Processing Ternary Sulfide Ceramics: Powder Preparation, Sintering, and Hot-Pressing

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Ceramic processing of various AB_2S_4 sulfides with the Th_3P_4 , CaFe₂O₄, and spinel structure types was investigated. These refractory sulfides show good sinterability when fired in flowing H₂S. They can be densified by a combination of hotpressing and hot isostatic pressing into theoretically dense ceramics.

I. Introduction

THE state-of-the-art ceramic materials used in infrared window applications are hot-pressed MgF₂ and hot-pressed or CVD ZnS and ZnSe. Although these highly developed materials have excellent optical properties, they have some limitations imposed by their generally low hardness, fracture toughness, and infrared cutoff. For this reason there is interest in alternative materials that might exhibit longer-wavelength infrared cutoffs, greater hardness, or other improved physical properties.

The ternary sulfides with generic formula AB_2S_4 contain many compounds of interest. Some seven structural families are represented but the two cubic families, the Th₃P₄ structure and the spinel structure, are of greatest interest because they are optically and mechanically isotropic. Reconnaissance of their vibrational spectra¹ shows that the ir modes responsible for intrinsic vibrational cutoff decrease linearly with increasing average cation coordination number. The one Th₃P₄-structure compound investigated in detail, CaLa₂S₄, promises to be an interesting alternative infrared window material.²

Preparation of polycrystalline optical materials is a fine-tuned exercise in ceramic processing, the first step of which is to examine conventional processing techniques. The present paper describes the powder and ceramic processing of CaLa₂S₄ and some other examples of the Th₃P₄, CaFe₂O₄, and spinel structures.



Fig. 1. Scanning electron micrograph of CaLa₂S₄ prepared by direct firing.

II. Powder Preparation

The ternary sulfides used in this study, mainly CaLa₂S₄, were prepared by dry-firing oxides and carbonates in H₂S. Batches were calculated according to the reaction:

$$CaCO_3 + La_2O_3 \cdot x H_2O + 4H_2S \rightleftharpoons CaLa_2S_4 + CO_2 + (4+x)H_2O \quad (1)$$

where $0 \le x \le 4$. The starting powder was placed in a polystyrene bottle with methylacrylic balls and mixed dry for 15 min to ensure homogeneity. The mixtures, contained in graphite or alumina boats, were placed into a fused silica tube contained in an electric tube furnace. After purging with argon, the furnace was heated to 800°C, H₂S gas was admitted through the furnace, the temperature was raised, and the materials were allowed to equilibrate at 1050°C for 120 h. The furnace was turned off and allowed to cool. At 800°C, the H₂S stream was cut off and argon was again admitted. This procedure inhibited sulfur precipitation in the hot zone and on the sample.

The resulting ternary sulfide powders were characterized by X-ray powder diffraction. Oxysulfides and CaS were sometimes observed as impurity phases. Oxysulfide formation could be suppressed by maintaining firing temperatures above 950°C; CaS in the products resulted from an La/Ca ratio <2.00 during initial mixing of raw materials. Exact weighing was difficult because of the hygroscopic character of La₂O₃. When CaS was found, the powder was boiled in deionized water for 0.5 h, which extracted the easily hydrated CaS. The powders were then refired in H_2S at 1000°C for 24 h to remove oxidation products and adsorbed water from the ternary sulfide. The end products were single-phase, well-crystallized ternary sulfides of 10 to 15 μ m particle size.

III. Powder Processing

Densification by any of the usual ceramic processing methods requires starting material with a small particle size and high surface energy. A series of powder processing experiments was made to analyze and understand the effect of different milling techniques on particle size and grain characteristics of CaLa₂S₄. During synthesis, $CaLa_2S_4$ sinters into large agglomerated particles (Fig. 1), which must be comminuted before further processing.

The material was first ball-milled with acrylic balls to break up the sintered aggregates. Samples of several grams were also handground for ≈ 15 min in an agate mortar. Hand grinding produced material with about the same particle size and surface area as did the fluid-energy mill. However, the particle size distribution was wider and the particles were decidedly less spherical than with the fluid-energy-milled material.

Table I. Particle Size/Surface Area of CaLa₂S₄ for Various Comminution Techniques

Comminution technique	SEM es partic (µm)	stimated le size Min/max	BET surface area (m ² /g)
Initial material	12.66	0.55	0.08
Ball-milled	9.5	0.42	0.143
Hand-ground	5.1	0.55	0.95
Fluid-energy-milled Fluid-energy-milled	5.0	0.54	1.0
and hand-ground	4.36		1.25
Attrition-milled	2.76	0.51	2.45

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Fig. 2. Particle size distributions for $CaLa_2S_4$ comminuted by methods indicated. Grain size is expressed in micrometers; size interval is 0.2 of a log unit.

One batch of the powder was run twice through a compressed-air fluid-energy mill. The mill had a partial-vacuum sample hopper which fed into a latex-lined collision chamber, where the particles collided with one another. The resultant particles were vented into the center exhaust tube, where they were collected in double polyester^{\dagger} cotton sample bags.

As an alternative approach to a homogeneous size distribution, $CaLa_2S_4$ was run for 3.5 h in a polyurethane-lined attrition mill using zirconium oxide pellets as the grinding medium and ethanol as the liquid medium. The particle size decreased to $\approx 2.8 \ \mu m$. Comparison of fluid-energy-milled and attrition-milled fractions shows that the attrition milling produces much more homogeneous particles.

Surface areas of powders comminuted by each method were measured by BET (Table I). Attrition milling produces about a factor of 30 increase in surface area over the original as-fired powder. Particle size distributions were determined by a computerdriven scanning electron microscope.³ In this method, each time the beam identifies a particle it stops, draws eight equally spaced cords through the approximate center point, and then averages the maximum and minimum cord lengths to produce a mean grain diameter and ellipticity. These averages in turn are averaged over all grains observed by the SEM, about 1000 grains in the samples measured here. Figure 2 shows the size distributions. All comminution methods produced log-normal distributions. As shown, attrition-milled material is skewed to the left with a decided excess of smaller particle sizes. The distribution in fluid-energy-milled particles is skewed to the right.

Each milling technique effectively reduced grain size, but also produced contamination. Fluid-energy milling could lead to surface oxidation due to exposure to the turbulent air stream. To minimize the amount of trapped oxygen, the material was refired in H₂S for 24 h at 1000°C. The powder prepared in the attrition mill was more yellow than the original material and emission spectroscopic analysis showed $\approx 1\%$ zirconia present in the sample. Contamination also occurred in the hand-ground sample. Samples dissolved in concentrated nitric acid produced 1 wt% silica as an insoluble residue. Overall, fluid-energy milling seems to produce the best powder for further processing.

IV. Sintering

The sinterability of the ternary sulfides was tested by firing green pellets in flowing H_2S .

The CaLa₂S₄ was processed in a fluid-energy mill and then carefully hand-ground. The particles had a mean size of 2.5 μ m



Fig. 3. (A) Dependence of bulk density of sintered CaLa₂S₄ plates and (B) increase of specimen grain size as functions of temperature.

and a surface area of 2.65 m²/g. The material compacted in a pellet press at 350 MPa produced an average green density of 2.85 g/cm³ or 63% of theoretical. The pellets were then sintered in a graphite furnace in a flowing H₂S atmosphere at various temperatures and times. During sintering, grain size and density increased and porosity decreased. A densification of $\approx 85\%$ was reached at a sintering temperature of $1500^{\circ} \pm 10^{\circ}$ C.

An increase in green density should increase the fired density. The pressure was increased to 760 MPa, forming a pellet with a green density 69% of theoretical. The material was again hand-ground and again pressed at 760 MPa, forming pellets with a green density of 72%.

The specimens were sintered in the form of small disks, one centimeter in diameter and a few millimeters thick. They were colored uniformly light yellow and were hard, compact, and robust. The measured bulk densities varied from 82 to 85% of theoretical density. Figure 3 shows the density of CaLa₂S₄ as a function of sintering temperature at a reference time of 90 min. Density increases with temperature up to $\approx 1500^{\circ}$ C and then levels off at $\approx 85\%$ of theoretical. Grain size increases rapidly with increasing temperature in a characteristic S-shaped pattern to $\approx 1500^{\circ}$ C, where further increase of temperature produces little further grain growth.

The effect of sintering time on bulk density and grain size of $CaLa_2S_4$ is shown in Fig. 4. Densification increases with longer sintering time, but then levels off; the final point at 300 min represents the maximum density achieved, $\approx 95\%$ of theoretical. Chemical reactions become important at long sintering times; beyond 200 min the pellets begin to turn black. Grain growth begins to level off at about the same sintering time as the density.

An SEM image of a chemically etched polished surface (Fig. 5) shows that the pores are almost entirely intergranular. Further decrease in pore volume will be rate-limited by very slow diffusion processes.

Unexpectedly, some of these samples showed evidence for melting at temperatures well below the previously determined melting

[†]Dacron, E. I. du Pont de Nemours & Co., Inc., Wilmington, DE.



Fig. 4. (A) Dependence of $CaLa_2S_4$ bulk density and (B) grain size on sintering time.



Fig. 6. (A) Dependence of $SrHo_2S_4$ density and (B) grain size on sintering temperature at a constant sintering time of 90 min.

points. Whether the onset of melting results from a drift from stoichiometry or from unknown reactions with the H_2S atmosphere can be determined only when more information is available on the CaS-La₂S₃ phase diagram.

Sintering experiments were also carried out with $SrHo_2S_4$, a CaFe₂O₄-structure compound. The density increased with temperature up to a maximum near 1550°C and then decreased to the onset of melting. Grain size increased and then leveled out at about the temperature at which maximum density occurs (Fig. 6).

Time is less critical in the sintering of $SrHo_2S_4$. Density increases only slightly with sintering time at 1500°C. Grain growth is very rapid during the early stages of sintering and pore closure occurs very early, allowing the density to plateau at 90 to 93% of the theoretical value. Scanning electron micrographs show the predominance of intergranular porosity in the sintered material. The grains also become less angular at high temperature.

V. Hot-Pressing

A selection of ternary sulfide compounds belonging to several structural families was hot-pressed (Table II). Most pressing was done at 20 MPa ram pressure, although some experiments used 28 MPa. Temperatures were varied and the final density was



Fig. 5. Scanning electron micrograph of $CaLa_2S_4$ sintered at 1550°C for 240 min, showing distribution of pore volume.

Structure	Compound	Leveling temp. (°C)	Elapsed time (min)	Density* (g·cm ⁻³)	Theoretical density (g·cm ⁻³)
Th ₃ P ₄	$\begin{array}{c} CaLa_2S_4\\ SrLa_2S_4\\ CaNd_2S_4\\ SrNd_2S_4\\ CaPr_2S_4\\ SrPr_2S_4\\ SrPr_2S_4\\ CaGd_2S_4\\ SrGd_2S_4\\ \end{array}$	1400 1400 1400 1400 1400 1400 1400 1400	6 6 6 6 6 6 6 6	4.38 4.44 4.68 5.00 4.80 4.30 5.24 5.30	4.526 4.823 4.884 5.178 4.737 5.051 5.367 5.634
CaFe-O	CaSm ₂ S₄ SrSm ₂ S₄ SrHo S	1400 1400	6 6	5.30 5.47 5.10	5.123 5.404
Spinel	$SrEr_2S_4$ $ZnSc_2S_4$	1430 1450 1400	6 7	3.13	3.308 5.470 3.274
Thiogallate	$MgYb_2S_4$ ZnGa ₂ S ₄	1400 1200	6 6	4.78 3.34	5.036 3.809

Table II. Hot-Pressing Experiments on Ternary Sulfide Compounds

*Maximum density observed with 20 MPa.

() 0

TEMPERATURE

1000<u>1</u> 3.2

34

3.6



Fig. 7. Densification of CaLa₂S₄ by hot-pressing. Asprepared material was obtained by direct reaction of oxalates with flowing H₂S; particle size is $\approx 12 \ \mu m$. Jet-milled starting material had a particle size of 5 μm and a particle size distribution as shown in Fig. 2. Holding time at final temperature was 5 min for as-prepared material and 6 to 7 min for jet-milled material.

3.8

DENSITY (g cm⁻³)

40

4.2

44

4.6

determined. Densification histories were recorded during the pressing run.

Hot-pressing was conducted in a resistance-heated uniaxial hotpress[‡] using graphite dies. The dies were coated with boron nitride to suppress interaction with the sulfides. About seven grams of samples were used to press a 2.5-cm disk to 0.5-cm thick. The die assembly was heated to 1450°C at a rate of 100°C/min and full pressure was applied at 450°C. Rapid initial compaction quickly leveled off and actual densification began at \approx 1100°C. The material continued to densify as time and temperature were allowed to level off, after which a steady state density was reached. The other compounds followed essentially the same behavior. The densification time was \approx 15 min.

The densification behavior for two CaLa₂S₄ powders is shown in Fig. 7. The as-prepared powders were obtained by dry-firing calcium and lanthanum oxalates and had grain sizes of ≈ 10 to 15 μ m. Increasing the ram pressure increased densification, but these materials did not reach theoretical density even at the highest temperatures used. Jet-milling produces a much-finer-grained material and greatly improves the densification, particularly at lower temperatures. Here again, however, the densification curves flatten out, and at 1450°C the fine-grained material at 20 MPa achieves about the same density as does the coarse-grained material at 41 MPa. It does not appear possible to achieve theoretical density

[‡]Advanced Vacuum Systems Inc., Woburn, MA.



Fig. 8. Microstructure of $CaLa_2S_4$ hot-pressed at 41 MPa and 1450°C for 5 min.

by hot-pressing alone, using these starting powders and short holding times (5 to 7 min). Hot-pressing with holding times of 30 min or more will produce 99.9% dense ceramics, but these ceramics are black.

The hot-pressed disks are hard and robust. Those that were pressed for short times (5 to 15 min maximum) are yellow, translucent solids, except $ZnSc_2S_4$, which is purple. If pressing was continued for more than 15 min, the disks generally blackened, beginning with an annular black zone around the perimeter of the disk. A 2-h pressing resulted in a completely black disk. The black materials are opaque in the infrared, as well as in the visible. Reduction of the sulfides by the action of the graphite dies probably causes the blackening. Reaction of graphite with the sulfides produces CS_2 , resulting in a shift in stoichiometry.

Figure 8 shows a typical microstructure for hot-pressed $CaLa_2S_4$. Substantial pore volume remains, but there are more closed pores and the overall permeability of the specimens is less than that of the sintered sulfide ceramics.

Hot-pressing proves to be an effective method of densifying ternary sulfides but its use is limited by the tendency of the materials to drift off stoichiometry. Table III compares some of the properties of the hot-pressed materials. Longer pressing times can produce theoretically dense materials but at the price of an unacceptable degradation of the optical properties.

VI. Hot Isostatic Pressing

Complete densification of stoichiometric ternary sulfide ceramics was achieved by hot isostatic pressing. Both sintered and hot-pressed ceramic disks were densified in the hot isostatic press, but only the hot-pressed samples could be fully densified.

Hot isostatic pressing was conducted in a specially designed unit constructed in this laboratory. The heating element, a molybdenum-wound alumina crucible (100 mm high and 50 mm ID), was enclosed within four sealed concentric ceramic and metal cans which act as convection barriers. This arrangement, which can be readily assembled for rapid specimen turnaround, has proved to be very efficient thermally. Samples were wrapped in

Table III. Comparison of Physical Properties of Sintered and Hot-Pressed CaLa₂S₄

	Sintered (1500°C 00 min)	Sintered (1500°C 150 min)	Sintered (1500°C 120 min)	Hot-pressed (20 MPa)	
Property	and cold-pressed (350 MPa)	and cold-pressed (350 MPa)	and cold-pressed (760 MPa)	1400°C, 15 min	1450°C, 30 min
Temperature (°C)	1500	1500	1500	1400	1450
Time (min)	90	150	120	15	30
Grain size (μm)	26	28.3	29	35	40
Density (g·cm ⁻³)	3.85	3.88	4.08	4.23	4.33
Density (% theor.)	85	86	90	93	96
Porosity (%)	14	14	10	6	4
Vickers hardness (GPa)	3.14	3.19	3.92	5.39	5.64

Table IV. Density of CaLa₂S₄ After Hot Isostatic Pressing

	Density (% theor.)	
Specimen	Before	After
Hot-pressed, fine-grained	95.6	100
Hot-pressed, coarse-grained	95.0	100
Cold-pressed and sintered	90.0	96.5
Cold-pressed only	65.0	85



Fig. 9. Microindentation hardness measurements for $CaLa_2S_4$ prepared by processing techniques indicated.

platinum foil and placed into a separate alumina crucible and then loaded into the furnace. The apparatus was evacuated and backfilled with argon to atmospheric pressure several times to remove any oxygen. The samples were heated to 1400°C at 12°C/min and held at temperature while a pressure of 20 MPa (2925 psi) was applied for 30 min. High-pressure argon was provided from a 41 MPa (6000 psi) cylinder and recycled after the hot isostatic pressing operation using two auxiliary low-pressure cylinders. About ten minutes was required to reach a working pressure of 20 MPa. Temperature was then lowered at 12°C/min to ambient and pressure was relieved to atmospheric.

The densification achieved by hot isostatic pressing is summarized in Table IV. The increase in density improves the hardness (Fig. 9). The combination of hot-pressing and hot isostatic pressing produces materials of maximum hardness which are close to the intrinsic values.

Figure 10 shows the microstructure obtained from the hotpressing/hot isostatic pressing combination. The pores in the hotpressed pieces are completely closed by hot isostatic pressing. There is also considerable grain growth and a great enhancement in the sharpness of the grain boundaries. It was not possible to densify either sintered or cold-pressed specimens as unenclosed disks in the hot isostatically pressed samples. The pore volume in the initial pieces must have been interconnected so that densification could not occur.

VI. Conclusions

Refractory ternary sulfides, particularly those belonging to the Th₃P₄, spinel, and CaFe₂O₄ structural families are amenable to conventional ceramic processing. The most significant problem in powder comminution is the tendency to form hydrated or oxidized layers on the surfaces of the reactive powders. These layers can be stripped by a second firing in flowing H_2S at temperatures



Fig. 10. Microstructure of $CaLa_2S_4$ (A) as-hot-pressed at 20 MPa and 1450°C and (B) hot-pressed followed by hot isostatic pressing at 24 MPa and 1400°C.

low enough (e.g. 1000°C) to suppress sintering and minimize particle growth.

The ternary sulfides can be sintered into compact, hard ceramics in flowing H₂S; the compounds remain stoichiometric. Densification of 90% was about the maximum obtained with starting materials prepared by direct firing of oxides and carbonates in flowing H₂S.

Hot-pressing with 20 to 40 MPa ram pressure at 1400° to 1550°C produces hard, compact ceramics. However, at pressing times necessary to achieve theoretical density, a reduction occurs due to reaction between the ternary sulfide and the graphite dies.

Theoretically dense ceramics with clearly developed grain structure could be obtained by hot isostatically pressing disks that had been previously hot-pressed for short times to achieve a closedpore structure. Grain boundaries of these materials are sharp and the SEM shows no residual pores. Ceramic CaLa₂S₄ has a 5.88 GPa Vickers hardness, the highest value observed in this study.

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