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# Preparation, Properties, and Development of Calcium Lanthanum Sulfide as an 8- to 12-micrometer Transmitting Ceramic

by  
Marian E. Hills  
*Research Department*

SEPTEMBER 1989

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NAVAL WEAPONS CENTER  
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## FOREWORD

This report documents work done on the development of calcium lanthanum sulfide ( $\text{CaLa}_2\text{S}_4$ ) as an infrared dome material for use in the 8- to 12- $\mu\text{m}$  region. The preparation and the optical, thermal, and mechanical properties of the ceramic are described. An extensive bibliography is provided.

The work was supported by the Missile Support Technology Block, NW2A, Program Element 62234N, and Project RS34W54 at the Naval Weapons Center.

This report has been reviewed for technical accuracy by Terence M. Donovan.

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CONTENTS

Introduction..... 3  
 Background..... 3  
 Bibliographic Information..... 3

Preparation of the Ceramic..... 4  
 Stoichiometry..... 4  
 Preparation of CaLa<sub>2</sub>S<sub>4</sub> Powder..... 4  
     Precipitation Route..... 4  
     Evaporative Decomposition of Solution (EDS) Route..... 4  
 Fabrication..... 4

Properties of the Ceramic..... 7  
 Optical..... 7  
 Thermal..... 7  
 Mechanical..... 7  
 Chemical Stability..... 8  
 Rain Erosion Resistance..... 8  
 Summary of the Data..... 8

References..... 10

Appendixes:  
 A. Bibliography..... 13  
 B. Processes for Calcium Lanthanum Sulfide Fabrication..... 23  
 C. Mechanical Strength of Various CaLa<sub>2</sub>S<sub>4</sub> Samples..... 31  
 D. Rain Erosion Testing of CaLa<sub>2</sub>S<sub>4</sub> Disks Coated with Ytria..... 37

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## INTRODUCTION

The purpose of this report is to document work done on the development of calcium lanthanum sulfide ( $\text{CaLa}_2\text{S}_4$ ) as an infrared (IR) dome material for use in the 8- to 12- $\mu\text{m}$  region. The work was supported by the Missile Support Technology Block of the Navy Exploratory Development Program.

## BACKGROUND

In the late 1970s an extensive survey of optical dome materials and some research effort were conducted by the General Electric Company, Philadelphia, Penna., and its subcontractors with funding from the Defense Advanced Research Agency (DARPA) under the Office of Naval Research (ONR) Contracts N00014-77-C-0649, N00014-78-C-0466, and N00014-80-C-0964, Advanced Optical Ceramics (References 1 through 4). Commencing under these contracts and continuing under other ONR contracts, W. B. White and others (References 5 through 9) at The Pennsylvania State University, University Park, Penna., studied the preparation and processing of various  $\text{AB}_2\text{S}_4$  sulfides with the  $\text{Th}_3\text{P}_4$  structure. The Office of Naval Research also funded work at Coors Porcelain Co., Golden, Colo., (References 10 and 11). Effort on the development of  $\text{CaLa}_2\text{S}_4$  as an IR dome material has been carried out most recently by the Research Division of the Raytheon Co., Lexington, Mass., under Naval Weapons Center (NWC) Contracts N60530-84-C-0170 and N60530-85-C-0172. The latter contract was supported by the Missile Support Technology Block of the Navy Exploratory Development Program; the work carried out with this support is reported here.

In addition to the work done in the United States, work on  $\text{CaLa}_2\text{S}_4$  has been funded and carried out by the British (References 12 through 15)

## BIBLIOGRAPHIC INFORMATION

All of the reports, papers, etc., resulting from the 1985 NWC contract with Raytheon are listed in Appendix A of this report. Many reports concerning  $\text{CaLa}_2\text{S}_4$  that resulted from earlier government contracts are also listed; hence, this extended list should give entrée to the results of other investigations of the preparation, properties, fabrication, and suitability of  $\text{CaLa}_2\text{S}_4$  as an IR dome material.

## PREPARATION OF THE CERAMIC

### STOICHIOMETRY

The material developed for IR dome/window material is not the stoichiometric compound  $\text{CaLa}_2\text{S}_4$  with  $\text{La}/\text{Ca} = 2$  but a material with the atomic ratio  $\text{La}/\text{Ca} = 2.7$  and more recently  $\text{La}/\text{Ca} = 18$ , which is often referred to as 90:10 material because this is the mole ratio of  $\text{La}_2\text{S}_3$  to  $\text{CaS}$ . In this report material will be referred to as  $\text{CaLa}_2\text{S}_4$  but this should be understood to refer to the non-stoichiometric material.

### PREPARATION OF $\text{CaLa}_2\text{S}_4$ POWDER

There are two routes to the preparation of the  $\text{CaLa}_2\text{S}_4$  powder from which the ceramic is fabricated.

#### Precipitation Route

Precipitation of mixed carbonates from an aqueous solution of  $\text{La}(\text{NO}_3)_3$  and  $\text{Ca}(\text{NO}_3)_2$  followed by heating of the precipitate in flowing  $\text{H}_2\text{S}$  is the method used by Raytheon and detailed in Appendix B.

#### Evaporative Decomposition of Solution (EDS) Route (developed by W. B. White of The Pennsylvania State University (Reference 8))

This method, used by the British, consists of spraying an aqueous solution of  $\text{La}(\text{NO}_3)_3$  and  $\text{Ca}(\text{NO}_3)_2$  into a hot furnace followed by heating the resulting oxide powder in flowing  $\text{H}_2\text{S}$ .

### FABRICATION

Two techniques have been used to fabricate  $\text{CaLa}_2\text{S}_4$  ceramic. Hot pressing of the powder was the first method used. The currently favored technique is to sinter the powder to closed porosity and to follow this with a containerless hot isostatic pressing (HIP).

Reproducibility of the product remains a problem, which is thought to be a result of variability of the powder. However, measurable properties of the powder which can be used to predict if a particular batch of powder will give a good ceramic piece have been impossible to identify.

Figure 1 is a schematic of the two approaches to making  $\text{CaLa}_2\text{S}_4$  ceramic. Figure 2 is the flow chart for the Raytheon process.

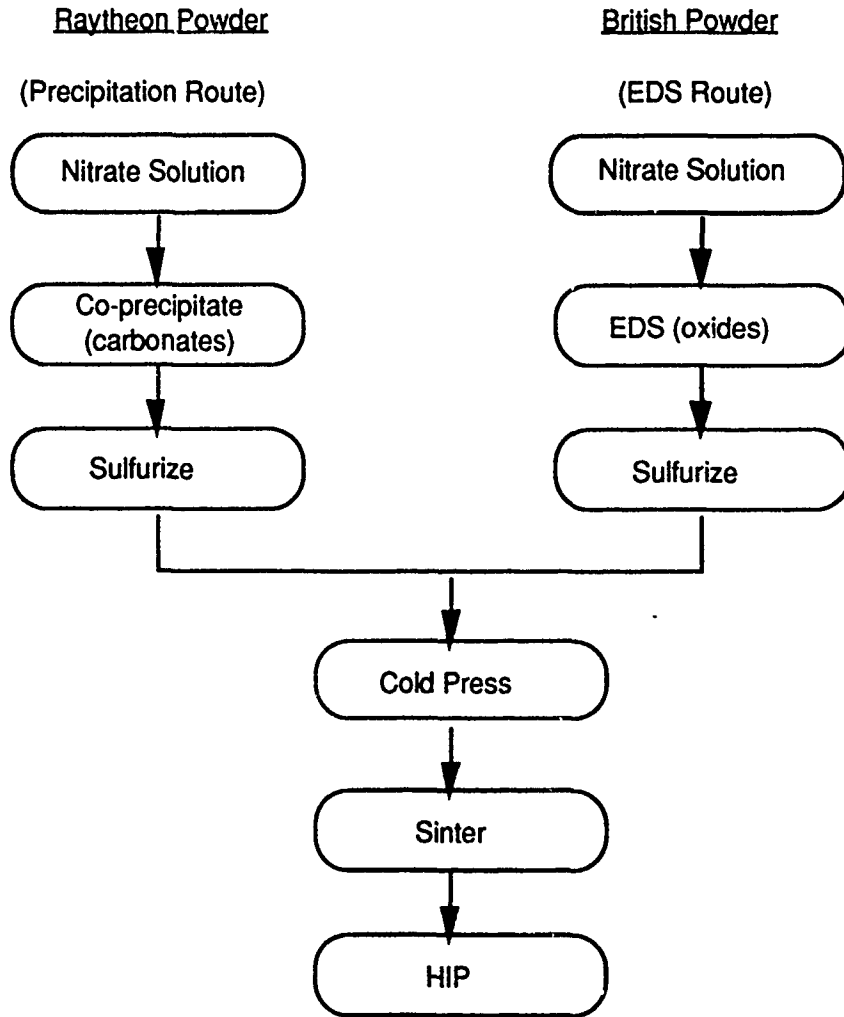


FIGURE 1. Powder Synthesis Routes.

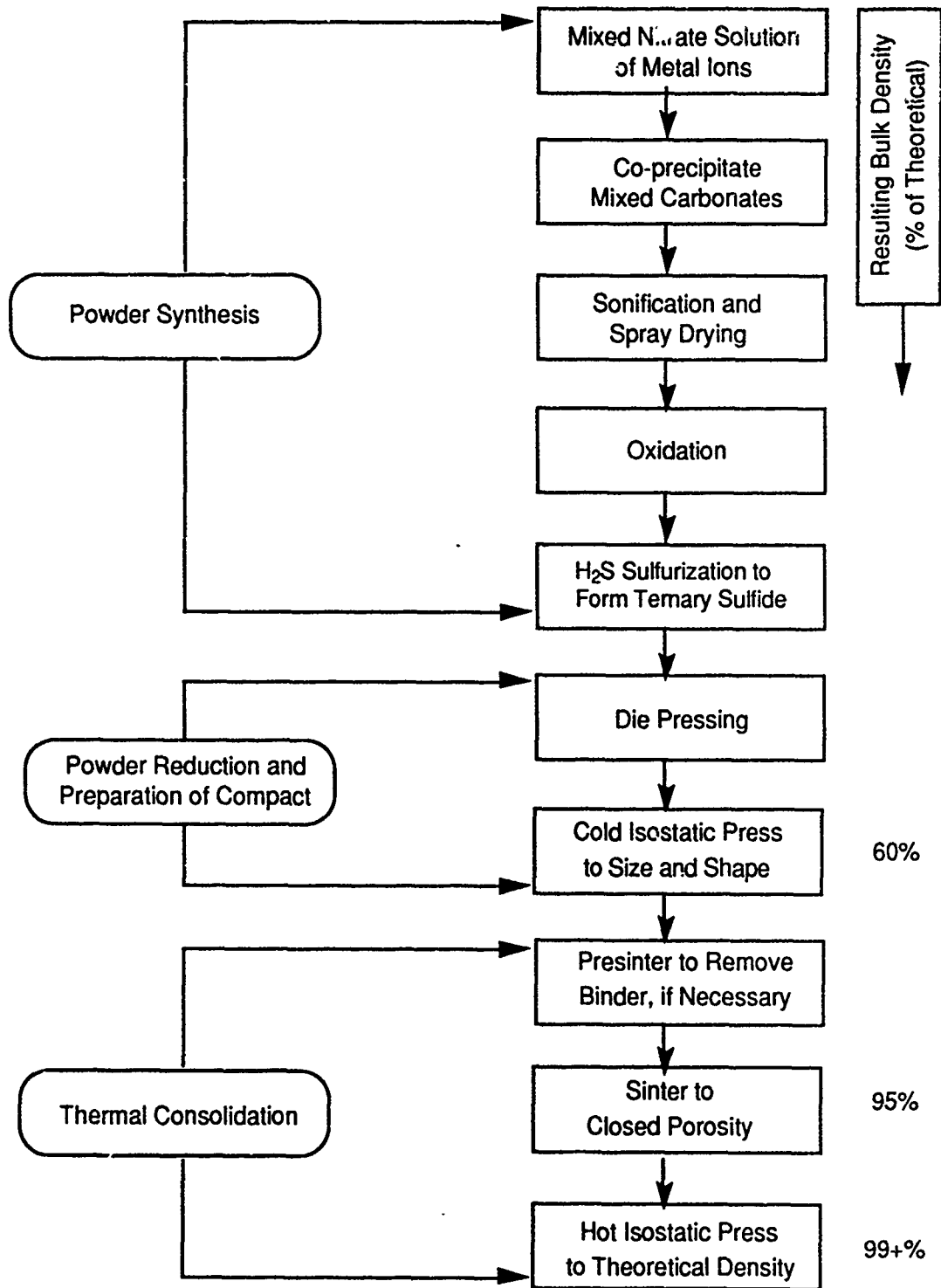


FIGURE 2. Flow Chart for Processing  $\text{CaLa}_2\text{S}_4$ .



## PROPERTIES OF THE CERAMIC

### OPTICAL

The long wavelength cutoff of  $\text{CaLa}_2\text{S}_4$  is greater than that of ZnS. Figure 3 shows the transmittance curves for  $\text{CaLa}_2\text{S}_4$  and ZnS.

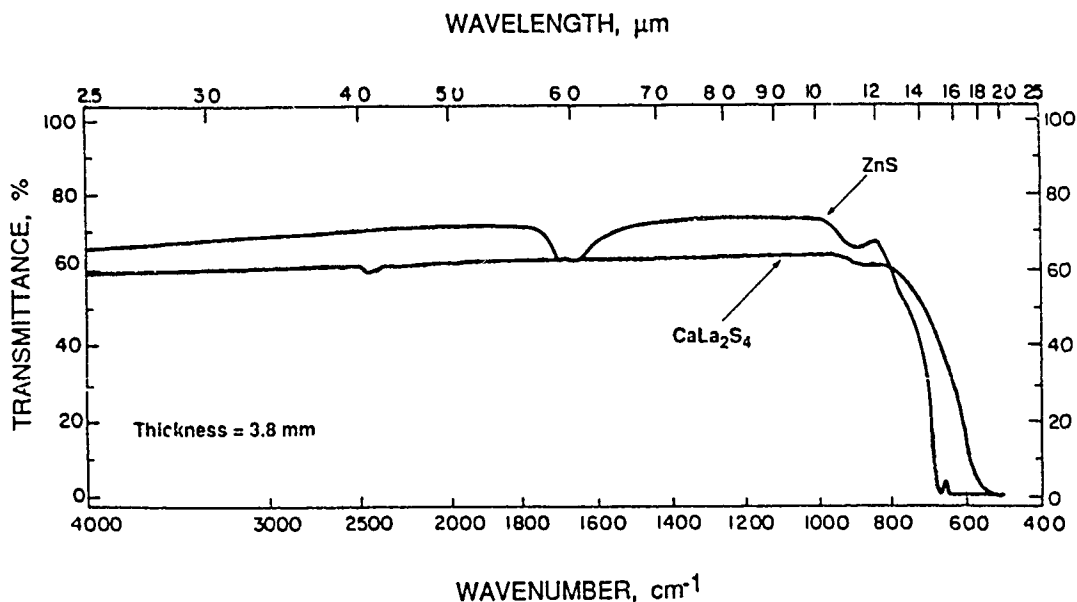


FIGURE 3. IR Transmittances (not corrected for reflection losses) of  $\text{CaLa}_2\text{S}_4$  and ZnS (Reference 16).

An absorption coefficient of  $0.1 \text{ cm}^{-1}$  has been achieved in the very lanthanum rich ceramic ( $\text{La}/\text{Ca} = 18$ ). Yttria can serve as an anti-reflection coating for calcium lanthanum sulfide.

### THERMAL

The thermal expansion coefficient is  $14.7 \times 10^{-6}/^\circ\text{C}$ , which is about twice that of ZnS. The thermal conductivity is  $1.7 \text{ Watts-m/m}^2\text{-K}$ , which is one-tenth that of ZnS. Both of these values make  $\text{CaLa}_2\text{S}_4$  more susceptible to thermal shock than ZnS.

### MECHANICAL

The flexural strength measured on bars 0.250 by 0.500 by 4.00 inches at room temperature is 7,240 psi (9,300 psi for ZnS). Biaxial flexure on disks 0.100-inch thick by 0.875-inch diameter gave  $12,515 \text{ psi} \pm 4,222 \text{ psi}$  for  $\text{CaLa}_2\text{S}_4$  and  $15,128 \text{ psi} \pm 3,209 \text{ psi}$  for ZnS. Although the values are different for the two test configurations and the standard deviations large, the ratio of the strengths of  $\text{CaLa}_2\text{S}_4$  to ZnS is about 80% for both methods.

Attempts to produce ceramic pieces having smaller grain size to try to increase the mechanical strength were not successful.

Data on the strength of various kinds of  $\text{CaLa}_2\text{S}_4$  are given in Appendix C and compared with data for ZnS. The data show the variability of the pieces.

### CHEMICAL STABILITY

Ceramic pieces of  $\text{CaLa}_2\text{S}_4$  are attacked by moisture at high humidity at 120°F. The resulting degradation can be prevented by coating the ceramic with yttria ( $\text{Y}_2\text{O}_3$ ). The yttria also serves as an anti-reflection coating and appears to increase the mechanical strength and rain erosion resistance of the  $\text{CaLa}_2\text{S}_4$  ceramic.

### RAIN EROSION RESISTANCE

$\text{CaLa}_2\text{S}_4$  appears to be more resistant to rain erosion than ZnS; however, the data are somewhat equivocal (References 16 and 17). In some rain erosion testing of yttria-coated  $\text{CaLa}_2\text{S}_4$  pieces, the coating did not adhere. In many cases there was almost complete removal of the coating after 5 minutes in a 1 in/h rainfield at 370 mph. The pieces were recoated and the test repeated; coating removal was more extensive than before. Some of the pieces were again recoated under different conditions and tested. This time the adhesion was much better than before. More information is given in Appendix D.

### SUMMARY OF THE DATA

Table 1 gives optical, mechanical, and thermal data for  $\text{CaLa}_2\text{S}_4$  and compares them with data for ZnS.

TABLE 1. Comparison of Properties of  $\text{CaLa}_2\text{S}_4$  ( $\text{La}/\text{Ca} = 2.7$ )  
and Raytran® ZnS (Standard Grade).

	Temperature	$\text{CaLa}_2\text{S}_4$	Reference	ZnS	Reference
<b>Optical</b>					
Absorption coefficient, $\text{cm}^{-1}$ at $10.6 \mu\text{m}$ (calorimetric)		0.12	18	0.3	18
Long wavelength cutoff, $\mu\text{m}^a$		11.5	19	10	19
<b>Mechanical</b>					
Knoop hardness, $\text{kg}/\text{mm}^2$ , 50 g load		570	18	250	18
Flexural strength, $\text{psi}^b$		7240	20	9300 <sup>c</sup>	21
Flexural strength, $\text{psi}^d$		12,515	22	15,128	22
Young's modulus, $10^6 \text{ psi}$		13.9	20	10.8 <sup>c</sup>	21
Impact damage threshold <sup>e</sup> (References 42 and 62)					
Bare, m/s		110-225	...	110	...
Yttria coated, m/s		180	...	120	...
<b>Thermal</b>					
Melting point, $^{\circ}\text{C}$		1810 <sup>f</sup>	...	1830	3
Specific heat					
Btu/lb- $^{\circ}\text{F}$	500 $^{\circ}\text{F}$	0.088	20	0.120 <sup>c</sup>	21
J/g- $^{\circ}\text{C}$	23 $^{\circ}\text{C}$	...	...	0.468	23
Expansion coefficient, $10^{-6}/^{\circ}\text{C}$					
	77-752 $^{\circ}\text{F}$	14.7	24	7.4	24
	70-1000 $^{\circ}\text{F}$	14.9	20	8.03 <sup>c</sup>	21
Conductivity, $\text{W}\cdot\text{m}/\text{m}^2\cdot\text{K}$					
	23 $^{\circ}\text{C}$	...	...	17	23
	77 $^{\circ}\text{F}$	1.7	24	17	24
	500 $^{\circ}\text{F}$	1.51	20	9.65 <sup>c</sup>	21
Density, $\text{g}/\text{cm}^3$		4.61	20	4.08	23
Refractive index, $10.6 \mu\text{m}$		...	...	2.193	25

<sup>a</sup> Corresponds to a 2% drop in transmittance for a piece 7.8-mm thick.

<sup>b</sup> Measured on bars 0.250 by 0.500 by 4.00 inch; 4-point bend.

<sup>c</sup> Measurement made on ZnS fabricated by CVD, Inc., Woburn, Mass.

<sup>d</sup> Measured on disks 0.100-inch thick with a diameter of 0.875 inch; biaxial.

<sup>e</sup> 1 damage site per 100 impacts, 2-mm water drop, 1 in/h rainfall.

<sup>f</sup> D. L. Chess and W. B. White. Presented at the Annual Meeting of the American Ceramic Society, 2 May 1984.

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NWC TP 7037

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**Appendix A**  
**BIBLIOGRAPHY**

The reports listed in this bibliography are grouped into three sections: Raytheon annual reports; other reports (excluding Raytheon quarterly reports) and open literature papers; and Raytheon quarterly reports. The reports in each section are listed chronologically.

Copies of the Raytheon annual reports have been placed in the Technical Library at the Naval Weapons Center.

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NWC TP 7037

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NWC TP 7037

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**Appendix B**

**PROCESSES FOR CALCIUM LANTHANUM SULFIDE FABRICATION**

This appendix is a copy of Appendix A of Reference 19. **Note:** In this appendix CLS is an abbreviation for calcium lanthanum sulfide.



The following is a detailed description of the fabrication processes for CLS optical ceramics as used at Raytheon at the completion of the current program.

#### A.1 PRECIPITATION OF CALCIUM LANTHANUM CARBONATE

##### A.1.1 Weigh Out Carbonate and Nitrates

The required amounts are calculated for each new lot of lanthanum or calcium nitrate. TGA is performed on the nitrate to determine water content. The amount of nitrate needed is calculated based on the water content and the composition desired. Significant variation in water content of different lots has been observed. The variation for the lanthanum nitrate has been from 4 moles to 8 moles of water. The calcium nitrate usually contains between 3 and 4 moles of water.

Listed below are the current amounts used for both the 2.7 and the 90:10 compositions.

For the 2.7 composition: (La:Ca ratio = 2.7)

278.2 g Ammonium Carbonate

322.9 g Lanthanum Nitrate (Based on  $\text{La}(\text{NO}_3)_3 \cdot 5.11 \text{H}_2\text{O}$ )

66.5 g Calcium Nitrate (Based on  $\text{Ca}(\text{NO}_3)_2 \cdot 3.76 \text{H}_2\text{O}$ )

For the 90:10 composition: (La:Ca ratio = 18)

222.0 g Ammonium Carbonate

353.4 g Lanthanum Nitrate (Based on  $\text{La}(\text{NO}_3)_3 \cdot 8.55 \text{H}_2\text{O}$ )

9.5 g Calcium Nitrate (Based on  $\text{Ca}(\text{NO}_3)_2 \cdot 3.76 \text{H}_2\text{O}$ )

The ammonium carbonate is placed in a 1400 ml beaker. The lanthanum and calcium nitrates are combined in a second 1400 ml beaker.

#### A.1.2 Dissolve the Nitrates and Carbonates in DI Water

Eight hundred ml deionized (DI) water is added to the carbonate and 900 ml of DI water to the nitrates. The mixtures are stirred at room temperature until all of the solid is in solution. The two solutions are each filtered using #44 Whatman filter paper.

#### A.1.3 Precipitating and Rinsing

The precipitation is performed by combining the two solutions with an ultrasonic horn. The carbonate is introduced first through the lower side port. When the cell is full, the nitrates are introduced through the bottom port. The sonicator is turned on and set to approximately 20% output. The precipitate exits the cell through the higher side port and is collected in a 4000 ml beaker.

When the process is complete, the precipitate is poured into a porcelain Buchner funnel and filtered using #5 Whatman filter paper. While the precipitate is filtering, it is also rinsed with 4000 ml of DI water. (It is important that the water level not drop below the precipitate during rinsing.) When no more water can be extracted, the precipitate is transferred to a Nalgene wide mouth jug. The precipitate is then dispersed with 60 g of Darvan 821A.<sup>1</sup> This slurry is rolled for one hour at 150 rpm.

#### A.1.4 Sonicating and Spray Drying

After rolling, the mixture is poured into a beaker and is kept stirring continuously. The mixture is then sonicated using the unit cell attachment shown in Figure A1. The mixture

<sup>1</sup> Darvan 821A is an ammonium based dispersant. It can be purchased from R. T. Vanderbilt Company, Inc., Norwalk, CT - 06855.

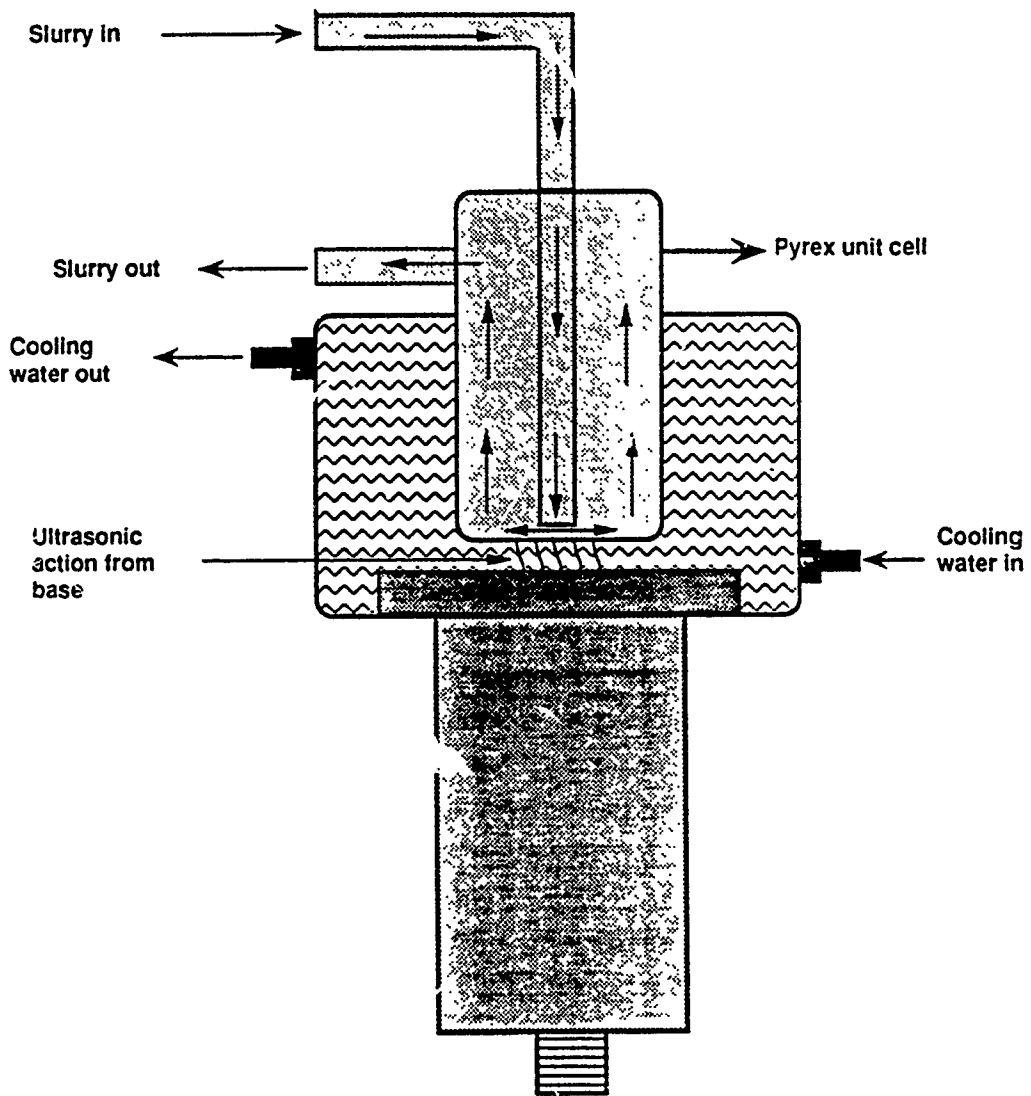


Figure A1. Drawing of Unit Cell Attachment for Sonicator.

is sonicated for three hours at a speed of 100 ml/min and a power output of approximately 20%. The mixture is then spray dried at a temperature of 170 to 180°C. The fine powder is collected and placed in a labelled jar.

#### A.2 OXIDATION

The powder is placed in an alumina crucible. The lid is raised slightly with small diameter alumina rods. The crucible is placed into an air furnace with a flow of oxygen. The furnace schedule is as follows:

Room Temperature (RT) to 875°C in 5 hours  
Hold at 875°C for 3 hours  
Cool to RT in 5 hours.

#### A.3 SULFURIZATION

After oxidation, the "clumps" of powder are broken up by shaking the powder in a closed jar. Then, 250 to 300 g of powder (1 batch) is placed in a quartz crucible. The crucible is placed in a quartz lined vacuum furnace and the furnace is pumped down with a mechanical pump. The firing schedule is as follows:

RT to 300°C in 6 hours (in vacuum)  
Hold at 300°C for 1 hour, while introducing H<sub>2</sub>S  
300°C to 925°C in 5 hour  
Hold at 925°C for 8 hours (gas flow off after 8 hours)  
Cool to RT in 7.5 hours (static H<sub>2</sub>S in furnace)

When the powder is removed from the furnace, the clumps are broken up by using the Spex mill with no media for 10 minutes. A sample of the powder is taken for X-ray diffraction analysis. The powder is now ready for processing into a ceramic.

#### A.4 SAMPLE FABRICATION

##### A.4.1 Die Pressing

To obtain the proper final size, a die large enough to accommodate shrinkage of the material during sintering and HIPping is chosen. Next, the proper charge for the die is weighed out. The powder is placed in the die and pressed at approximately 800 psi.

##### A.4.2 Isostatic Pressing

The sample is placed in a rubber bag suitable for isopressing. The bag is evacuated and sealed. The sample(s) are then isopressed at 25,000 psi. After pressing, the edges of the sample are wiped with a lint free cloth to remove the markings left by the die. The sample is labelled, using a scribe. The sample is now ready for sintering.

#### A.5 SINTERING

The samples are sintered in a vacuum furnace according to the following schedule:

RT to 600°C in 9 hours (in vacuum)  
Hold at 600°C for 1 hour while introducing H<sub>2</sub>S gas  
600 to 1000°C in 3 hours  
Hold at 1000°C for 5 hours  
1000 to 1150°C in 1.25 hours  
Hold at 1150°C for 4 hours (gas off after 4 hours)  
Cool to RT in 10 hours (static H<sub>2</sub>S in furnace)

After sintering, the density of each sample is measured using the Archimedes method. If the sample has a density greater than 93%, it is ready to be HIPped. If not, it must be resintered.

A.6 HIPPING

The samples are placed in an alumina crucible and HIPped according to the following schedule:

RT to 990°C in 2.5 hours

Hold at 990°C and 29,000 psi (Argon) for 3 hours

Cool to RT in 5 hours

The density of each sample is again measured after HIPping.

A.7 SAMPLE FINISHING

The samples are finished by coring to a specified diameter, if necessary, grinding (using 40, 12 and 5  $\mu\text{m}$  alumina) and polishing (using 0.3  $\mu\text{m}$  alumina) to give the proper final thickness and required optical finish.

**Appendix C**

**MECHANICAL STRENGTH OF VARIOUS  $\text{CaLa}_2\text{S}_4$  SAMPLES**

Samples 0.100-inch thick with a diameter of 0.875 inch were fabricated from three kinds of  $\text{CaLa}_2\text{S}_4$  powder: Raytheon La/Ca = 2.7, Raytheon La/Ca = 18, and British Drug House (BDH), Poole, Dorset, United Kingdom, La/Ca = 18. Disks were also made from standard Raytheon vapor-deposited ZnS. The strength of the pieces was determined using the biaxial flexure method; the same fixture was used for all of the tests. The data (Reference 19) are presented in Tables C-1 through C-4. There is considerable variability in the mechanical strength of the specimens. The data are summarized in Table C-5 (Reference 22). **Note:** The tables in this appendix were taken, with some modification, from Raytheon reports (References 19 and 22).

TABLE C-1. Optical and Mechanical Properties of Calcium Lanthanum Sulfide Samples (Raytheon 2.7:1).<sup>a</sup>

Sample No.	% Transmittance		Biaxial flexure strength, psi	Knoop hardness	Average grain size, $\mu\text{m}$
	1 $\mu\text{m}$	10 $\mu\text{m}$			
207-2	37.5	62.0	10,172	...	...
207-3	38.0	61.5	...	...	...
207-4	35.5	60.2	10,928	500	8.13
207-5	37.0	61.6	19,628	500	8.23
207-8	36.0	57.5	...	...	...
207-9	39.7	62.7	...	...	...
207-10	26.3	61.4	12,875	...	...
207-11	37.0	62.3	8,970	498	16.67
			Mean 12,515		
			Standard deviation 4,222		

<sup>a</sup> From Reference 19 with modifications.TABLE C-2. Optical and Mechanical Properties of Calcium Lanthanum Sulfide Samples (Raytheon 90:10).<sup>a</sup>

Sample No.	% Transmittance		Biaxial flexure strength, psi	Knoop hardness	Average grain size, $\mu\text{m}$
	1 $\mu\text{m}$	10 $\mu\text{m}$			
125-1	18.7	60.3	9,081	504	25.65
125-2	21.0	59.3	7,698	...	...
125-3	21.0	60.3	4,589	504	41.65
125-4	18.0	59.0	12,955	504	47.64
125-5	16.3	60.6	7,463	...	...
125-7	22.0	59.9	9,636	...	...
			Mean 8,570		
			Standard deviation 2,773		

<sup>a</sup> From Reference 19 with modifications.



TABLE C-3. Optical and Mechanical Properties of Calcium Lanthanum Sulfide Samples (BDH 90:10).<sup>a</sup>

Sample No.	% Transmittance		Image resolution, m $\mu$ r	Biaxial flexure strength, psi	Knoop hardness	Average grain size, $\mu$ m	Lattice parameter, $\text{\AA}$
	1 $\mu$ m	10 $\mu$ m					
B-3	57.8	65.8	0.820	15,786	504	9.53	8.719
B-6	59.8	66.8	0.731	11,774	...	...	...
B-8	41.5	66.3	0.820	12,166	507	15.51	8.719
B-11	36.5	65.2	1.03	11,810	...	...	...
B-12	58.0	66.7	0.651	10,776	500	11.50	8.719
B-13	54.7	65.4	0.731	10,971	...	...	...
			Mean	12,214			
			Standard deviation	1,829			
B-2	59.8	66.5	0.651	20,259 <sup>b</sup>	658	...	...
B-5	59.0	66.5	0.651	18,592 <sup>b</sup>	...	...	...
B-7	58.7	66.9	0.651	12,814 <sup>b</sup>	...	...	...
B-9	57.7	66.6	0.731	9,889 <sup>b</sup>	652	...	...
B-10	59.3	66.7	0.731	10,888 <sup>b</sup>	...	...	...
			Mean	14,488			
			Standard deviation	4,665			

<sup>a</sup> From Reference 19 with modifications.

<sup>b</sup> Strength test performed after yttria coating was applied.

NWC TP 7037

TABLE C-4. Mechanical Properties of Zinc Sulfide Samples (Raytheon ZnS).<sup>a</sup>

Uncoated				Coated with yttria	
Sample No.	Biaxial flexure strength, psi	Knoop hardness	Average grain size, $\mu\text{m}$	Sample No.	Biaxial flexure strength, psi
Z-1	15,535	...	...	Z-20	12,066
Z-2	20,709	228	4.52	Z-21	13,371
Z-3	15,375	232	5.03	Z-22	14,196
Z-4	14,235	...	...	Z-23	14,818
Z-5	12,876	228	...	Z-24	16,393
Z-6	16,843	...	...	Z-25	18,845
Z-7	14,054	...	...	Z-26	19,621
Z-8	10,457	...	...	Z-27	19,937
Z-9	20,436	...	...	Z-28	20,984
Z-10	12,453	...	...	Z-29	21,808
Z-11	16,865	...	...	Z-30	22,492
Z-12	11,702	...	...	Z-31	23,150
	Mean 15,128				18,140
	Standard deviation 3,209				3,823

<sup>a</sup> From Reference 19 with modifications.

TABLE C-5. Summary of Biaxial Flexure Strengths.<sup>a</sup>

	ZnS	Calcium lanthanum sulfide		
	Raytheon	BDH, 90:10	Raytheon, 90:10	Raytheon, 2.7:1
<u>Uncoated</u>				
Average strength	15,128	12,214	8,570	12,515
Standard deviation	3,209	1,829	2,773	4,222
High	20,709	15,786	12,955	19,628
Low	10,457	10,776	4,589	8,970
Count	12	6 6	5	
Grain size, $\mu\text{m}$	4 - 6	9 - 16	25 - 50	8 - 17
<u>Coated with yttria</u>				
Average strength	18,140	14,488	...	...
Standard deviation	3,823	4,664	...	...
High	23,150	20,256	...	...
Low	12,066	9,889	...	...
Count	12	5...	...	...

<sup>a</sup> From Reference 22 with modifications.

## Appendix D

### RAIN EROSION TESTING OF $\text{CaLa}_2\text{S}_4$ DISKS COATED WITH YTTRIA

For rain erosion testing, 42  $\text{CaLa}_2\text{S}_4$  ceramic disks 0.875-inch diameter by 0.100-inch thick were fabricated from BDH 90:10 powder ( $\text{La}/\text{Ca} = 18$ ) produced via the EDS route. The disks were coated on one side with yttria ( $\text{Y}_2\text{O}_3$ ).

Twenty of the 42 samples were eroded for 5 minutes at 370 mph (165 m/s) and a 90-degree angle of impact in a 1 in/h rainfield at the Materials Laboratory Rain Erosion Test Facility (Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio). The coating failed on three-fourths of the samples; for one-half of the samples, the coating removal was 50% or greater. This was not expected; Raytheon had previously coated  $\text{CaLa}_2\text{S}_4$  with yttria and had not run into adhesion problems. Nearly all of the samples tested had subsurface ring fractures. The coating failure precluded the use of the specimens for planned mechanical strength testing. The comments given in the test report by Charles J. Hurley of the test facility are listed in Table D-1. Samples 4412-n (where n is a number) were coated in the first group. After they were coated, the target in the coating apparatus broke. Samples coated after the target was replaced suffered greater coating loss during the rain erosion test. All samples, eroded and uneroded, were returned to Raytheon where the coatings and remnants of coatings were removed along with a thin layer of ceramic. The pieces were then coated on the reverse side. Some of these pieces were again subjected to rain erosion at 370 mph for 5 minutes. Coating removal was even more extensive than before. The comments given in the test report by Charles J. Hurley of the test facility are listed in Table D-2.

The samples were again returned to Raytheon. Raytheon used the samples to study the effect of coating parameters on the adhesion of yttria on  $\text{CaLa}_2\text{S}_4$ . Rain erosion tests showed that some conditions gave better adhesion. The study of the coating parameters was not part of the NWC contract and the results will be reported separately by Raytheon.

NWC TP 7037

TABLE D-1. Rain Erosion Test of Ytria-Coated CaLa<sub>2</sub>S<sub>4</sub>. 370 mph, 5 minutes and a 90-degree angle of impact, 1 June 1988.

AFWAL <sup>a</sup>	User ID	Comments
23411	4412-1	Subsurface ring fractures/pitting/localized coating removal (~5%)/coating erosion failure
23412	4412-2	Subsurface ring fractures/localized coating removal (~1%)/coating erosion failure
23413	4412-6	Subsurface ring fractures/localized coating removal (~1%)/coating erosion failure
23414	4412-9	Subsurface ring fractures/localized coating removal (~1%)/pitting/cratering/coating erosion failure
23415	4412-7	Subsurface ring fractures/localized coating removal (~1%)/coating erosion failure
23416	4434-4	95% coating removal/coating erosion failure
23417	4434-1	Subsurface ring fractures/pitting/30% coating removal/coating erosion failure
23418	4434-7	Subsurface ring fractures/95% coating removal/coating erosion failure
23419	4434-6	Subsurface ring fractures/pitting/95% coating removal/coating erosion failure
23420	4434-11	Subsurface ring fractures/pitting/50% coating removal/coating erosion failure
23421	4912-4	Subsurface fractures/pitting/40% coating removal/specimen cracked/erosion failure
23422	4912-6	Subsurface ring fractures/pitting/95% coating removal/internal fracture/coating erosion failure
23423	4934-2	Subsurface ring fractures/pitting/95% coating removal/coating erosion failure
23424	4934-10	Subsurface ring fractures/pitting/60% coating removal/coating erosion failure
23425	4934-6	Subsurface ring fractures/pitting/localized coating removal/coating erosion failure
23426	4405-3	Subsurface ring fractures/pitting/95% coating removal/coating erosion failure
23427	4934-8	Subsurface ring fractures/pitting/85% coating removal/coating erosion failure

<sup>a</sup> See footnote at end of table.

TABLE D-1. (Contd.)

AFWAL <sup>a</sup>	User ID	Comments
23428	4934-11	Pitting/specimen cracked/40% coating removal/coating erosion failure
23429	4405-2	90% coating removal/coating erosion failure
23430	4405-4	Subsurface ring fractures/pitting/30% coating removal/coating erosion failure

<sup>a</sup> Wright Research and Development Center formerly Air Force Wright Aeronautical Laboratories identification number.

TABLE D-2. Rain Erosion Test of Recoated CaLa<sub>2</sub>S<sub>4</sub> Samples. 370 mph, 5 minutes, and 90 degree angle of impact, 15 November 1988.

AFWAL <sup>a</sup>	User ID	Comments
24381	4412-7	Prior substrate exposure on reverse side/pre-existing surface defects/subsurface ring fractures/slight pitting/100% coating removal/coating erosion failure
24382	4434-2	Pre-existing surface defects/subsurface ring fractures/surface microcracks/slight pitting/100% coating removal/coating erosion failure
24383	4412-8	Subsurface ring fractures/surface microcracks/slight pitting/cratering/100% coating removal/coating erosion failure
24384	4412-9	Prior substrate exposure on reverse side/pre-existing surface defects/subsurface ring fractures/surface microcracks/slight pitting/cratering/100% coating removal/coating erosion failure
24385	4412-10	Subsurface ring fractures/surface microcracks/slight pitting/approximately 100% coating removal/coating erosion failure
24386	4412-11	Subsurface ring fractures/surface microcracks/slight pitting/100% coating removal/coating erosion failure
24387	4434-4	Subsurface ring fractures/surface microcracks/slight pitting/approximately 100% coating removal/coating erosion failure
24388	4434-7	Prior substrate exposure on reverse side/pre-existing surface defects/subsurface ring fractures/surface microcracks/slight pitting/approximately 100% coating removal/coating erosion failure

<sup>a</sup> See footnote at end of table.

NWC TP 7037

TABLE D-2. (Contd.)

AFWAL <sup>a</sup>	User ID	Comments
24389	4912-2	Subsurface ring fractures/surface microcracks/slight pitting/cratering/approximately 100% coating removal/coating erosion failure
24390	4912-5	Subsurface ring fractures/surface microcracks/slight pitting/approximately 100% coating removal/coating erosion failure
24391	4934-2	Prior substrate exposure on reverse side/pre-existing surface defects/subsurface ring fractures/surface microcracks/slight pitting/approximately 100% coating removal/coating erosion failure
24392	4934-4	Prior substrate exposure on reverse side/pre-existing surface defects/subsurface ring fractures/surface microcracks/slight pitting/approximately 100% coating removal/coating erosion failure
24393	4934-5	Subsurface ring fractures/surface microcracks/slight pitting/approximately 100% coating removal/coating erosion failure
24394	4934-8	Prior substrate exposure on reverse side/pre-existing surface defects/subsurface ring fractures/surface microcracks/slight pitting/approximately 100% coating removal/coating erosion failure
24395	4405-2	Subsurface ring fractures/surface microcracks/slight pitting/cratering/approximately 100% coating removal/coating erosion failure
24396	4405-3	Subsurface ring fractures/surface microcracks/slight pitting/cratering/approximately 100% coating removal/coating erosion failure
24397	4405-5	Subsurface ring fractures/surface microcracks/slight pitting/approximately 100% coating removal/coating erosion failure
24398	4405-6	Subsurface ring fractures/surface microcracks/slight pitting/cratering/3 internal fractures/approximately 100% coating removal/coating erosion failure

<sup>a</sup> Wright Research and Development Center formerly Air Force Wright Aeronautical Laboratories identification number.

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