic pH (~ 5.5) was used to prevent the precipitation of the rare earth hydroxides. A reducing H_2 atmosphere was generated with the rare earth metal or a mixture of $R.E.Cl_3$ and Al metal. When reducing conditions were maintained throughout the run, it was quite certain in the case of Eu that the predominant R.E. ion in the solution was Eu^{2+}. However, the partition coefficient of Eu^{2+} between grossular and solution may be low, probably lower than for Eu^{3+} based on size differences, Eu^{3+} 1.02 Å, Eu^{2+} 1.09 Å, Ca 0.99 Å. Charge balance with $R.E.^{3+}$ substitution can be achieved either by forming a defect structure with 2 $R.E.^{3+}$ substituting for 3 Ca^{2+}, incorporation of hydroxyl groups, or by coupled substitution $R.E.^{3+}Al^{3+} = Ca^{2+}Si^{4+}$. Changing the hydrogen pressure or redox potential alters the Eu^{2+}/Eu^{3+} ratio in solution, but does not alter the partition coefficient. In most cases Eu^{3+} substitution appeared to be favored. Similar comments apply to ytterbium and samarium. The ratio $R.E.^{3+}/R.E.^{2+}$ in solution, however, should decrease in the order Eu> Yb> Sm in the same order as their decreasing stability toward oxidation.

The grossular and doped grossular crystals grown under this contract and submitted to Dr. Nicolai at its conclusion are listed in Table 4 along with some of their characteristics. Included are: fully synthetic crystals of undoped and Eu-doped grossular up to 3 mm x 5 mm x 9 mm; overlays of synthetic grossular doped with Eu, Sm and Yb on an Asbestos, Quebec natural grossular seed plate; overlays of Eu-doped and Sm-doped $Ca_3Ga_2Si_3O_{12}$ garnet, the gallium analogue of grossular; glasses of grossular composition containing 5 wt.-% Sm_2O_3 (Sm^{3+}) and 1 wt.-% Eu_2O_3 (Eu^{3+}); spontaneously nucleated micro-crystals of Eu-doped and Sm-doped grossular of high purity; a seed plate of natural grossular from Asbestos, Quebec. The fully synthetic crystals were grown by cutting out the natural grossular seed plate after an initial growth period and carrying out subsequent growth runs on that fully synthetic seed plate. The crystals are divided into three Groups. Group I includes the best doped grossular crystals where optimum reducing conditions were maintained and where divalent R.E. ion doping was believed to be successful. As discussed in Section I, the presence of $R.E.^{2+}$ was not established in any of the crystals by fluorescence spectroscopic methods. The Eu-doped grossular overlay, #12206-32-1, was compared to the seed material by a differential spectroscopic method and showed a residual absorption band in the ultraviolet at 315 mμ, consistent with a known absorption band for Eu^{2+}.

Those crystals marked with an asterisk in Table 4 were examined by fluorescence and emission spectroscopy by Dr. Ohlmann at Westinghouse. The two samples of Sm-doped grossular, #12206-63-1 and 12206-63-4 in Group I, are those for which Dr. Ohlmann reports conflicting data with respect to the identity of the dopant ion. They were analyzed in this laboratory by emission spectrographic techniques and found to contain 0.1 wt.-% Sm. Based on fluorescence spectra, Dr. Ohlmann identifies Eu^{3+} in 12206-63-1, and Eu^{3+} + Sm^{3+} in 12206-63-4, and suggests that the samples were mislabelled. Without additional reanalysis of the same crystals the point must remain unsettled.

Any additional research work on the hydrothermal synthesis of grossular garnet should be directed in the following areas.

1. Improve chemical purity. High-purity glasses and doped glasses used as nutrient source and high-purity, all-synthetic seed plates generated.

2. Improve optical quality. Adjust growth rate and other growth parameters to minimize "wisps" containing liquid-gas inclusions and crystal inclusions.

3. Investigate the dopant systems, Sm^{2+} and Mn^{2+}, with emphasis on Sm^{2+}. Doping with Mn^{2+} should offer no technical difficulties. Improve the Eu^{2+}-doped crystals to eliminate any possible traces of trivalent europium to establish the inherent spectroscopic characteristics of Eu^{2+} in grossular. Investigate different concentration levels of the activator ions (0.01, 0.1% and higher).

4. Grow high-purity, high quality, crystals doped with Sm^{2+}, Eu^{2+}, and Mn^{2+}, fully synthetic, and of sufficient size (about 3 x 10 x 10 mm) for spectroscopic measurements.

5. Measure fluorescence and absorption specra of final Sm^{2+}-, Eu^{2+}-, and Mn^{2+}-doped crystals.

6. Investigate electron spin resonance spectra as an alternate method of determining the valency of Sm and Eu in the doped crystal.

All of the preceding appear to be technically feasible. Additional research effort however only seems warranted if there is high incentive for use of grossular as a host lattice for laser crystal application.

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TABLE 1

Characteristics of Natural Grossular Nutrient and Garnet Seed Materials

Composition	Locality	Quality	Color	Analysis
*Grossular	Lake Jaco, Chihuahua, Mexico	Translucent to opaque, contains microcracks	Pale pink and green dodecahedra	Ca 26.8, Al 10.6, Si 18.3 Fe 2.3 wt.-%, Mn n.d. 1) a_o = 11.883 ± .003 Å
Grossular	Asbestos, Quebec	Excellent, transparent, free of microcracks	Pale pink dodecahedra	Mx ~ 0.5, Fe ~ 0.6, Ti 0.00, V 0.00, Cr 0.00 wt.-%
Almadine ($alm_{82}pyr_{18}$)	India	Transparent	sherry-violet	a_o = 11.535 Å, d = 3.983 g/cc, R.I. = 1.765 ± .005
Almadine ($alm_{82}pyr_{18}$)	Madagascar	Transparent	port wine	a_o = 11.518 Å ± .004, d = 4.194, R.I. = 1.81 ± .01

* Source of all natural grossular nutrient used as mesh in growth experiments.

1) n.d. = not determined

TABLE 2

Mineralizers Investigated for Hydrothermal Growth of Grossular

A. Phase Stability Studies:

Grossular Crystallized:	No Grossular Crystallized:
NH_4Cl	H_3BO_3
NH_4Br	40% $(NH_4)_2CO_3$
$CaCl_2 \cdot 2H_2O$	5, 10% $AlCl_3$
5, 10, 20% $CaCl_2$	0.6% $LiCl + NH_4OH$
Ammoniacal 10, 20% $CaCl_2$ (pH ~ 10)	40% K_2CO_3
0.2% $NH_4F + NH_4OH$	1% $NH_4Cl + NH_4OH$
Conc. NH_4OH	1.8% $LiF + NH_4OH$
	10% LiOH
	10% NaOH

B. Growth on Grossular Seed (Thermal Gradient Method):

Growth on Seed:	No Growth on Seed:
10, 20% $CaCl_2$	10% $CaCl_2$, 400-500°C.
5% $CaCl_2$-NH_4OH (pH 11.5)	10% NH_4F
10% $CaCl_2$-NH_4OH (pH 10)	10% NH_4Br
0.2% NH_4F-NH_4OH (pH 11.5)	weakly acidic 10, 30% NH_4Cl
6% NH_4Cl	
5N NH_4Cl	
Conc. NH_4OH (pH 12.8)	

Except where indicated crystallization temperature 550-650°C., usually 600°C.

TABLE 3

Preferred Processes for Hydrothermal Growth of Grossular

Temperature, °C. Seed	Temperature, °C. Nutrient	Gradient ΔT	% Fill	Pressure, psi	Mineralizer	Metal	Nutrient	Solubility	Reaction Geometry 1)	Linear Growth Rate and Quality
A.	Thermal Gradient Method:									
590	660	10°/cm.	70	45,000 External	a. 20% $CaCl_2$ b. 20% $CaCl_2$ 10% $R.E.Cl_3$	--- Al, R.E. metal	Nat. gross., glass of grossular	Normal	Seed top, nutrient bottom, separated by 8-10 cm., microreactors	0.4 mm/day max., 0.25 mm/day sustained Quality poor with nat. gross. nutrient due to Fe impurities; very good with glass nutrient.
640	540	5-10°/cm.	35	< 10,000 Estim.	a. 10% $CaCl_2$ b. 10% $CaCl_2$	--- R.E. metal	Same as above	Retrograde	Nutrient top, seed bottom separated by 8-10 cm., microreactors	0.15 mm/day max., 0.05 mm/day sustained Quality same as above.
B.	Oxide Diffusion Method:									
550	570	20°	50	~ 14,000 Estim.	a. 6% NH_4Cl b. 6% NH_4Cl	--- R.E. metal, 0.5 wt.-% based on nutrient solids	$CaCO_3$ $Al(OH)_3$, quartz	Normal?	Mixed nutrient in bottom, seed in top, gold baffle in between, separation of seed and nutrient ~ 3 cm. max., Pt or Au-lined Morey vessel	0.04 mm/day sustained, quality very good.
640	530	~ 100°	40	~ 10,000,	a. 10% $CaCl_2$ b. 10% $CaCl_2$	--- R.E. metal	1/4" pellets $Ca(OH)_2$, $Al(OH)_3$, quartz mixture	Retrograde?	Seed on frame in bottom, gold baffle in between, nutrient pellets stacked on top of gold baffle; separation of nutrient and seed ~ 1 cm., Pt or Au-lined Morey vessel	0.02 mm/day sustained, quality very good.

---

1) Preferred seed material in all cases is high quality natural grossular from Asbestos, Quebec (see Table 1).

TABLE 4

Hydrothermal Grossular Crystals

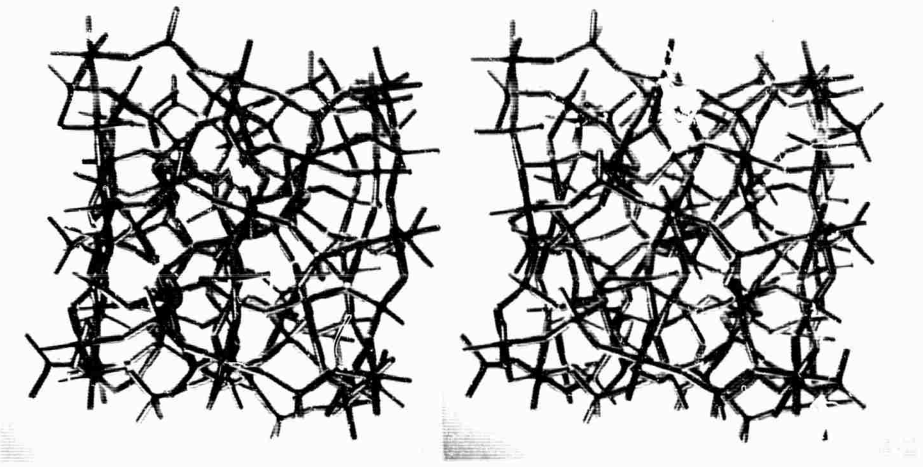
Sample Number	Dopant Ion	Wt., Gm.	Description
GROUP I:			
---	none	---	Natural grossular seed plate from Asbestos, Quebec. Mn $\sim$ 0.5 wt.-%, Fe $\sim$ 0.6 wt.-%; Ti 0.00%, V 0.00%, Cr 0.00%.
12223-79	none	$\sim$ 0.28	All synthetic hydrothermal grossular. Nil fluorescence in the visible.
*12223-87-1	Eu	$\sim$ 0.31	All synthetic hydrothermal Eu-doped grossular. Grown under reducing conditions. Weak pink fluorescence. Probably Eu^{+2} plus Eu^{+3} Eu = 1.1 wt.-%, Fe $\sim$ 0.01 to 0.1 wt.-%.
*12206-27-2	Eu	---	Overlay of synthetic hydrothermal Eu^{+3}-doped (possibly some Eu^{+2}) grossular on natural grossular seed plate (above). Strong pink-orange fluorescence. Emission spectrum analysis of overlay shows Eu $\approx$ 0.01%. a_o = 11.834 Å.
*12206-32-1	Eu	---	Overlay of synthetic hydrothermal Eu^{+2}-doped grossular on natural grossular seed plate (above). Nil fluorescence in the visible. Emission spectrum analysis of overlay shows Eu $\approx$ 0.1 wt.-%.
*12206-63-1	Sm	---	Overlay of synthetic hydrothermal Sm-doped grossular on natural grossular seed plate, Sm = 0.1 wt.-%. Total overlay thickness 31 mils. Deep pink fluorescence (visual observation) under UV excitation (3650 Å). a_o = 11.818 Å.
*12206-63-4	Sm	---	Overlay of synthetic hydrothermal Sm-doped grossular on natural grossular seed plate, Sm = 0.1 wt.-%. Total overlay thickness = 16 mils, seed thickness 24 mils. Deep pink fluorescence (visual observation) under UV excitation (3650 Å).

TABLE 4, cont'd.

Sample Number	Dopant Ion	Wt., Gm.	Description
GROUP II:			
*12223-100	Eu	0.135	Overlay of synthetic hydrothermal Eu-doped $Ca_3Ga_2Si_3O_{12}$ garnet on natural grossular seed plate (above). Eu ≈ 1%. Grown under reducing conditions using Eu metal for dopant source. Seed thickness 0.75 mm; seed + overlay 1.50 mm thick. Probably Eu^{+3} + Eu^{+2} (?).
12223-101B	Yb	0.123	Overlay of synthetic hydrothermal Yb-doped grossular on natural grossular seed plate (above). Yb ≈ 1%. Seed thickness 0.99 mm; seed + overlay 1.32 mm. Grown under reducing conditions using Yb metal as source of Yb. Overlay bright blue in color.
*12223-94	Sm	---	Glass of $Ca_3Al_2Si_3O_{12}$ composition containing 5 wt.-% Sm_2O_3. Fluoresces yellow-orange.
12223-102	Eu	---	Glass of $Ca_3Al_2Si_3O_{12}$ composition containing 1 wt.-% Eu_2O_3.
12223-101A	Sm	0.116	Overlay of synthetic hydrothermal Sm-doped garnet of $Ca_3Ga_2Si_3O_{12}$ composition on natural grossular seed plate (above). Sm ~ 1 wt.-%. Seed thickness 0.81 mm. Overlay + seed 1.46 mm thick. Grown under reducing conditions using Sm metal as dopant source. Probably contains Sm^{+3} + Sm^{+2} (?).
*12223-95	Sm	0.1355	Overlay of synthetic hydrothermal Sm-doped grossular on natural grossular seed plate (above). Sm ≈ 1 wt.-%. Seed thickness 0.80 mm. Seed + overlay 1.20 mm. Grown under reducing conditions using Sm_2O_3 in a glass of $Ca_3Al_2Si_3O_{12}$ compositions as nutrient. Probably contains Sm^{+3} + Sm^{+2} (?).

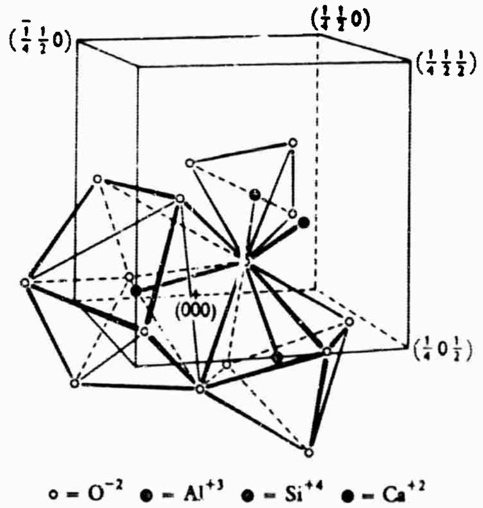
TABLE 4, cont'd.

Sample Number	Dopant Ion	Wt., Gm.	Description
GROUP III:			
12206-40-8	Eu	---	Spontaneously nucleated micro-crystals of Eu-doped grossular (0.1 wt.-% Eu). Grown under reducing conditions. Probably Eu^{+2} + some Eu^{+3}.
12206-64-1	Sm	---	Spontaneously nucleated micro-crystals of Sm-doped grossular (0.1 wt.-% Sm). Grown under reducing conditions. Probably Sm^{+2} + Sm^{+3}.



Stereoscopic photograph of a model of the aluminosilicate framework in $Ca_3Al_2Si_3O_{12}$ viewed normal to (100). Tetrahedral or d sites are shown as the centers of the wire tetrahedra, octahedral or a sites at the centers of the octahedra. Ca atoms in c sites are not shown.

(Gibbs and Smith, 1963)



The coordination polyhedron of Si, Al and Ca in grossular are shown with the polyhedron around Ca as a nearly cubic hexahedron.

(Abrahams and Geller, 1958)

Figure 1

Figure 2

Hydrothermal Vessels

a. Microreactor vessel is constructed of Stellite 25 and has a 1/4 inch diameter axial hole drilled within 1 inch of bottom. The nut secures a cone-in-cone seal at the top of the vessel. At the left is a gold tube which is sealed at both ends and serves as an inert reactant container.

b. The Kennedy vessel on the left has an internal volume of 50 cc and is fitted with a tapered seal for ease of assembly. The Inconel X Lens Ring vessel shown on the right has an internal volume of 50 cc. Thick walled gold crucibles like that shown in the center can be used inside either vessel as an inert reactant chamber.

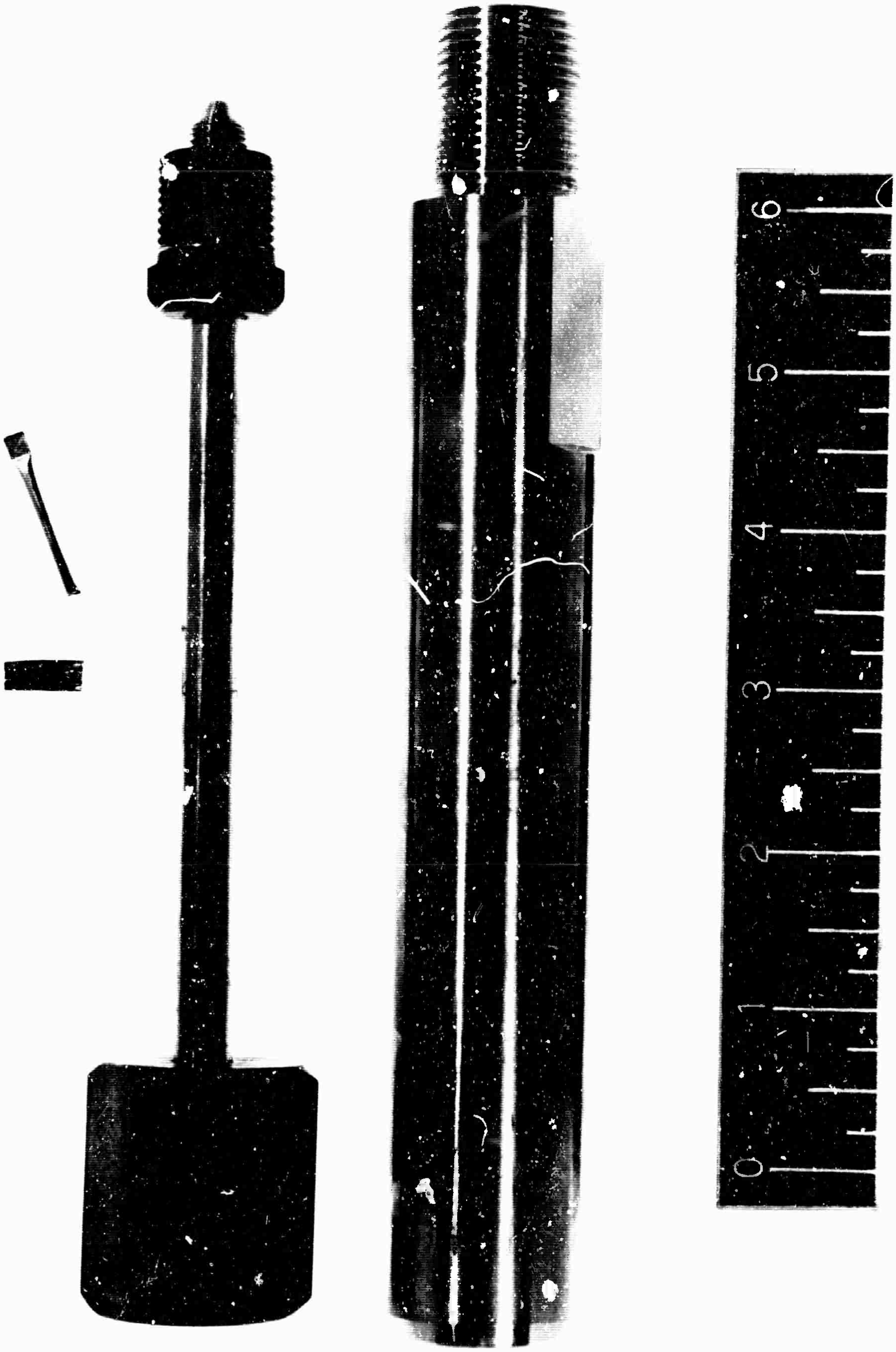
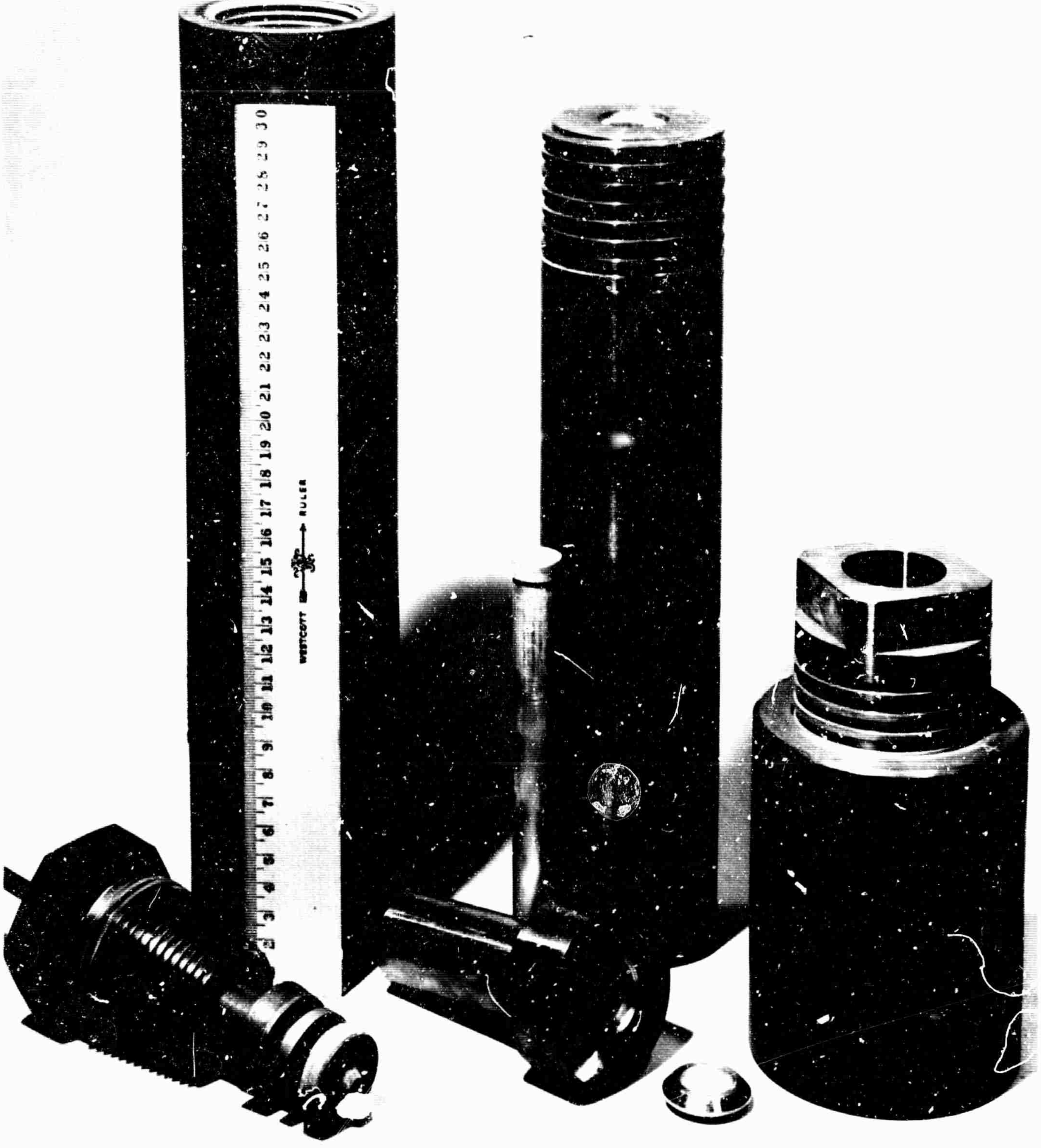


Figure 2A



VESSELS USED FOR HYDROTHERMAL CRYSTAL GROWTH

Figure 2B

FIGURE 3

HYDROTHERMAL GROSSULAR CRYSTALS

(see also Table 4)

a.

Overlays of Sm-doped grossular on natural grossular seed plate; l. to r. 12,206-63-1, 12223-95, 12206-63-4; good quality growth.

b.

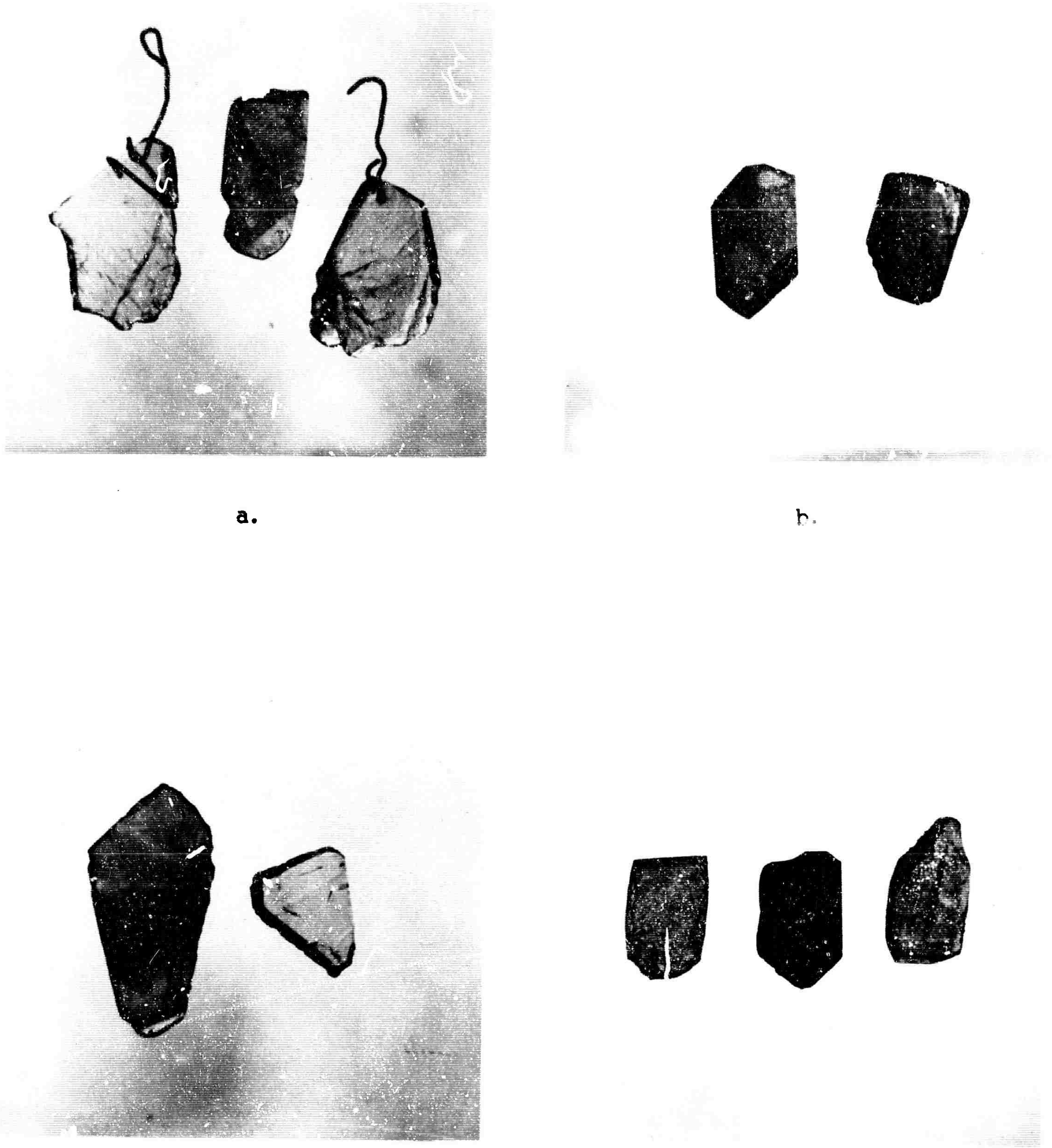
Fully synthetic hydrothermal grossular crystals; l. undoped, 12223-79, 0.28 g; r. Eu-doped under reducing conditions, 12223-87-1, 0.31 g; poor quality due to significant Fe impurities.

c.

Overlays of Eu-doped grossular on natural grossular seed plate; l. 12206-27-2, r. 12206-[illegible]-1; good quality growth.

d.

Overlays of synthetic grossular in natural grossular seed plate; l. to r., Eu-doped $Ca_3Ga_2Si_3O_{12}$, 12223-100; Yb-doped grossular, 12223-101B; Sm-doped $Ca_3Ga_2Si_3O_{12}$, 12223-101A.



a.

b.

c.

d.

Figure 3

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Union Carbide Corporation, Linde Division
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2a REPORT SECURITY CLASSIFICATION
Unclassified

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3 REPORT TITLE

HYDROTHERMAL GARNET CRYSTALS-FINAL SUMMARY REPORT

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)
Final Report - July 16, 1964 - July 15, 1965

5 AUTHOR(S) (Last name, first name, initial)

Flanigen, E. M. (Miss)

6 REPORT DATE
December 27, 1966

7a TOTAL NO OF PAGES
43

7b NO. OF REFS
22

8a CONTRACT OR GRANT NO.
Nonr-4657(00)

b. PROJECT NO.
ARPA Order 306-62

c.
Code 4730

d. Task No. NR-017-718

9a ORIGINATOR'S REPORT NUMBER(S)

Hydrothermal Garnet II-66

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13 ABSTRACT

The aim of this research was the hydrothermal growth of single crystals of grossular garnet, $Ca_3Al_2Si_3O_{12}$, containing divalent activator ions such as Eu, Sm, Gd, Ce and Mn. Such crystals were desired as possible new laser materials with efficient pumping and high fluorescent yield characteristics. Hydrothermal processes were successfully developed for growth of synthetic grossular on seeds and have yielded good quality fully synthetic crystals up to 3 mm x 5 mm x 9 mm. Incorporation of the rare earth ions Eu, Sm and Yb into the lattice under reducing conditions was achieved, but excitation and fluorescence spectra indicated the presence of only trivalent rare earth ions in the grossular crystals.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Laser						
Optical Maser						
Hydrothermal Crystal Growth						
Fluorescence						
Garnet						
Grossular						
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