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Final Technical Report

on

GROWTH OF NEW MATERIALS FOR SOLID STATE LASER APPLICATIONS

with a supplemental study on

THE GROWTH OF $ZnGeP_2$ BY THE VERTICAL BRIDGMAN METHOD

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ABSTRACT

This is the final technical report on the cooperative NASA program "Growth of New Materials for Solid State Laser Applications," covering the period from 9-1-86 through 3-31-91. The first two and one half years of the program, from 9-1-86 through 3-31-89 was devoted to the development of new eye-safe laser sources. Single crystal fibers of rare earth doped and co-doped YAG were grown by the laser-heated pedestal growth method, characterized for their structural properties and supplied to NASA/Langley for spectroscopic evaluation. From 4-1-89 through 3-31-91, research focused on the growth of zinc germanium phosphide for nonlinear optical applications in the IR. The vertical Bridgman growth process was evaluated as a means to achieve better control over the short wavelength optical absorption in this material that adversely affects 2 μm-pumped optical parametric oscillators.

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I. INTRODUCTION

This is the final technical report on the cooperative NASA program "Growth of New Materials for Solid State Laser Applications," covering the period from 9-1-86 through 3-31-91. The first two and one half years of the program, from 9-1-86 through 3-31-89 was devoted to the development of new laser sources. Funding for this part of the program amounted to $120K. From 4-1-89 through 3-31-91, research focused on the growth of zinc germanium phosphide for nonlinear optical applications in the IR with supplemental funding of $96K.

A. New Materials for Solid State Lasers

The driving force for the initial program was the need to develop new laser sources in the 2-3 μm (eyesafe) wavelength range for lidar and other measuring/sensing applications. The spectroscopic properties of the known dopant/host combinations that emit in this wavelength range are complex, and measurements on a number of host materials doped with varying amounts of activator ions were required to develop useful laser sources. The program involved preparation and growth of a selection of these new laser materials at the Center for Materials Research (CMR), Stanford University. Optical evaluation, the task of unraveling the complex interrelationships between the lasing ions, any charge transfer codopant and the host matrix, were carried out primarily at NASA Langley. The materials preparation effort at CMR included participation by both professionals and graduate students.

It was originally proposed that we prepare single crystal fiber specimens from two classes of materials: congruently melting oxides, and halides with a variety of activator ions. However, the strong interest in rare earth-doped YAG and related materials at NASA Langley led us to concentrate exclusively on growing doped and codoped single crystal YAG fibers at Stanford. Our research on these and related materials was based on the laser-heated pedestal growth (LHPG) method which was available at only a few institutions in this country. This technique, which has been described fully in a number of our publications, [for example, see reference(1)], has a number of major advantages for growing crystals of congruently melting oxides. It is a containerless process so that impurity pickup from crucibles is avoided. It is a quick and relatively easy method for the growth of small single crystal rods with controlled doping levels. This growth capability provided an opportunity to looking again at some of the materials first grown during the early 1970's, as well as entirely new host/dopant combinations. While doping is relatively straightforward with the LHPG method, control of dopant valence state and site preference were more challenging, necessitating atmospheric control and/or co-doping with a charge compensating species.

The material of principal interest was co-doped YAG with Ho^{3+} as the activator ion, such as Ho, Er:YAG and Ho,Tm:YAG. This material had been reported to lase around 2.09 μm(2). In fact, Ho,Tm:YAG was grown in the early 1970's(3) and used for preliminary fluorescence measurements. Our purpose was to obtain high optical quality, 1 μm diameter rods with a range of carefully controlled doping levels, permitting more extensive optical spectroscopic studies which were needed to evaluate Ho,Tm:YAG's potential as a solid state diode-pumped laser.

A variety of sub-millimeter single crystal fibers of doped YAG with different dopants in varying concentrations were prepared and suppied to NASA/Langley for evaluation.

B. Growth of $ZnGeP_2$

When originally proposed, the program's second phase was to emphasize improving the crystal growth yield of high quality $AgGaSe_2$, an important material for nonlinear frequency conversion in the IR. Growth technology was to be improved through the use of shaped crucibles and melt stirring, and the development of a better model for the heat-treatment processing of that material. The program's emphasis, however, was immediately shifted to the growth and characterization of $ZnGeP_2$ when that material's potential for 2μm-pumped OPOs was realized. The first objective involved establishing a synthesis procedure for preparing $ZnGeP_2$ charges with carefully controlled compositions. The second objective involved a determination of whether the vertical Bridgman growth technique could be used to grow $ZnGeP_2$, and whether it offered advantages over the horizontal Bridgman method which had been used for the early growth studies on this material. The third objective involved a determination of the influence of melt composition on the short wavelength (1μm) optical absorption that was (and still is) seen in varying degrees in virtually all $ZnGeP_2$ crystals irrespective of the growth technique used.

$ZnGeP_2$ theoretically is transparent from 0.7-12 μm. However, melt grown crystals typically display considerable short wavelength band-edge optical losses with absorption coefficients rising rapidly at wavelengths shorter than 1 μm, as shown in fig. 3. 2μm-pumped OPOs do not require a high degree of transparency in the 1 μm region for operation. However, optical absorption here is felt to correlate strongly with lower levels of 2 μm absorption which does have a strong effect on OPO performance. In addition, 1 μm absorption was significantly easier to measure for quantitative comparison, and we focused on that waveband in order to compare the various preparative procedures investigated in this program.

$ZnGeP_2$ melts congruently at 1025° C in equilibrium with a vapor phase consisting essentially of phosphorus at a pressure of 3.5 atmospheres(4), as shown in fig. 4. Early growth experiments by other researchers utilized vitreous carbon boats inside sealed quartz ampoules for both synthesis and growth experiments. This was due to the reported reactivity of the molten constituents with fused quartz (5). $ZnGeP_2$ had also been reported to undergo a solid-state phase transition at 950° C, op. cit. The high temperature modification was presumed to have a sphalerite structure, but its existence has not yet been verified. Others found no evidence of such an event in DTA experiments(6) Literature reports indicate that crystals grown by the horizontal Bridgman method from charges slightly richer in ZnP_2 (by 1.5%) had lower short-wavelength optical absorption than crystals grown from stochiometric melts.(5) Knowing that the vertical Bridgman method offered the advantage of greater control over vapor phase losses from the growing crystals within the growth ampoules than did the more commonly-used horizontal Bridgman method, we sought to compare the effects of 1.) controlling the phosphorus pressure to compensate for losses to the free volume over the melts, and 2.) adding excess ZnP_2 into the quartz ampoules during the synthesis process, on the optical properties in the 1 μm spectral region.

II. TECHNICAL REPORT

A. Growth of Rare-Earth Doped YAG

The main program's objectives were the preparation of high quality, single crystal YAG rods containing the dopants listed in Table I.

Table I

Item	Host	Dopants (concentration in At %)
1	YAG	Ho (0.5%)
2	YAG	Ho (0.4%), Tm (6%)
3	YAG	Ho (0.5%), Tm (6%)
4	YAG	Ho (0.5%), Tm (1.5%)
5	YAG	Tm (6%)
6	YAG	Pr (0.5%)
7	YAG	Dy (0.5%)

Successful preparation of high optical quality, single crystal fibers for spectrographic evaluation was known to be strongly dependent on the availability of uniformly doped and optimally dense starting material. Doped single crystal feedstock is optimum. However, for most of the specific target materials, it was not readily available and so, for each case, we were faced with the need to prepare accurately-doped feedstock.

After initial, relatively unsuccessful, experiments in growing high optical quality specimens from hot-pressed ceramic feedstock, we concluded that the use of single crystal feedstock offered significant advantages. We therefore obtained undoped "white" YAG single crystal from Union Carbide. Feedrods were prepared by microcenterless grinding, and growth experiments were undertaken. Undoped YAG fibers 0.7-1.0 mm in diameter were prepared from 1.1 mm diameter feedstock. Occasionally, cracking was observed after growth. In these experiments, laser power limitations prevented us from achieving a flat growth interface and we presume, therefore, that there was some degree of radial strain in the fibers. Reducing the feedstock diameters to 0.7 mm and growing the samples in somewhat smaller dimensions with flatter growth interfaces minimized strain fields and totally eliminated the cracking.

Ho-doped YAG. A technique for doping source rods by coating the surfaces with appropriate quantities of holmium oxide was then developed. A slurry containing Ho_2O_3

and Al_2O_3 in molar ration 3:5 was prepared using gum arabic as a binder and ethyl alcohol as a vehicle. This was applied to the source rods using several methods, air dried, and fired at 1250° C for 6 hours to drive off the organic binder. Spraying, dipping and painting with a fine brush were all evaluated. Painting under a microscope seemed to give the most uniform and controllable coats. Weight added was then used to determine the amount of holmium added to the surface of the source rod. Adhesion of the Ho_2O_3:Al_2O_3 powders after firing was good. Vacuum evaporation was not used to apply a metallic Ho:Al layer to the source rods because of the reactivity of holmium metal with air.

Fibers of Ho:YAG were then grown by the LHPG method. Ho_2O_3 and Al_2O_3 appeared to be stable during this procedure: no obvious volatilization or condensate was detected. Growth parameters were explored and a range of dopant concentrations used. Fibers grown at rates of 0.3 mm/min or slower appeared to have minimal cracking and few internal defects. Fibers grown faster all contained excessive cracking. A slower growth rate, 0.3 mm/min, was adopted as a standard growth rate for holmium-doped YAG. This permitted us to assess the effects due to radial strain caused by growth interface curvature and composition caused by changes in doping level. Holmium doped fibers currently being grown at 0.3 mm/min in air appear to be quite uniform and of excellent optical quality, Fig. 1.

Election microprobe analysis (EMA) was used initially to calibrate the dopant application process for Ho:YAG fibers. Our first fibers were a little above target value and reduced surface

Table II

Ho:YAG Growth Conditions

Target Level (Ho^{+3})	Fiber No.	Surface Concentration (molar)	Measured Bulk Concentration (molar)
0.5 M %	4	11.2 M %	3.96 M %
	9	2.6 M %	0.89 M %
	12	1.4 M %	0.90 M%

Eff = 0.35

dopant levels were needed, Table II. Dopant levels achieved in a later series of fibers were also estimated using EMA analysis, and were found to be above target levels as well. The reason for this discrepancy was not understood and further EMA was carried out on well known standards to sort out the phenomena involved. Ultimately, we assumed a doping incorporation efficiency factor around 35%. The efficiency of dopant added to dopant incorporated should be 100%, if no losses occur during growth, according to LHPG (float zone) theory. We never did determine the reason for the apparent efficiency of only 35%, and continued to address the question as the program proceeded.

Tm-doped YAG and Ho-Tm-doped YAG. Thulium doping concentrations in the crystals of interest were in the 1.5-6.0 M % range. Starting materials containing 6.0 M % Tm^{3+} were initially investigated using the same surface application method described above and a slurry containing Tm_2O_3 and Al_2O_3 in a 3:5 molar ratio. It was found that the estimated surface dopant layer was excessively thick using the brush-on method. Difficulty was encountered in coating the feedstock with adequately thick layers having good uniformity along their lengths. Adhesion after sintering was good, but single crystal fiber morphology was poor. Diameter and straightness were difficult to control. Due to the thickness of the dopant layer, incorporation into the molten zone was nonuniform. This caused major perturbations to the molten zone volume and resulted in the major diameter fluctuations.

We ultimately used 6.0 M % Tm^{3+} bulk single crystal YAG from Union Carbide as feedstock and as a substrate for the selective application of Ho_2O_3 dopant. Control fibers grown directly from the 6 M % Tm^{3+}-doped single crystal stock were of excellent quality. Somewhat higher growth rates were used than had been possible in our earlier experiments on singly-doped Ho:YAG fibers, Table III. Longitudinal and axial sections, Fig. 2a, b revealed no evidence of voids or inclusions. Dark field microscopy consistently revealed strain fields along the [111] fiber axes, but they did not display the three-fold symmetry characteristic of growth in this direction. It was concluded that the weak strain fields shown in Fig. 2b were an artifact of the mounting medium which is also in the optical path as a thin film sandwiched on one side by a glass substrate.

Samples of Tm:YAG and Ho:Tm:YAG were analyzed to determine approximate doping levels. The same doping efficienty (35%) was assumed for holmium incorporation in 6% Tm:YAG until actual measurements become available. Using this doubly-doped series of YAG fibers, we also investigated the effects of oxygen in the ambient atmosphere during growth. Samples of Tm:YAG and Ho:Tm:YAG were prepared in both argon and air ambients. Structurally and microscopically, both sets of fibers looked to be of excellent quality in both longitudinal and axial thin sections. Samples were shipped to NASA/Langley for fluorescence and absorption spectroscopic evaluation..

TABLE III

Ho:Tm:YAG Growth Conditions

Target Doping Level	Sample No.	Atmosphere	Pulling Rate	Diameter	Surface Concentration (molar)
6% Tm	#10	Air	0.94 mm/min	400~430 μm	-0-
6% Tm	#14	Ar (15CFH)	0.94 mm/min	400 μm	-0-
6% Tm 0.5% Ho	#23	Air	0.94 mm/min	390~420 μm	1.49
6% 0.5% Ho	#25	Ar (15CFH)	0.94 mm/min	380~420 mm	1.49

Pr- and Dy-doped YAG. Experiments using the slurry application method to dope YAG with Pr_2O_3 were totally unsuccessful. Little or no adhesion occurred during the sintering procedure and the powders fell off the feedrods both during and after the sintering process. Since Pr- and Dy-doped YAG was far down in the list of materials desired, no further experiments were carried out.

B. Growth of $ZnGeP_2$ Crystals

1. Experimental Procedures

Synthesis - Experiments on $ZnGeP_2$ focused heavily on the preparation of completely reacted starting materials with controlled composition, with the main objective being to determine the effects of stoichiometry on the optical properties. Starting materials were all in high purity elemental form, and they were handled as little as possible during weighing and sealing (of the nominal 20 g charges) into 25 mm ID fused silica synthesis ampoules. Two types of synthesis boats were initially evaluated: glassy carbon boats originating from Fluorocarbon, and machined high density UF - 4S graphite from

Ultracarbon. No differences in yields or purity were apparent and the machined graphite boats were used for the duration of the program because they cost less. A two temperature vapor transport process, similar to that used for the synthesis of $AgGaS_2$(7) was used for the synthesis of $ZnGeP_2$. The advantage of this technique is that it minimizes the chance of building up excess phosphorus pressure in the synthesis ampoule before chemical reaction. However, due to the presence of a relatively high equilibrium vapor pressure containing P_4 (and probably Zn) over molten $ZnGeP_2$, a finite amount of the phosphorus and zinc can remain in the vapor phase over the melt, leaving the solidifying charge deficient in both. Condensed droplets on the walls of our reaction vessels suggested that this, in fact, happened, and it introduced a degree of uncertainty in the composition of the synthesis product which was subsequently used as a charge for the crystal growth process. Analysis of the condensed droplets indicated that they consisted primarily of red phosphorus. Small quantities of ZnP_2 were also found. (Two-temperature, vapor phase equilibration with one or two excess constituents was thought to be a feasible approach to achieving precise control over product composition. However, such studies were beyond the scope of the program.) In many cases, explosions occurred during the synthesis procedure. This was known to be a common occurrence when developing a workable synthesis process for $ZnGeP_2$, and it added a dimension of additional cost, frustration and the time to clean up and rebuild the apparatus after each event. Working out a controllable charge synthesis procedure consumed a sizeable fraction of this supplementary program on $ZnGeP_2$.

The Zn:Ge ratio in the charges used subsequently for growth was controlled in the synthesis step by adjusting the weight of the high purity elemental starting materials and assuming that the losses of Zn were minimal. We also studied the effects of phosphorus losses to the vapor phase during synthesis by adding excess phosphorus calculated to to provide overpressures of 3.5 atm of P_2 or P_4 over the charges to determine if minor phosphorus losses to the free volume in the ampoules had an appreciable effect on the optical properties.

Crystal Growth - Crystals were grown from stoichiometric charges and from charges with 1.5 % excess ZnP_2. $ZnGeP_2$ crystals were grown in two sizes, 6-7 mm diameter with boules weighing approximately 12 g, and 12-14 mm diameter with boules weighing close to 25g. Growth ampoules were coated internally with carbon by the pyrolysis of hexane in order to minimize reaction between the $ZnGeP_2$ charges and the fused silica walls, and they were sealed under vacuum. All growth ampoules were of the self-seeding type, and were double encapsulated because self-seeded boules typically contained several grains, and differential expansion between the grains usually led to self-seeding type, and were double encapsulated because self-seeded boules typically contained several grains, and differential expansion between the grains usually led to fracturing of the quartz ampoules during cooling from high temperatures. Growth rates of 1 cm/day were used.

2. Results

Synthesis - Charge synthesis was reasonably successful using the procedure detailed in fig. 5. In all cases, however, a small percentage of the synthesized charges was lost during removal from the quartz ampoules. This added a slight degree of uncertainty to the exact charge compositions used for the subsequent growth experiments. Quartz ampoules of nominal wall thicknesses (1.5 mm) were adequate to contain the few atmospheres of phosphorus overpressure present. Table IV summarizes the synthesis (and the crystal growth) experiments carried out during the program.

Table IV

Synthesis and Growth Experiments on $ZnGeP_2$

Run	**Experiment**	**Conditions**	**Results**	**Absorption at 1 mm (cm^{-1})**
15a	Synthesis	3.5 atm P_2	7 wt % unrecovered, good XRD pattern	NA
15b	Growth	Vacuum	Poly, badly cracked, (15 g)	NA
15c	Growth	Vacuum	Large grain poly, (10 g)	43 cm^{-1}
15d	Growth	Vacuum	Large grain poly, (7.8 g)	12 cm^{-1}
16a	Synthesis	3.5 atm P_4	5 wt % unrecovered, good XRD pattern	NA
16b	Growth	Vacuum	Near single crystal, (18.9 g)	12 cm^{-1}
17a	Synthesis	3.5 atm P_4, 1.5% excess ZnP_2	8 wt % unrecovered, good XRD pattern	NA
17b	Growth	3.5 atm P_4	Large grain, poly, twins, (42.2 g)	12 cm^{-1}

Crystal Growth - Crystals typically contained a few grains and, as a consequence of differential thermal expansion, fractured in varying degrees. Grain selection was not found to be particularly effective as solidification proceeded. Figure 6a shows the best 12 mm dia boule grown during the program, and fig 6b shows a series of cross-sectional slices that reveal internal cracks, twins caused by mechanical stresses, and grain boundaries. These were not considered to be serious problems as our previous experience with $AgGaSe_2$(7) has shown that these effects can be eliminated through the use of seeds. Cross-sections were sufficient to obtain optical absorption spectra on all of the samples grown which was our primary objective.

Optical Characterization - We analyzed each crystal for its short wavelength optical absorption using boule cross-sections a few millimeters in thickness and a Perkin Elmer Lambda 9 spectrophotometer. Typical absorption spectra are shown in fig. 7a-7e. All of our crystals displayed optical absorptions in the 12 - 45 cm^{-1} region at 1 μm. (Lower values, in the range of 8-9 cm^{-1} had been reported earlier by Buehler and Wernick(5) in crystals grown under near-isothermal conditions with 1.5% excess ZnP_2, and in the range of 5-6 cm^{-1} in crystals grown at lower temperatures, again under isothermal conditions, using Bi as a solvent. Their results suggested that the anomolous short wavelength absorption in $ZnGeP_2$ might be due to point defects caused by high temperature equilibrium deviations from stoichiometry.) In our experiments which were carried out in somewhat higher temperature gradients, 1 μm absorption coefficients (12 cm^{-1}) in crystals grown from charges with stoichiometric quantities of ZnP_2 (crystal 16b), were as low as coefficients measured on crystals synthesized with 1.5% excess ZnP_2 under similar P_4 compensation (crystal 17b). The vertical Bridgman technique is necessarily a moderate to high temperature gradient technique, and we were not able to test the effects of low thermal gradients on short wavelength transparency in order to compare with the results in (5). Our results, however, were not inconsistent with stoichiometry playing a significant role in the short wavelength absorption process. Figure 8 summarizes our findings.

3. Conclusions

Although we were able to grow $ZnGeP_2$ crystals with optical absorption coefficients as low as other melt grown crystals reported in the literature, no clear advantage in reducing 1 μm optical absorption appeared to be offered by the vertical Bridgman growth technique compared to the horizontal process. The horizontal process is, in fact, somewhat better suited to low temperature gradient operation which has already produced material with slightly lower 1 μm optical absorption. Further work involving the development of seeding techniques for the vertical method was, therefore, not proposed.

absorption in $ZnGeP_2$ crystals grown from melts synthesized under 3.5 atm. of P_2. The results, however, were not better than those of first-grown boules grown from charges synthesized under higher phosphorus overpressures. Nor, as this same figure shows, did we detect any differences due to the addition of excess ZnP_2 to the charges during synthesis. From these results, we concluded that reducing 1 μm optical absorption coefficients below 10 cm^{-1} by only controlling charge composition did not appear to be a promising approach compared to post growth annealing in atmospheres with excess zinc and phosphorus, which was part of a concurrent study carried out at Lockheed/Sanders(8).

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IV. FIGURE CAPTIONS

Fig. 1. Holmium doped YAG single crystal fiber grown at 0.3 mm/min. Doping application level was 11.2 M%. The as-grown quality appears good. In b) the dark irregular banding is due to lighting effects from small diameter changes, and not to changes in optical density of the fiber..

Fig. 2. Cross-sectional dark field optical micrographs of YAG single crystal fibers:
a) Longitudinal section 6% Tm:YAG grown in air,
b) Axial section 6% Tm:YAG grown in air,
c) Longitudinal section 0.5% Ho:6% Tm:YAG grown in air,
d) Axial section 0.5% Ho:6% Tm:YAG grown in air.

Fig. 3. Optical absorption spectrum of $ZnGeP_2$.

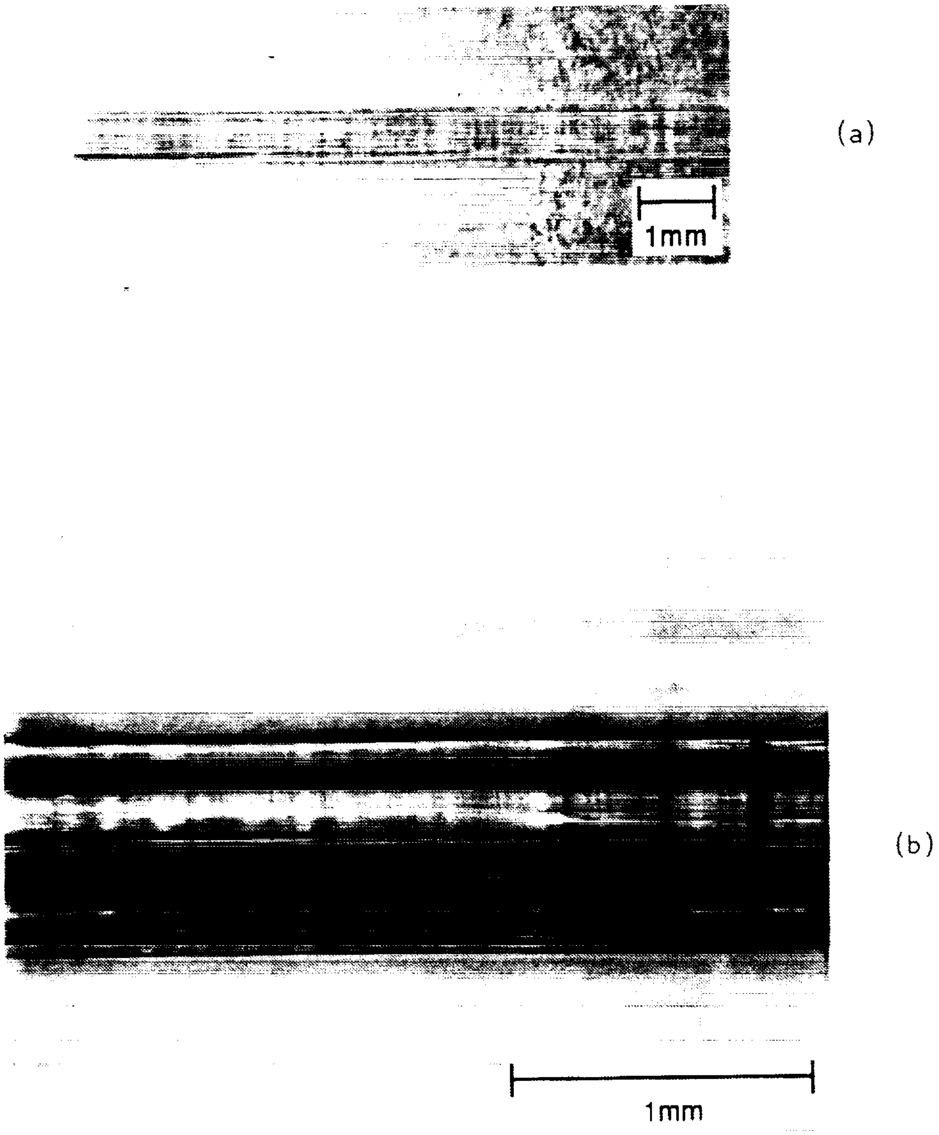
Fig. 4 Phase equilibria in the ZnP_2-Ge pseudobinary system(4).

Fig. 5 Procedure developed for synthesizing $ZnGeP_2$ with good control over charge composition.

Fig. 6 $ZnGeP_2$ crystal (17b) grown by the vertical Bridgman method.
a.) As-grown boule,
b.) Cross-sectional study showing multiple grains, twins and cracks due to differential thermal expansion between the various grains.

Fig. 7 Absorption spectra of $ZnGeP_2$ crystals appearing in Table IV.
a.) Crystal 15c,
b.) Crystal 15d,
c.) Crystal 16b,
d.) Crystal 17b - top, and
e.) Crystal 17b - bottom.

Fig. 8 Summary of the effects of starting composition and phosphrous compensation on optical absorption in $ZnGeP_2$ crystals.



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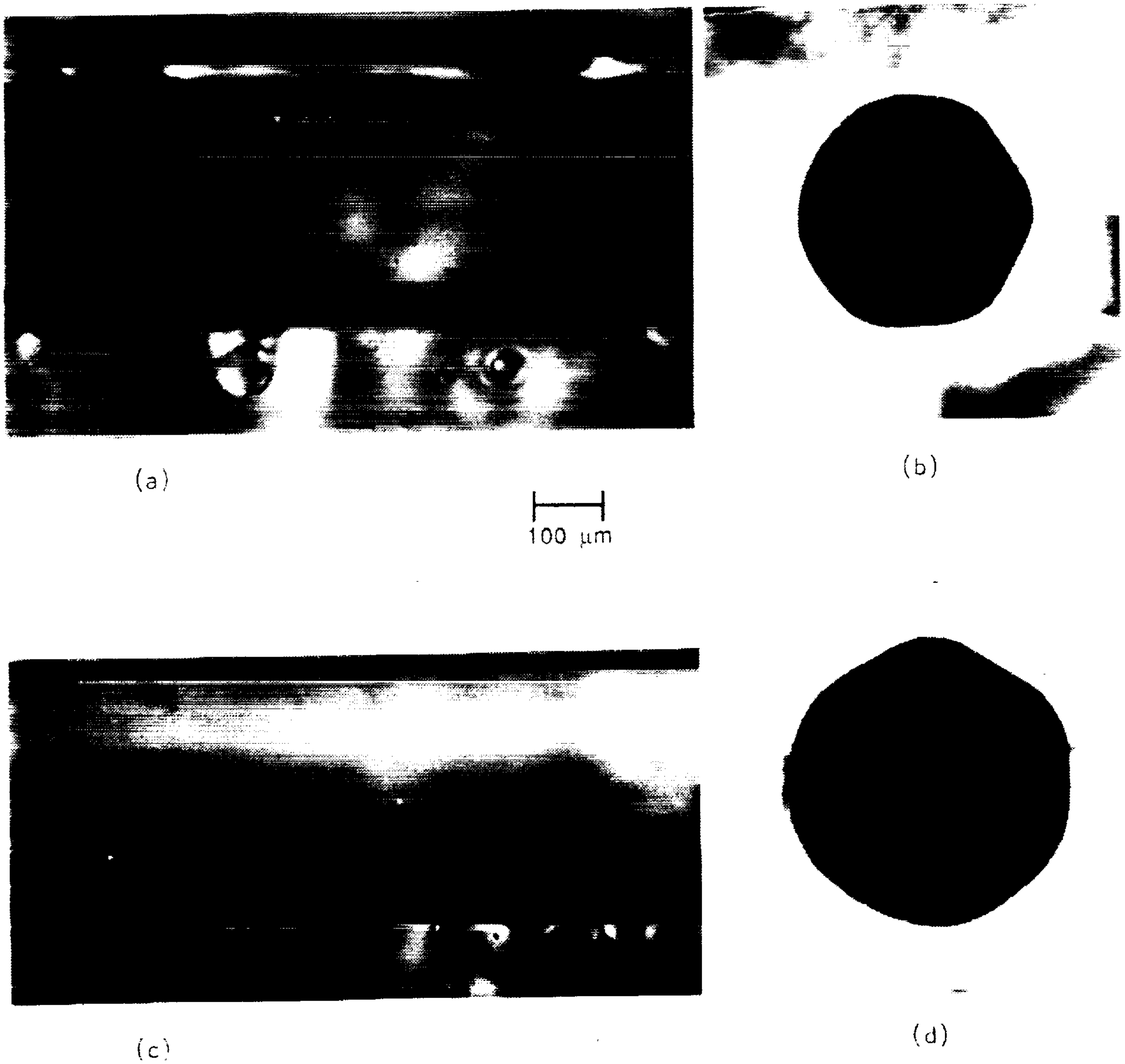

Fig. 2. Cross-sectional dark field optical micrographs of YAG single crystal fibers:
a) Longitudinal section 6% Tm:YAG grown in air,
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c) Longitudinal section 0.5% Ho:6% Tm:YAG grown in air,
d) Axial section 0.5% Ho:6% Tm:YAG grown in air.

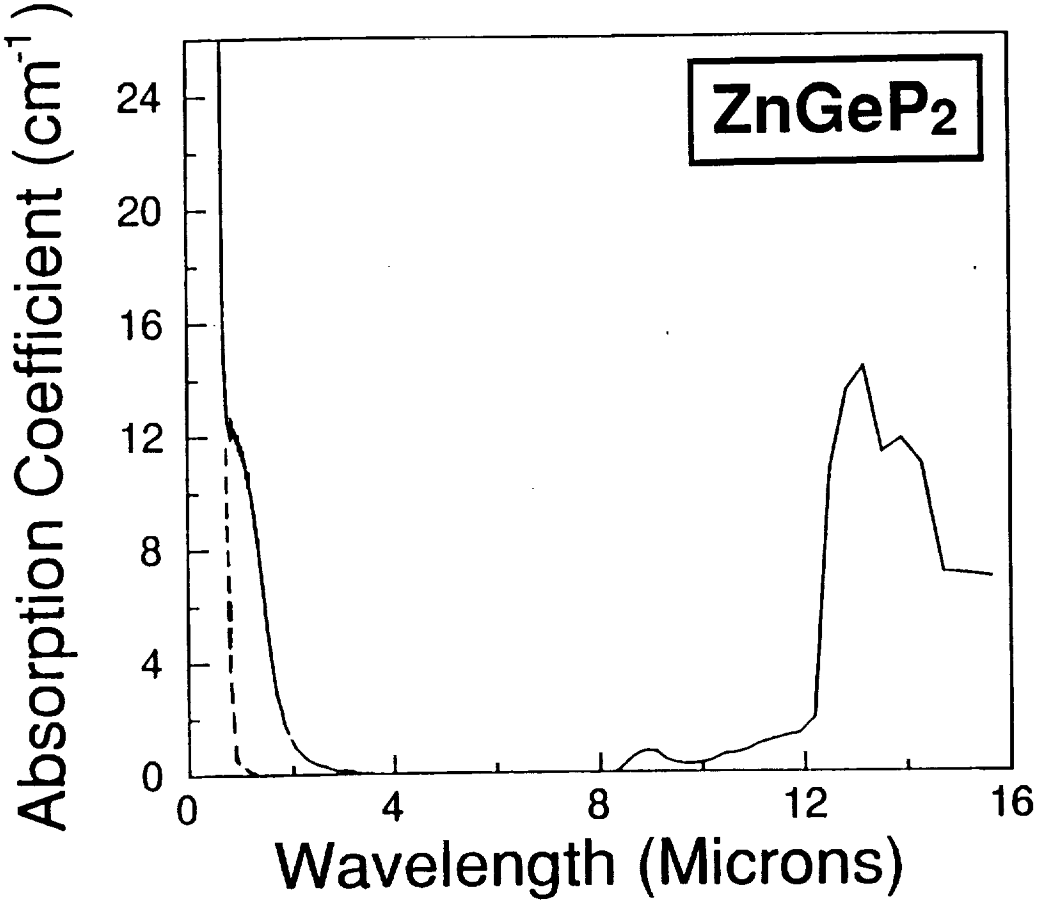

Fig. 3. Optical absorption spectrum of $ZnGeP_2$.

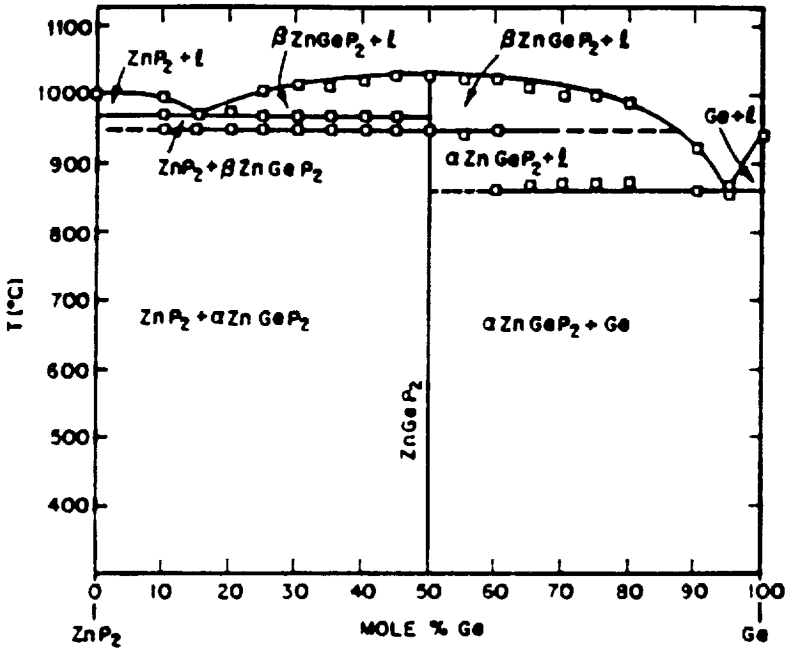

Fig. 4 Phase equilibria in the ZnP_2-Ge pseudobinary system$^{(5)}$.

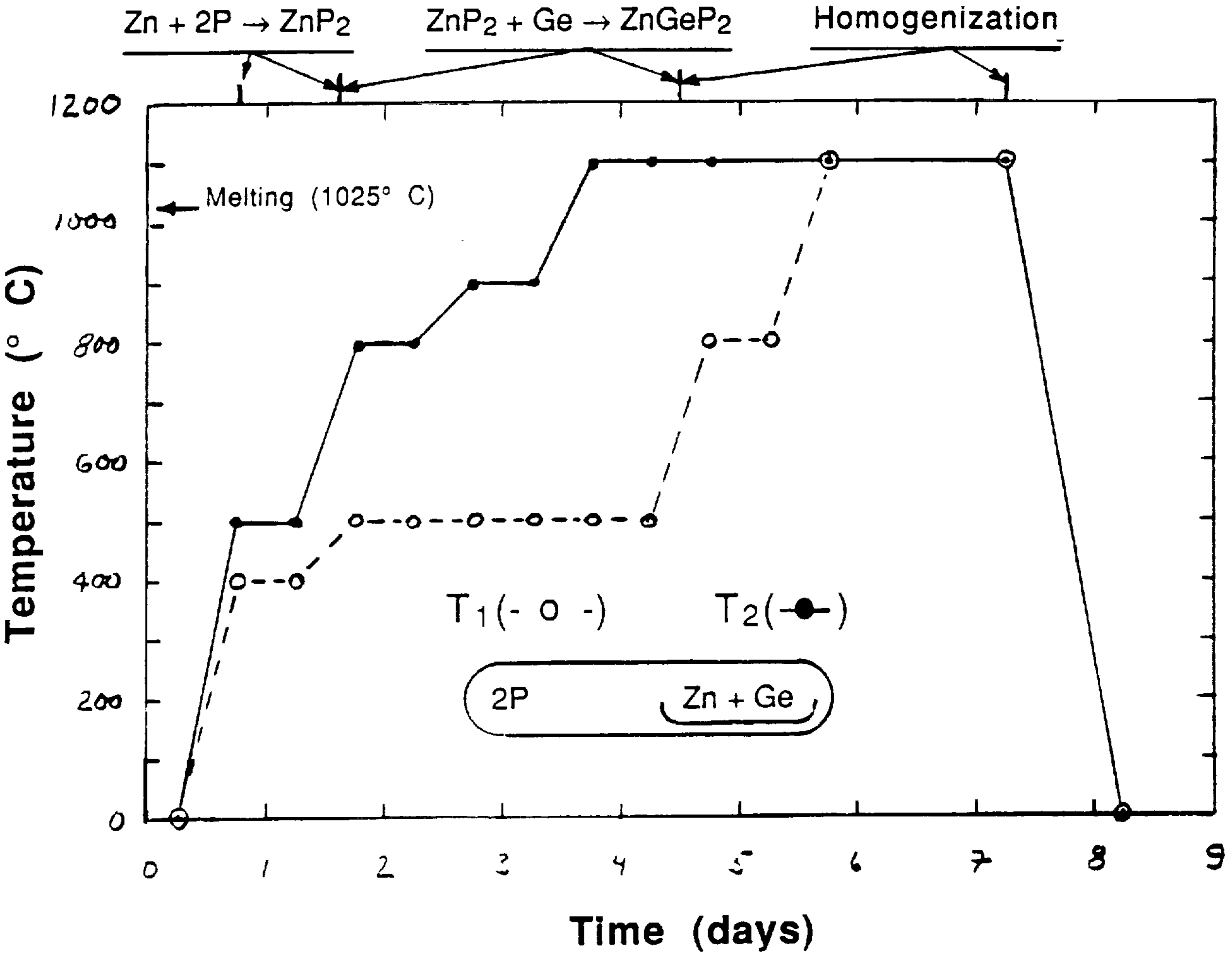

Fig. 5 Procedure developed for synthesizing $ZnGeP_2$ with good control over charge composition. Reactants were vacuum sealed in a fused silica ampoule with the matetallic constituents contained in an open machined graphite boat shown schematically.

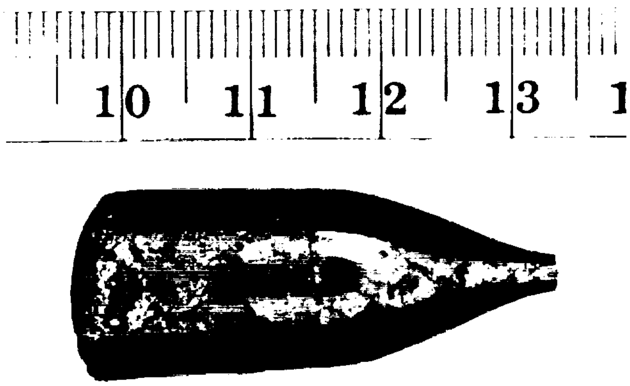

Fig. 6 $ZnGeP_2$ crystal (17b) grown by the vertical Bridgman method.
a.) As-grown boule.

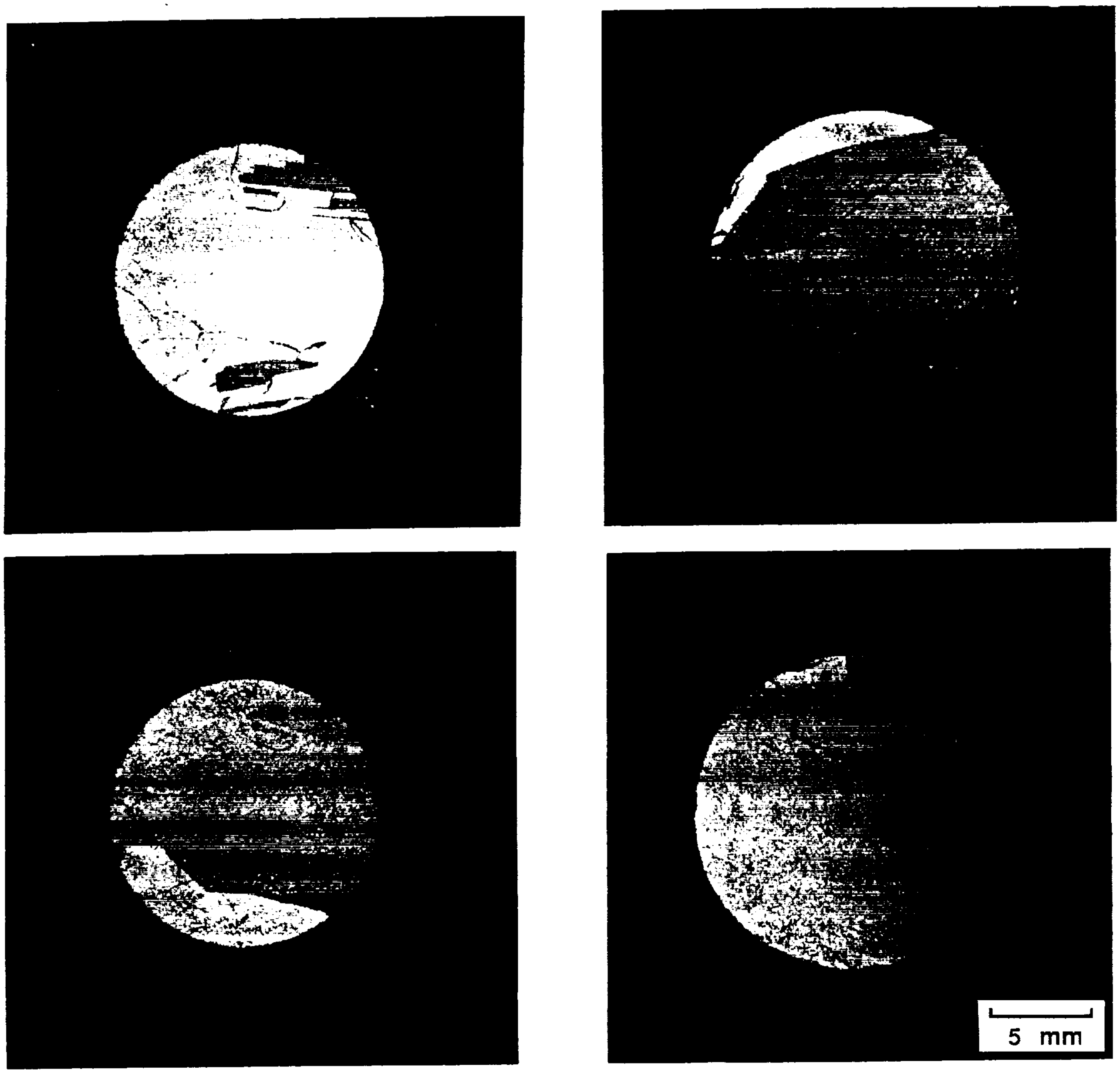

Fig. 6 $ZnGeP_2$ crystal (17b) grown by the vertical Bridgman method.
b.) Cross-sectional study showing multiple grains, twins and cracks due to differential thermal expansion between the various grains.

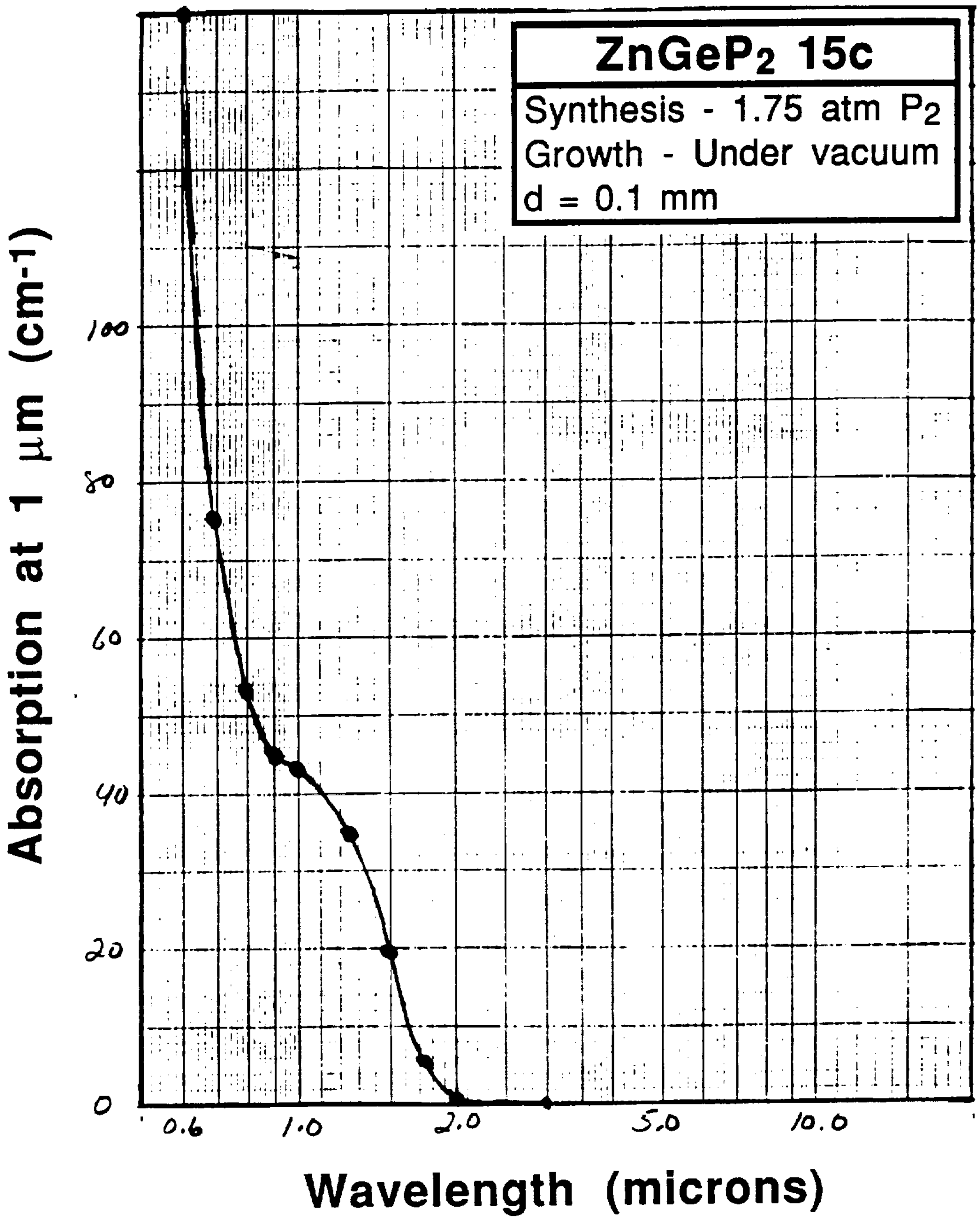

Fig. 7 Absorption spectra of ZnGeP$_2$ crystals appearing in Table IV.
a.) Crystal 15c.

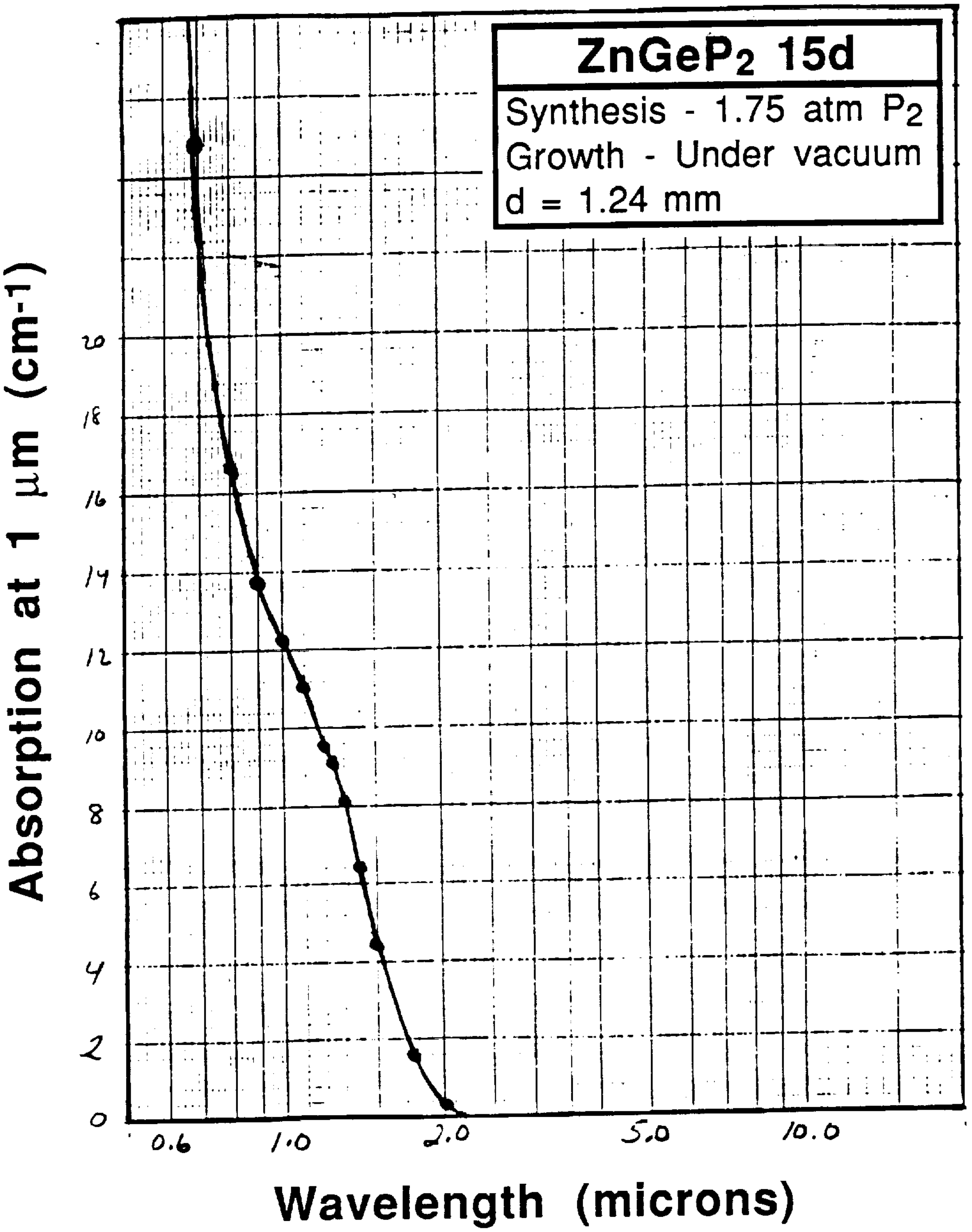

Fig. 7 Absorption spectra of $ZnGeP_2$ crystals appearing in Table IV.
b.) Crystal 15d.

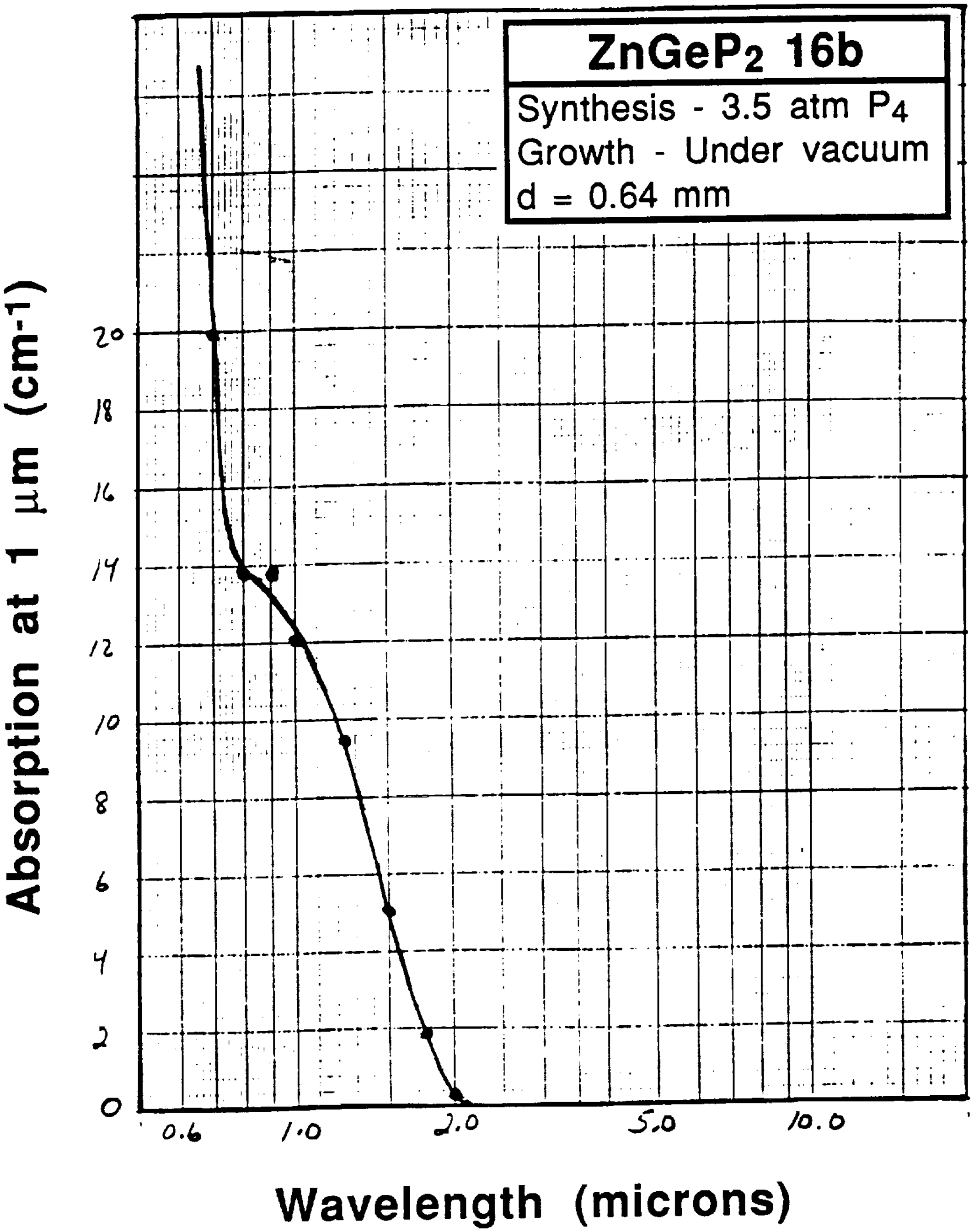

Fig. 7 Absorption spectra of $ZnGeP_2$ crystals appearing in Table IV.
c.) Crystal 16b.

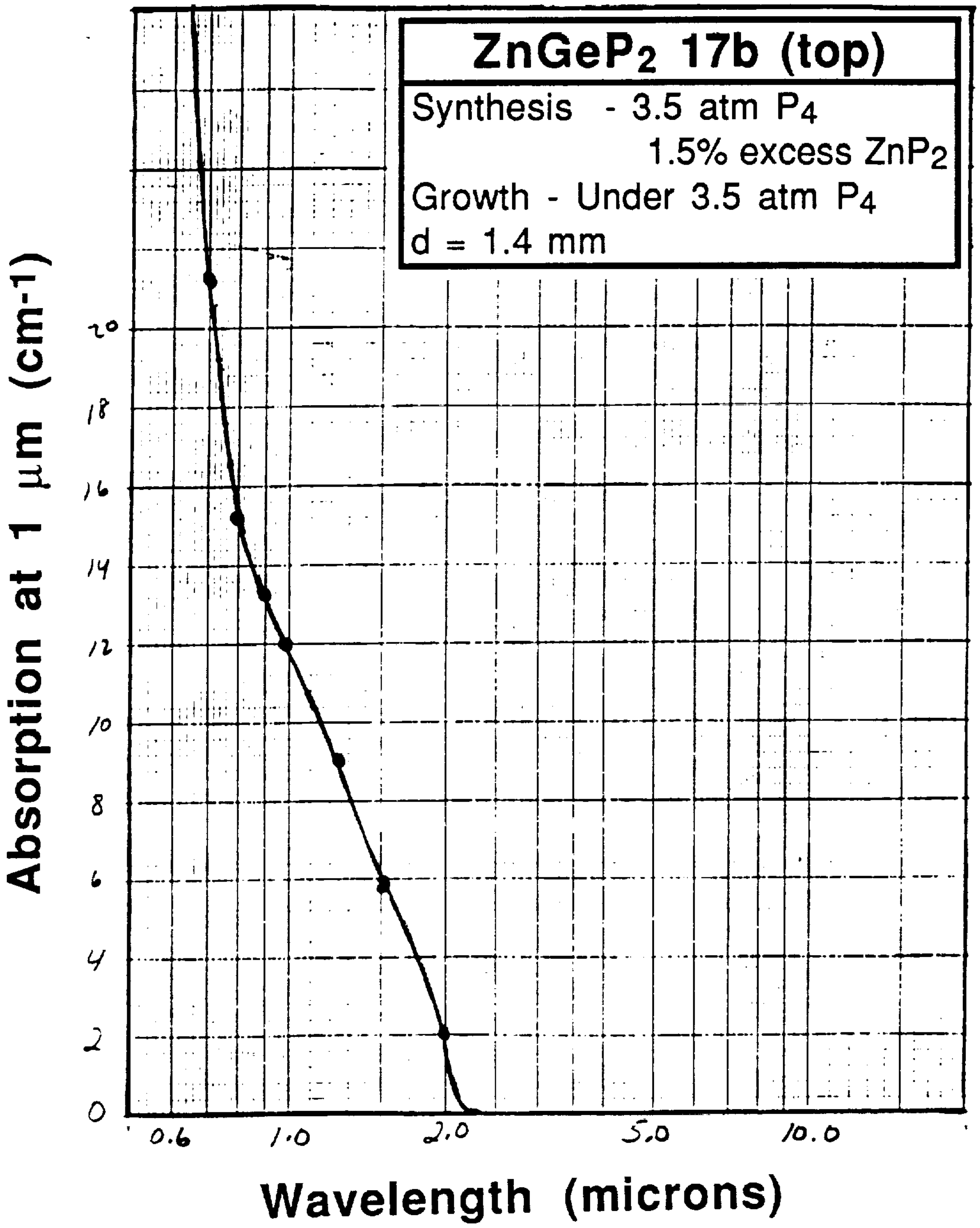

Fig. 7 Absorption spectra of $ZnGeP_2$ crystals appearing in Table IV.
d.) Crystal 17b - top.

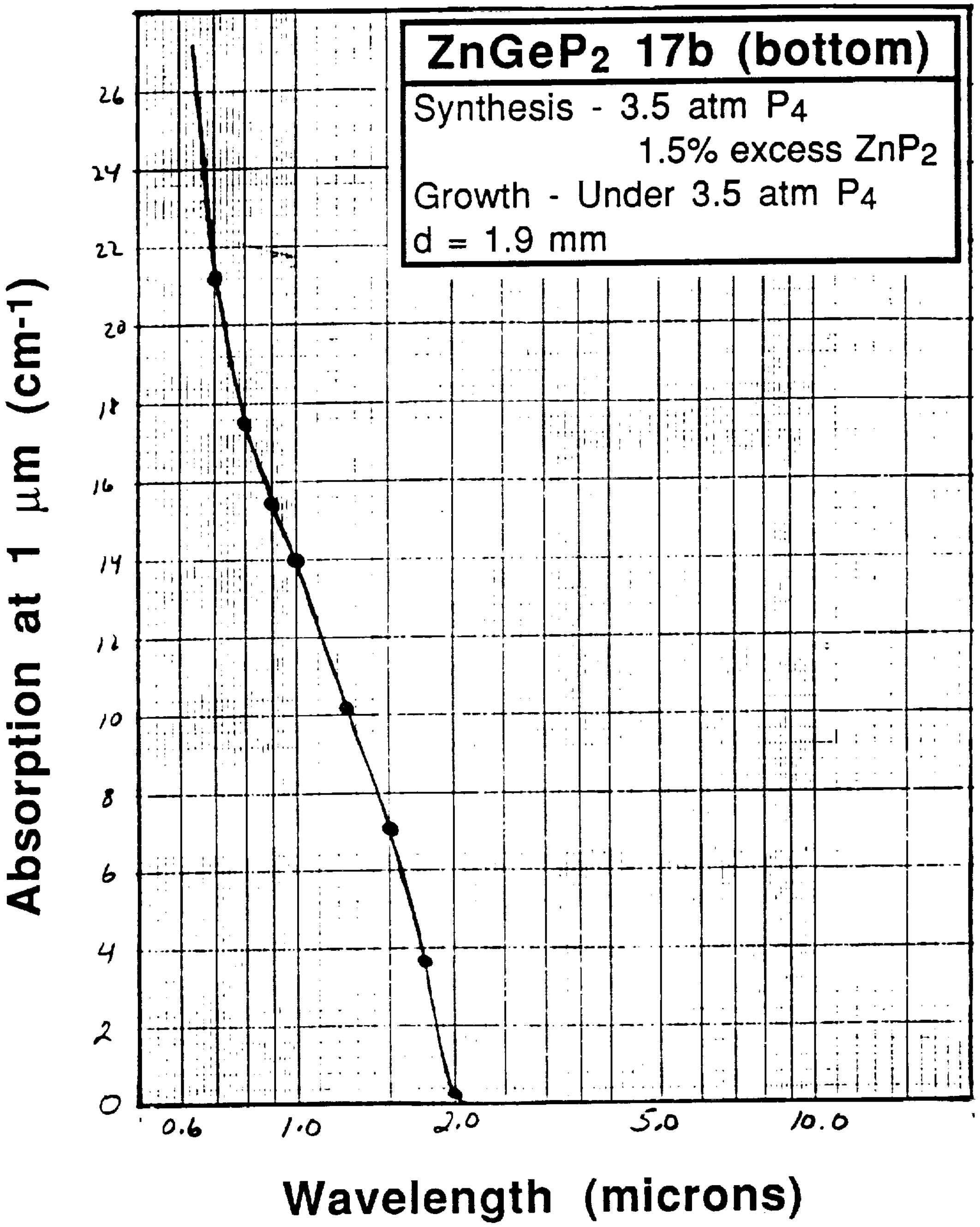

Fig. 7 Absorption spectra of $ZnGeP_2$ crystals appearing in Table IV.
e.) Crystal 17b - bottom.

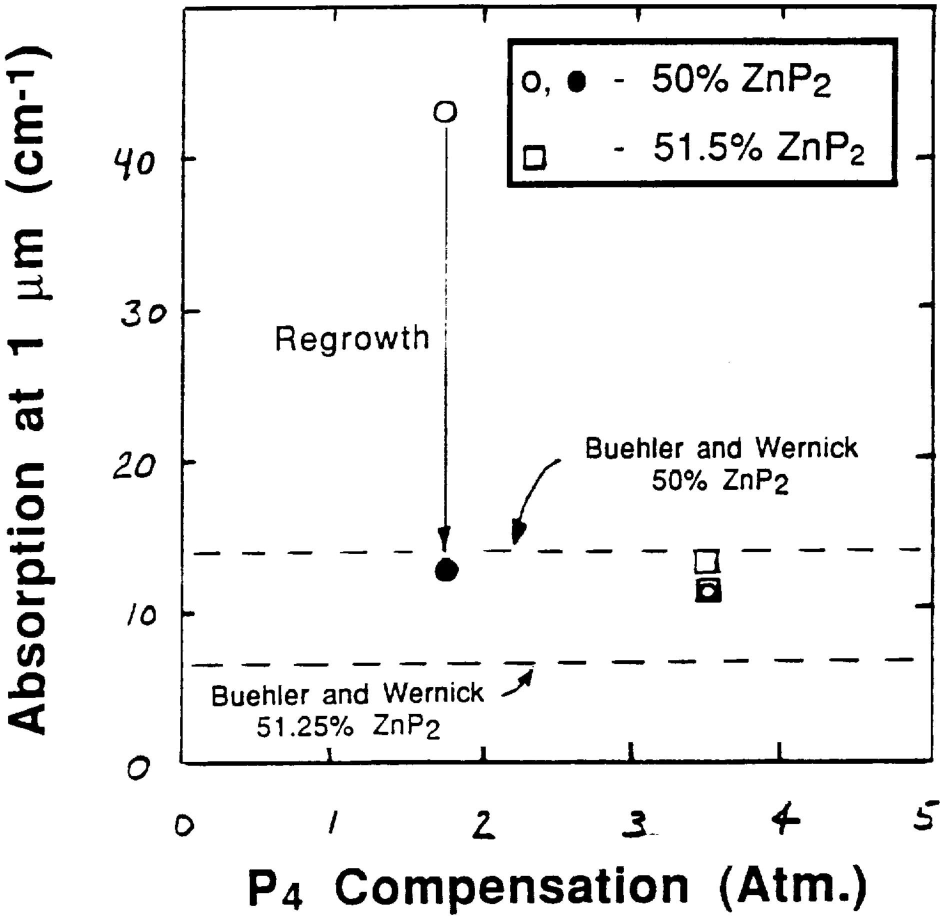

Fig. 8 Summary of the effects of starting composition and phosphrous compensation on optical absorption in $ZnGeP_2$ crystals.

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This is the final technical report on the cooperative NASA program "Growth of New Materials for Solid State Laser Applications," covering the period from 9-1-86 through 3-31-91. The first two and one half years of the program, from 9-1-86 through 3-31-89 was devoted to the development of new eye-safe laser sources. Single crystal fibers of rare earth doped and co-doped YAG were grown by the laser-heated pedestal growth method, characterized for their structural properties and supplied to NASA/Langley for spectroscopic evaluation. From 4-1-89 through 3-31-91, research focused on the growth of zinc germanium phosphide for nonlinear optical applications in the IR. The vertical Bridgman growth process was evaluated as a means to achieve better control over the short wavelength optical absorption in this material that adversely affects 2 µm-pumped optical parametric oscillators.

14. SUBJECT TERMS Solid State laser materials, co-doped YAG, single crystal YAG fibers; $ZnGeP_2$, zinc germanium phosphide, nonlinear infrared materials

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