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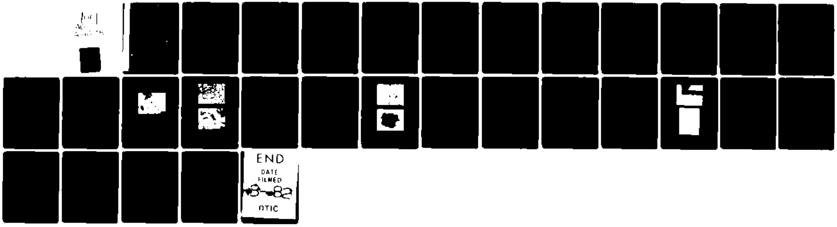

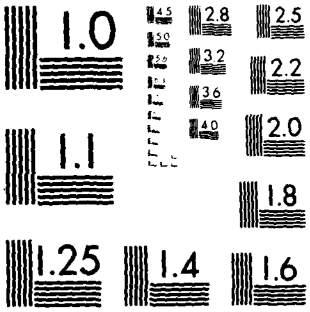
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FABRICATION STUDIES OF TERNARY RARE EARTH SULFIDES FOR INFRARED APPLICATIONS

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RAYTHEON COMPANY
RESEARCH DIVISION
WALTHAM, MA 02254

MAY 1981

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FINAL TECHNICAL REPORT
for Period 1 June 1980 to 31 May 1981

Prepared for
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Homogeneous, phase pure powders of cubic $CaLa_2S_4$ have been synthesized. The process developed has yielded powder with very fine particle size without the need for milling or mixing. The processing time has also been substantially reduced. It appears that the purity and morphology of these powders will allow one to produce highly transparent window blanks using standard sintering and/or hot isostatic pressing techniques.

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Although initial single crystal growth experiments have failed to produce useful samples, other approaches remain to be explored. However, it now appears that the more direct powder processing methods will be capable of producing optical quality material and, in fact, is the approach of more practical interest.

FOREWORD

This report was prepared by Raytheon Company, Research Division, Waltham, Mass., under Contract No. N00014-80-C-0430, entitled, "Fabrication Studies of Ternary Rare Earth Sulfides for Infrared Applications." This work was administered under the direction of the Office of Naval Research, Arlington, VA. Lt. Cmdr. Wayne Savage was the project monitor.

At Raytheon Research Division, this work was performed in the Advanced Materials Department. Dr. Randal W. Tustison was the Program Manager and Principal Investigator.

The author would like to take this opportunity to thank Mr. Ken Saunders and Mr. Joe Medici for their competent technical assistance and enthusiasm throughout the course of the project. In particular, Mr. Saunders has done an excellent job in leading the powder processing effort. He would also like to thank Mr. Dwight Howe for performing x-ray analysis of the synthesized material as well as Mr. Wai Tye for taking the SEM micrographs. The author is also grateful for the assistance of Ms. M. Ridge in preparing this manuscript as well as all of the quarterly reports.

During the course of this investigation the author benefitted greatly from technical discussion with Dr. J. Pappis, Manager of the Advanced Materials Department, Dr. W. Moser of Badger Co. and Dr. P. Miles of Raytheon Missile Systems Division, who originally suggested this project.

This Final Technical report covers work performed during the period 1 June 1980 to 31 May 1981. This report was given the Raytheon internal number S-2925.

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SECTION I
INTRODUCTION

There has been a long standing need for an optical material that is both transparent in the spectral range 0.4 to 14 microns and capable of withstanding the harsh environment imposed by high-speed flight through the lower atmosphere. The search for such a material has been painstaking and generally unsuccessful. While alkali-halides have served as ideal wide band windows in the ultraviolet, visual, near and far infrared in laboratory equipment, they are generally weak and/or water soluble and hence cannot serve as external optics on airborne systems. On the other hand, silicon and germanium are both more durable materials but silicon exhibits too great a multiphonon absorption between 8 and 12 microns to be used as a monolithic window, while germanium develops strong free carrier absorption at temperatures above 40°C. The nearest practical approach to a true multispectral window has been the development at Raytheon Company of CVD forms of ZnSe and ZnS. While ZnS has been demonstrated to be more durable than germanium and has been chosen as the window and dome material for current state-of-the-art infrared systems such as PAVE TACK and IIR Maverick, it is of limited use at wavelengths beyond 11 μm due to its intrinsic multiphonon edge absorption. On the other hand, highly transparent ZnSe shows surface erosion and internal fractures under raindrop impact at air speeds beyond 400 mph. However, preliminary work at Penn State University[1] indicates that ternary rare-earth (TRE) sulfide compounds having the cubic Th_3P_4 structure (e.g., $CaLa_2S_4$, $SrNd_2S_4$ etc.) hold promise of both enhanced transparency (visible to 18 μm) as well as increased durability (e.g., Vickers $\geq$ 500). Unfortunately, the present state-of-the-art of hot pressed TRE sulfides[1] provides a minimum scatter/absorption level of about 14 cm^{-1} at a wavelength of 17.5 microns (25% internal transmittance in a 1 mm thick sample). This compares to less than $10^{-3} cm^{-1}$ in the maximum transparency range of CVD ZnSe used in laser optics and the goal of $10^{-2} cm^{-1}$ sought in high quality FLIR optics, a level that is approached by the best CVD ZnS. Clearly, major advances in present fabrication techniques are needed in order to realize in practice the potential of TRE sulfides.

The initial thrust of this investigation has been two-fold. The first objective was to satisfy a need for small, fully dense samples of TRE sulfides (specifically $CaLa_2S_4$) for definitive optical and mechanical evaluation. This would be of greater value in assessing the ultimate potential of these materials as infrared, visual, and ultraviolet windows. Secondly, to further densify and thereby increase the optical transparency of the material produced by conventional hot pressing methods by subjecting the same to hot isostatic pressing. The following summarizes the results during the past contractual period and recommends additional areas of experimentation.

SECTION II
PROGRESS SUMMARY

2.1 TRE Sulfide Synthesis

A major portion of the experimental effort has been directed toward the production of high purity $CaLa_2S_4$ powder. This is of primary importance considering the fact that this serves as the source material for subsequent hot pressing and single crystal growth experiments. It was also apparent from the literature that the production of "phase pure" $CaLa_2S_4$ is a difficult task, the major impurities being mono and oxysulfides. Generally these sulfide compounds are present as a result of incomplete sulfurization, $La_2O_2S_2$ and La_2O_2S being intermediate products.[2]

The most commonly used procedure for compounding $CaLa_2S_4$[1] involves the dry firing of La_2O_3 and $CaCO_3$ in flow H_2S at temperatures in excess of 1000°C. The apparatus used during the present investigation is illustrated schematically in Figure 1. With the exception of the quartz reaction chamber and ground quartz joint, all fixtures were teflon including stopcocks and solenoids. Prior to each experiment the apparatus was throughly leak tested. Either H_2S or CS_2 can be used as the primary reactant and was metered into the reaction chamber along with He. This chamber was lined with a graphite furnace tube and the powder charge (La_2O_3 + $CaCO_3$) was contained in a vitreous carbon boat so that the cavity around the powder was entirely carbon. While some authors feel that the presence of carbon helps to inhibit the formation of the non-cubic beta phase[3] careful experimentation has shown this not to be correct and was done here only to provide a relatively inert environment during firing, isolating the charge from the quartz reactor tube which tends to devitrify with prolonged use.

The raw materials used were supplied primarily by A. D. Mackay but a list of potential suppliers is presented in Table 1. All starting powders

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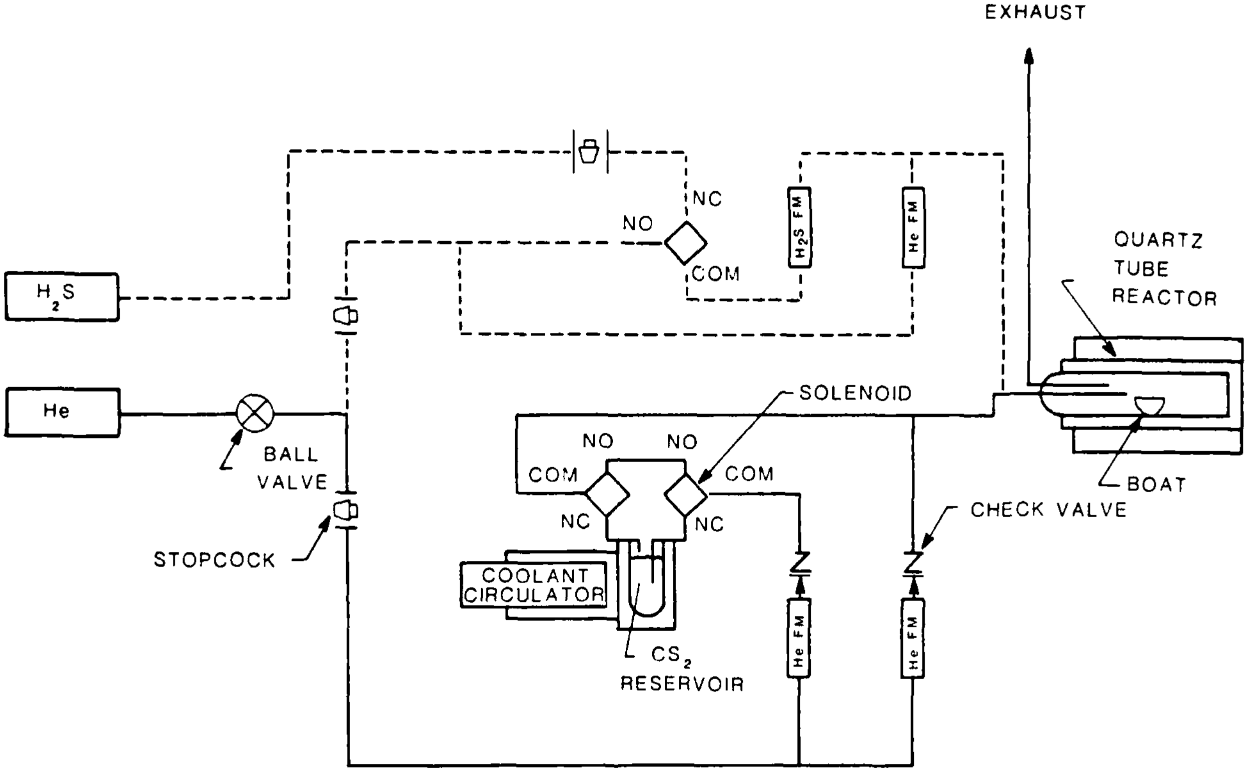

Figure 1. TRE sulfurization system.

TABLE 1

PARTIAL MATERIALS SOURCE LIST

Compound	Type	Supplier	Quantity	Approx. Cost/gm
La_2O_3	99.9	Cerac, Inc.	230 gm	0.08
	99.99	Electronic Space	100 gm	0.59
	99.99	Research Chemicals	1000 gm	0.02
	99.99	United Mineral	100 gm	0.35
	99.99	A. D. Mackay	1 lb	0.08
	99.99	Molycorp., Inc.	1/2 lb	gratis
	ultrapure	Ventron/Alfa	25 gm	0.89
	99.997	Research Chemicals	100 gm	0.20
	99.999	United Mineral	100 gm	0.50
	99.9999	Ventron/Alfa	5 gm	7.50
	99.9999	Atomergic	1 lb	1.43
LaS_2	99.9	A. D. Mackay	100 gm	3.15
La_2S_3	99.99	A. D. Mackay	100 gm	2.67
	99.99	Gallard-Schelsinger	50 gm	4.00
	99.99	Electronic Space	50 gm	4.20
$CaCO_3$	prim.std.	Scientific Products	1/2 lb	0.11
	ultrex	J. T. Baker (VWR)	100 gm	1.35
	99.98	A. D. Mackay	200 gm	1.20
	99.98	Cerac, Inc.	200 gm	0.58
	99.9975 (puratronic)	Ventron/Alfa	25 gm	2.08
	99.999	Atomergic	100 gm	3.00
	99.999	Gallard-Schlesinger	25 gm	3.40
CaS	99.99	A. D. Mackay	200 gm	0.47
	99.9	Electronic Space	100 gm	1.95
	99.99	Gallard-Schlesinger	100 gm	0.75

were baked out for a minimum of 24 hours in a vacuum drying oven before use. This was very important as La_2O_3 is hydroscopic and the unknown adsorption of water from the air will result in a non-stoichiometric mixture. Prior to firing, La_2O_3 and $CaCO_3$ were removed from the drying oven and weighed out in the correct proportions in a N_2 dry box. This mixture was then placed into a 4 ounce jar and mixed on a Spex mixer for 10 minutes. Approximately a 5 g charge was then placed into the reactor and a He purge was established while the remaining mix was returned to the drying oven. Firing times varied from 5 to 100 hours at temperatures between 1000° and 1060°C.

X-ray diffraction patterns of three of the fired powders are shown in Figure 2. These particular samples were all fired for 36 hours under three different conditions. Three phases are evident in each of the patterns, cubic $CaLa_2S_4$, cubic CaS, and orthorhombic La_2S_3. Strong oxysulfide reflections disappear after approximately 5 hours firing. The degree to which $CaLa_2S_4$ has been formed can be estimated by comparing the CaS(200) reflection with the neighboring (310) reflection of $CaLa_2S_4$. After firing for 36 hours in H_2S at 1000°C (b) the CaS reflection is relatively pronounced while the same treatment with CS_2 (a) converts substantially more material. From a thermodynamics viewpoint, sulfurization via CS_2 is preferable because it yields a larger free energy change.[4] This is evident by comparing 2a and 2b. However, all of the powders prepared with CS_2 contained very fine particles of carbon as a contaminant. To avoid this complication, H_2S was used in all latter sulfurizations. The "best" maerial (c) was obtained by increasing the firing temperature from 1000°C to 1060°C.

W. B. White's[1] prescription for $CaLa_2S_4$ synthesis followed a similar format, extending these firing times to 4-5 days. He reports that after this time phase pure powders were produced. Following this lead, the firing time was extended to 100 hours and the diffraction pattern of the resultant powder is shown in Figure 3. Even after 100 hrs there is still some evidence of CaS and non-cubic La_2S_3 in the pattern. A second diffraction pattern was taken after the same powder had been intentionally doped with 5 percent CaS. Based

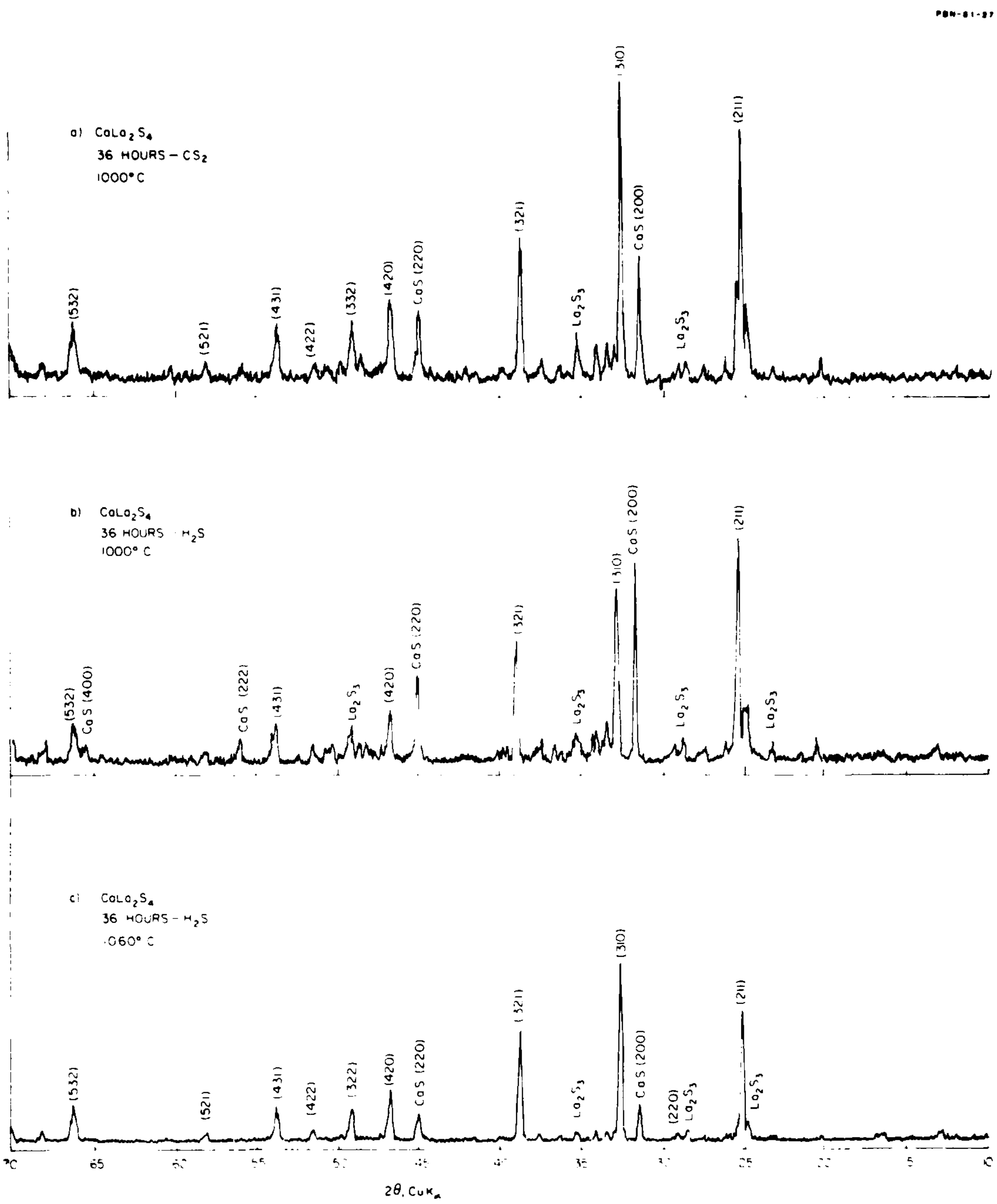

Figure 2. X-ray diffraction patterns for three powders fired under different conditions. Three phases are present in each pattern.

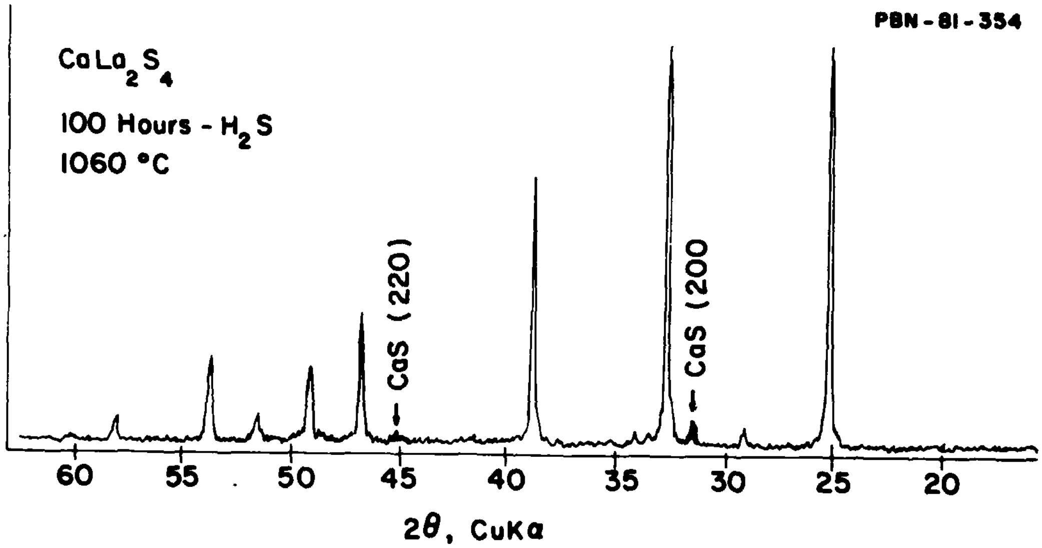

Figure 3. X-ray diffraction pattern of CaLa$_2$S$_4$ fired for 100 hours at 1060°C. Small amounts of CaS (and presumably La$_2$S$_3$) are still present.

on the increase in the CaS (200) peak intensity on doping it is estimated that the reflection evident in Figure 3 represents 3-5 percent CaS by weight with a detection sensitivity of about one percent. SEM micrographs of the powder before and after firing along with microprobe analysis revealed one problem. There exists a definite bi-modal particle size distribution with $CaCO_3$ crystal cubes 15 microns on an edge interspersed with large agglomerates of La_2O_3 typically 150 microns in diameter (Figure 4). The non-intimate nature of the mixture inhibits the complete transformation of $CaLa_2S_4$, a process relying on solid state diffusion. A much more intimate, homogeneous starting mixture was deemed desirable. The simplest approach involved passing of the starting powders through a 400 mesh sieve prior to mixing and firing. In fact this did reduce the amount of residual CaS. Jet milling of the starting materials was also attempted and while this greatly reduced the particle size, impurities from the lining of the mill were introduced.

There are several alternative methods that can be used to produce very fine homogeneous powders. Four techniques of particular interest are, (1) vapor phase reaction, (2) sol-gel processing, (3) freeze drying, and (4) co-precipitation. In the case of $CaLa_2S_4$, vapor phase reaction is limited by the lack of volatile compounds from which to choose reactants, while the sol-gel method generally requires more extensive apparatus. The latter two approaches seemed most appropriate and direct.

The method of co-precipitation was chosen because it was a very simple and potentially economical process. Two precipitation processes are currently being investigated, co-precipitation of mixed carbonates and mixed sulfates. Initial results are very encouraging. Two SEM micrographs are presented in Figure 5, one (5a) showing the mixed carbonate product as-precipitated and (5b) the original mixture of La_2O_3 + $Ca\ CO_3$, for the sake of comparison. An X-ray diffraction pattern of the precipitate shows a considerable amount of line broadening indicating that a large fraction of the particles present are a few hundred angstroms or less in diameter. Surface area analysis (Table 2) confirms the fact that a large reduction in particle size has taken place (relative to the oxide-carbonate mix) as the surface area has been increased

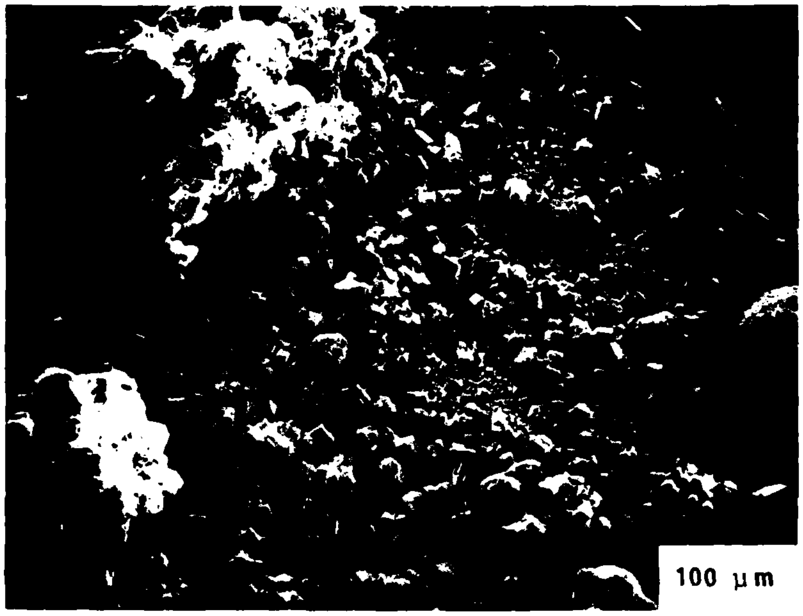

Figure 4. SEM micrograph of a mixture of La_2O_3 and $CaCO_3$ before firing. The small cubes are $CaCO_3$. The La_2O_3 particles vary dramatically in size from fine powder (background) to the large agglomerates, 200X.

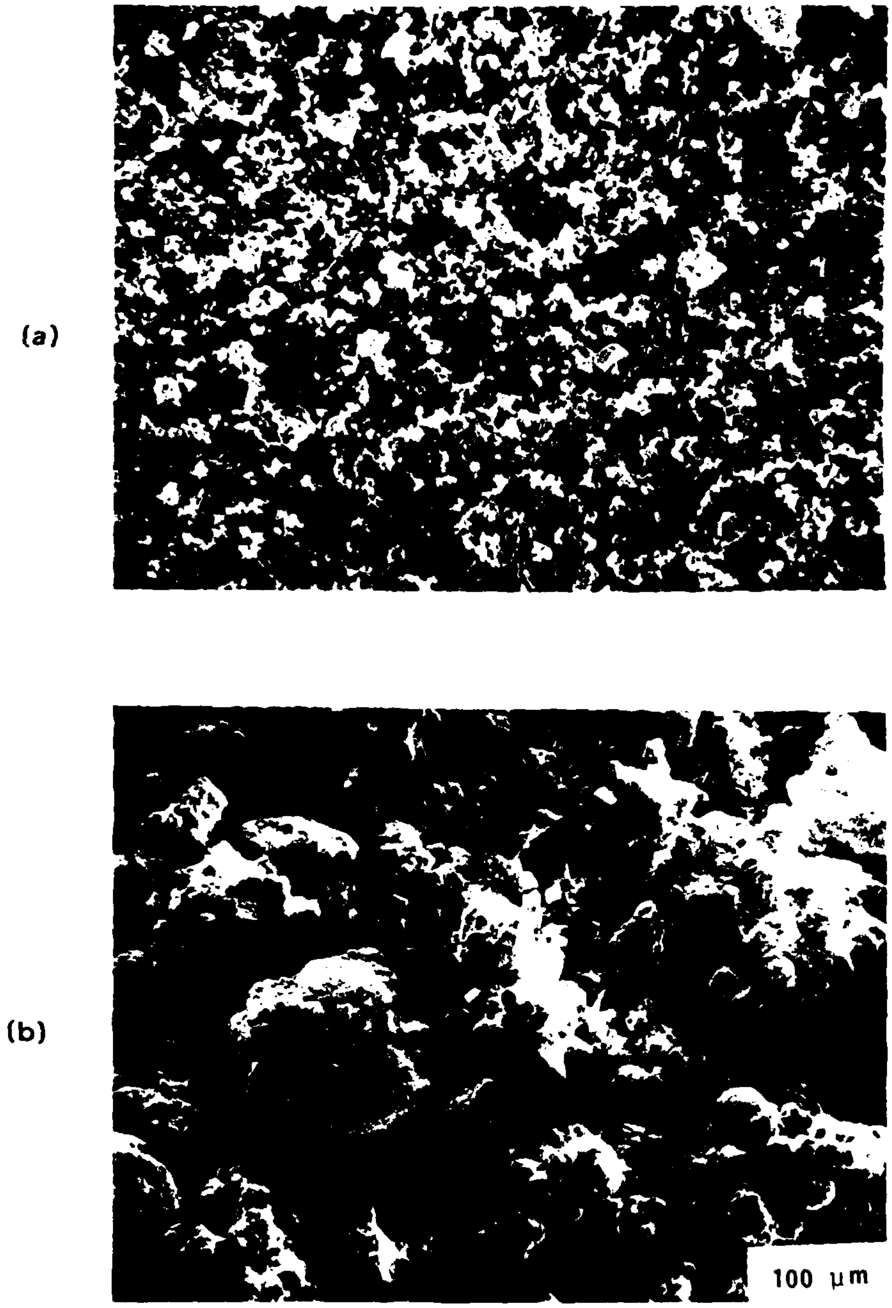

Figure 5. Two SEM micrographs showing, (a) the mixed carbonate powder, as-precipitated and, for comparison, (b) the much coarser mixture of $CaCO_3$ + La_2O_3 as shown in Figure 4, 200X.

TABLE 2

SURFACE AREA OF SEVERAL POWDERS AS MEASURED BY N_2 ADSORPTION*

Compound	Supplier	Grade	Surface Area (m^2/g)
$CaCO_3$	J. T. Baker	Ultrex	0.61
	A. D. Mackay	99.98	0.88
La_2O_3	Research Chemicals	99.99	0.73
	A. D. Mackay	99.99	0.58
	Research Chemicals	99.997	0.72
Ca-La-CO_3	Raytheon precipitate	-----	35.6
Ca-La-SO_4	Raytheon precipitate	-----	7.6
$CaLa_2S_4$	W.B. White-ball milled	-----	0.5(2)
$CaLa_2S_4$	W.B. White-fluid energy milled	-----	1.0(2)
$CaLa_2S_4$	W.B. White-attrition milled	-----	2.5(2)

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*Micromeritics Instrument Corp.; Automatic Surface Area Analyzer, Model 2200.

50 fold ! Figure 6a is a SEM micrograph of the same powder after firing for 36 hours in H_2S at 1060°C. Although coarsened, the particles appear rounded and of approximately the same size, averaging 2-5 microns in diameter. Unfortunately there was not a sufficient quantity of this powder available to carry out a surface area analysis. For comparison, 6b is a similar micrograph of a $CaLa_2S_4$ particle as shown in Ref 2 at the same magnification. Clearly, a substantial particle size reduction has been achieved without the need for milling which can introduce impurities. The X-ray diffraction pattern of this material suggests that it is single phase $CaLa_2S_4$ (Figure 7) produced after firing for only 36 hours at 1060°C. More recently, "phase pure" powders have been produced in as little time as twelve hours at 1060°C, while patterns identical to Figure 3 can be produced in just a few hours. Although many process parameters can be varied to further reduce the particle size (increase surface area) these initial results are very encouraging and suggest that the sinterability of $CaLa_2S_4$ has been substantially increased.

2.2 Sintering

Sintering experiments are underway in an attempt to produce highly transparent samples. In contrast to the hot pressed samples that are typically blackened to some degree during processing, those that have been cold pressed and then sintered in H_2S are light yellow in color and have been fired to 90% theoretical density (Ref. 2). Since densification is driven, in part, by the high surface free energy of the starting powder, one can anticipate that the high surface areas of the precipitated/sulfurized powders reported here will lead to sintered samples of at least as high a density, if not higher. Following sintering, if needed, full densification can be achieved via isostatic pressing, eliminating the need for the use of hot pressing as a prelude to the H.I.P. treatment. Hence, sintering of the co-precipitated powders is being pursued with the idea that, (1) optical quality samples may be produced via sintering alone, an inherently simple process, or (2) sintering could be followed by H.I.P. treatment, the processing combination eliminating hot pressing.

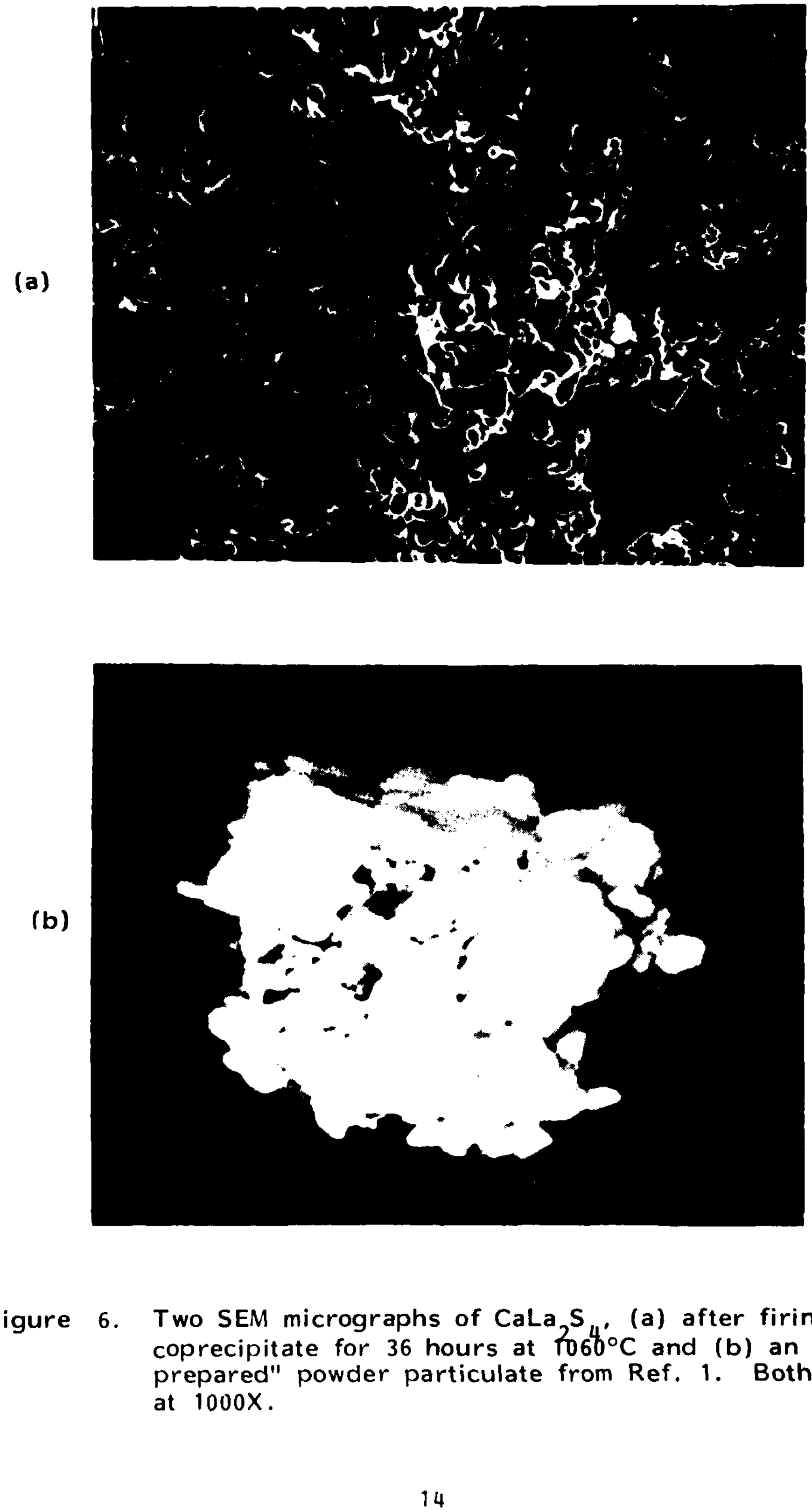

Figure 6. Two SEM micrographs of CaLa$_2$S$_4$, (a) after firing the coprecipitate for 36 hours at 1060°C and (b) an "as-prepared" powder particulate from Ref. 1. Both taken at 1000X.

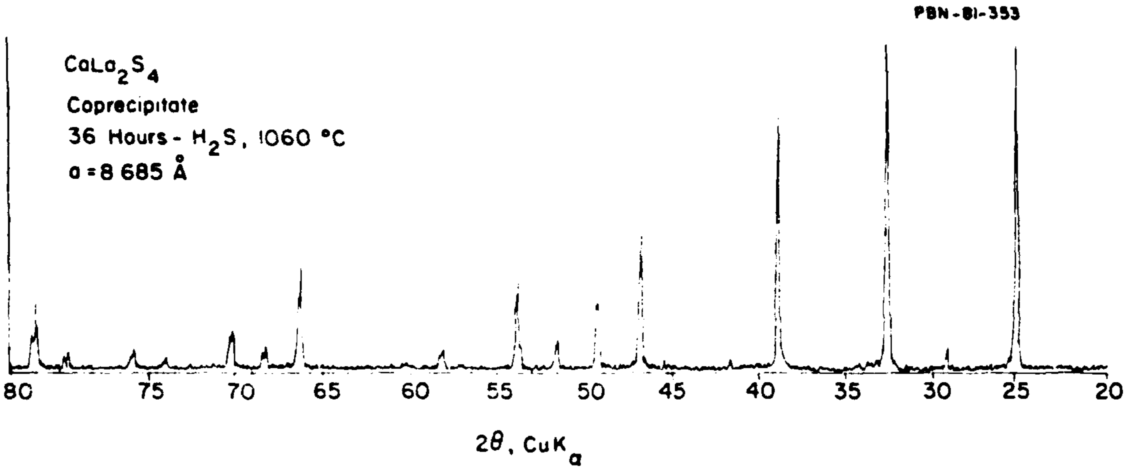

Figure 7. X-ray diffraction pattern of phase pure $CaLa_2S_4$ obtained after firing for 36 hours at 1060°C. The lattice parameter determination was obtained using a high angle extrapolation method.

2.3 Hot Pressing

One of the initial objectives of this program was to extend the state-of-the-art in the hot pressing of TRE sulfides. Attempts by other investigators have been plagued by time dependent deviations from stoichiometry and reaction of the powder with the die material.

Since the success of these experiments depends in large part on the availability of pure staring material, the beginning of hot pressing experiments has been delayed until sufficiently pure [illegible]$_2S_4$ could be produced. With the advent of the co-precipitated powders these experiments are now underway. Boron nitride coated dies are being prepared and will be used in an attempt to minimize the powder/die reactions. Hopefully, deviations from stoichiometry can be eliminated by controlling the ambient atmosphere during pressing and/or minimizing the pressing (densification) time. Again, the fine co-precipitated powders should be optimum.

2.4 Hot Isostatic Pressing

The most transparent samples reported to date have been produced via H.I.P. treatment (Ref. 1). As has been demonstrated with a variety of materials, under certain conditions can remove residual porosity present (as well as other deficiencies), in particular, improve the transparency of optical materials significantly.

We are currently in the process of establishing a laboratory for hot isostatic pressing and expect the delivery of a press in May. Although the temperature/pressure/volume parameters are interrelated, this piece of equipment will have, for example, the capability of processing pieces 8 inches in diameter at 30,000 psi and up to 2000°C. Hence, we will have available to us a previously unexplored temperature/pressure regime.

2.5 Single Crystal Growth

A primary objective of this program as stated in the introduction has been to provide fully dense, high quality samples of $CaLa_2S_4$ for definitive optical and mechanical evaluation. Single crystals would be ideal for this purpose. A closed tube vapor transport process was proposed as a technique for producing such samples. Historically single crystals of a number of ternary sulfide compounds had been produced via this method. The halogen elements were chosen as the most likely transporting agents, again based on available literature information. A relatively large crystal growing ampoule was designed, an example of which is shown in Figure 8. The diameter-to-length ratio was large in order to maximize vapor transport via convention by lowering the convection threshold pressure.[5] Pressures around 2 atm were also used in order to encourage transport via convection ($I_2 = 5$ mg/cm^3). The few previously reported attempts at crystal growth all suggested that the reactivity of the quartz ampoule during growth was a problem. To reduce this activity a thin coating of carbon was formed on the interior of the ampoule by the pyrolysis of benzene at 800°C. The preparation and charging of an ampoule was a long and tedious process, an outline of which is given here for the sake of completeness.

GROWTH AMPOULE PREPARATION

1. The ampoule is fabricated from 34 X 30 quartz tubing with a fire polished 60° nucleation tip and attached, charging side arm nipple (Figure 8a).

2. Ampoule is thoroughly cleaned in 1:1 HF:HNO_3 solution and rinsed in methanol and deionized water.

3. Ampoule is evacuated to 10^{-3} torr and heated to a glow with a torch.

4. Interior of the growth ampoule is coated with a thin carbon coating at 800°C via pyrolysis of C_6H_6.

5. The charging side arm nipple is cut open and the side arm is welded on (Figure 8b).

6. Ampoule is thoroughly washed with acetone, methanol and deionized water.

7. Ampoule is evacuated to 10^{-6} torr and heated to a glow.

8. $CaLa_2S_4$ is loaded into the ampoule and I_2 (or Br_2) into the side arm and the side arm is sealed off.

9. The halogen transporting agent is chilled with LN_2 while the ampoule containing $CaLa_2S_4$ is evacuated to 10^{-6} torr at 100°C.

10. The halogen material is transferred to the ampoule by gently heating the side arm while cooling the ampoule tip with LN_2.

11. The side arm is sealed off, followed by the ampoule.

Initially the ampoule was heated in a reverse temperature gradient, the tip being 130° hotter than the butt end. This drove any residual powder away from the nucleation point. The experiment was begun by positioning the ampoule in the grow position, the tip being 20° to 30° cooler than the source which was held at 1000°C. All runs lasted three (3) days after which the ampoule was again placed in a reverse temperature gradient as the furnace was cooled down so that the transporting material condensed in the ampoule end opposite the growing crystals.

Although these experiments are still continuing, the results to date are not encouraging. While I_2 is an effective transporting agent at these

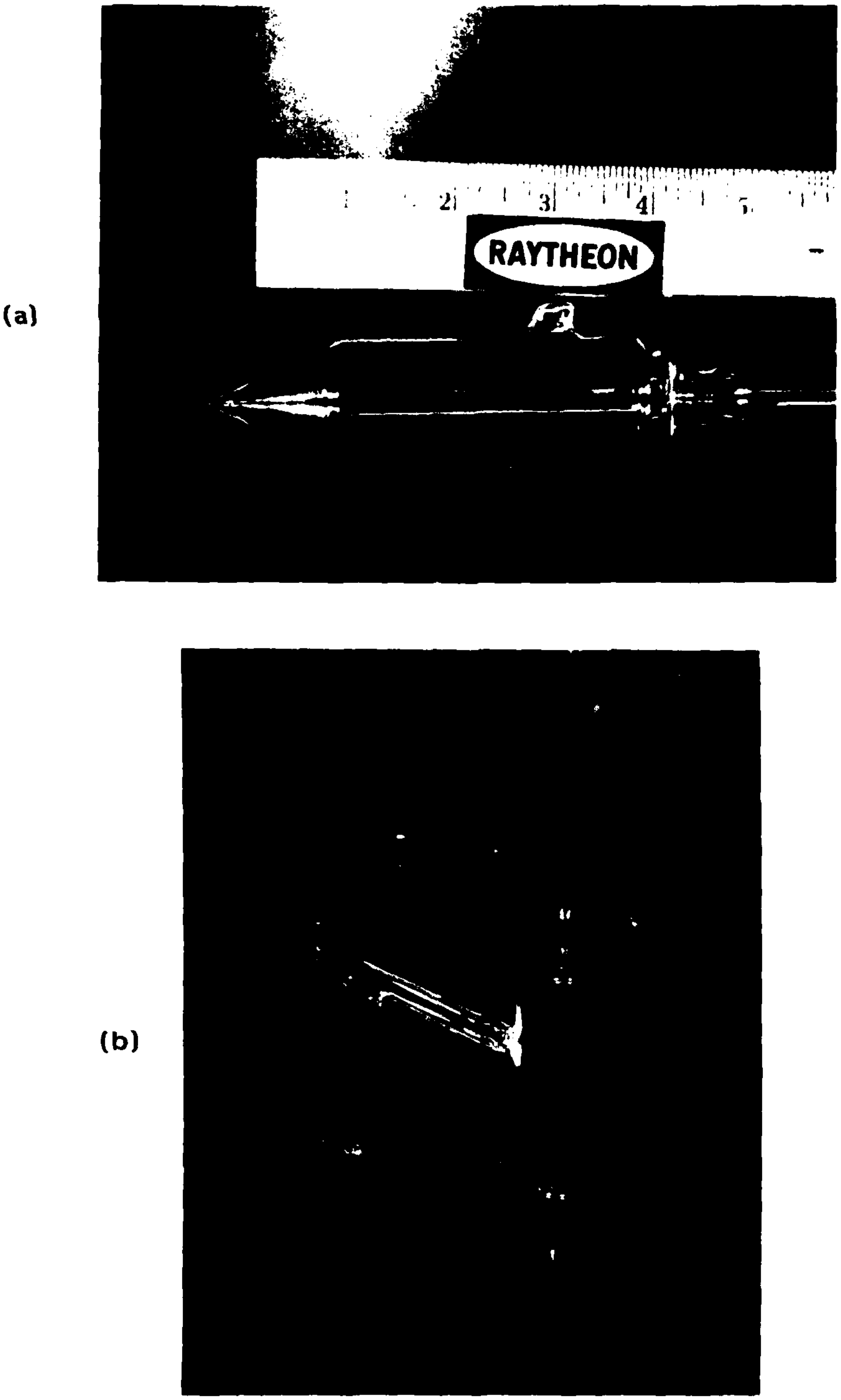

Figure 8. A typical crystal growing ampoule, (a) after forming and (b) after coating with carbon. The side arm has been attached.

growth temperatures, stable iodosulfides (probably La) are formed and are still present at room temperature in the form of polycrystalline deposits. I_2 may still be a useful transporting agent at higher temperatures where the iodosulfide compounds are unstable. Br_2 ($CaBr_2$) was also used in place of I_2 but not noticeable transport occurred.

SECTION III

CONCLUSIONS AND RECOMMENDATIONS

3.1 Accomplishments

Powder preparation via co-precipitation has been established as the most successful method yet reported for the production of phase-pure $CaLa_2S_4$. Using this technique, very fine, homogeneous powders have been produced without the need for milling or mixing. Sulfurization times have been reduced by at least an order of magnitude below previously reported schedules. This represents a breakthrough in $CaLa_2S_4$ materials preparation. While sintering/hot pressing studies are just beginning, based on the morphology of the precipitated powder one can conclude that the sinterability of $CaLa_2S_4$ has been greatly enhanced. This may eventually eliminate the use of hot pressing altogether, a more costly process that has been plagued with sample darkening.

Single crystal growth experiments have generally been unsuccessful although other possible growth techniques have not been fully explored, such as organo-metallic decomposition or flux growth. However, with the development of the co-precipitated, high purity powders it now appears that optical quality samples of $CaLa_2S_4$ can be directly obtained by applying conventional powder processing.

3.2 Recommendations

The most transparent samples of $CaLa_2S_4$ yet produced have been hot pressed samples that were subsequently hot isostatically pressed.[1] We have advocated this approach in the original proposal and still feel that when this method is combined with either sintering or hot pressing the result will be a significant increase in the transparency of TRE sulfides. With the potential that co-precipitation has for producing very fine powders we are enthusiastic about this approach.

However, all of the parameters involved in the powder synthesis process must be quantitatively evaluated, including specifically precipitation chemistry as well as firing times and temperatures, with the objective of optimizing powder particle size, shape and particle size distribution. Based on surface area measurements as well as particle sizes, it appears that the sinterability of the $CaLa_2S_4$ (and probably the phase purity) has been substantially improved. This will have to be verified experimentally, and those studies are in progress. Ideally, optical quality material might be produced via sintering alone, however, sintering could be used as a prelude to hot isostatic pressing to yield transparent samples. This combination would be very attractive from a batch processing point of view.

REFERENCES

1. W. B. White, "Advanced Optical Ceramics, Phase II, p. 111, Annual Report, June 1, 1979-May 31, 1980. Contract No. N00014-78-C-0466.

2. T. Toide, T. Utsunomiya, M. Sato, Y. Hoshino, T. Hatano and Y. Akimoto, Nippon Kagaku Kaishi, 12, 2438 (1972).

3. M. Cutler and J. F. Leavy, Physical Review, 133, no. 4, A1153 (1964).

4. J. R. Henderson, M. Muramoto and E. Loh, Journal of Chemical Physics, 47, No. 9, 3347 (1967).

5. F. Jona and G. Mandel, J. Phys. Chem. of Solids, 25, 187 (1964).

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