

Phase equilibria and processing of infrared optical ceramics on the join CaLa_2S_4 - La_2S_3

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Processing techniques have been developed for the fabrication of optically transparent, theoretically dense CaLa_2S_4 – La_2S_3 ceramics with a potential application as windows for the mid-infrared. Extreme care is needed to avoid oxygen. Best results were obtained by pre-sintering in an $\text{H}_2\text{S}/\text{H}_2$ atmosphere followed by hot-isostatic pressing. Microstructures, hardness measurements, and infrared absorption spectra serve to characterize the various processing procedures.

Key words: IR windows, Hot pressing, Phase equilibria, Thorium phosphide structures.

Introduction

Calcium lanthanum sulfide is a refractory material with a melting point above 1800 °C. It has shown some promise as an IR window material [1-3]. CaLa_2S_4 crystallizes in the cubic Th_3P_4 structure, space group $I\bar{4}3d$, which is optically isotropic making it useful as a polycrystalline optical material. The processing of CaLa_2S_4 and other sulfide optical ceramics is a difficult problem because, although the compounds are generally refractory, they are not stable in air at high temperature, take up oxygen, and drift off stoichiometry.

It has been found that there is a continuous solid solution between the nominally stoichiometric CaLa_2S_4 and $\gamma\text{-La}_2\text{S}_3$ which has a defect Th_3P_4 structure. There is little or no solid solution on the calcium-rich side of the compound. The precipitation of CaS as a hygroscopic second phase is one of the processing problems in the preparation of stoichiometric CaLa_2S_4 . For this reason it has been found useful to prepare materials on the lanthanum-rich side of the join [4]. The processing of the stoichiometric compound [5, 6] uses a combination of sintering in flowing H_2S and hot isostatic pressing of suitable powder preparations. Finding suitable powders has been challenging and much research has been done [7-10]. The sintering characteristics of the end-member sesquisulfides have also been investigated [11].

The development of CaLa_2S_4 and related compounds as practical optical ceramics was interrupted by the discovery of CVD diamond in the late 1980s. Diamond windows had the potential of better physical properties, optical properties, and chemical stability so that the thrust of optical and IR window research was focused on diamond. The refractory

sulfides remain intriguing materials for which not all questions have been answered. The present paper is concerned with ceramics formed along the CaLa_2S_4 - La_2S_3 join (tie-line) and discusses the phase equilibria and ceramic processing of materials with these compositions.

Phase Equilibria

Background

Some of the difficulties in determining the phase diagram along the join between CaS and La_2S_3 are illustrated in Fig. 1 for the similar SrS - La_2S_3 system. On the Sr-S (or Ca-S) side of the diagram there is only a single compound, SrS, with the cubic halite structure. It is an insulator. On the La-S side of the diagram, however, are at least six, possibly seven intermediate lanthanum sulfides. LaS also

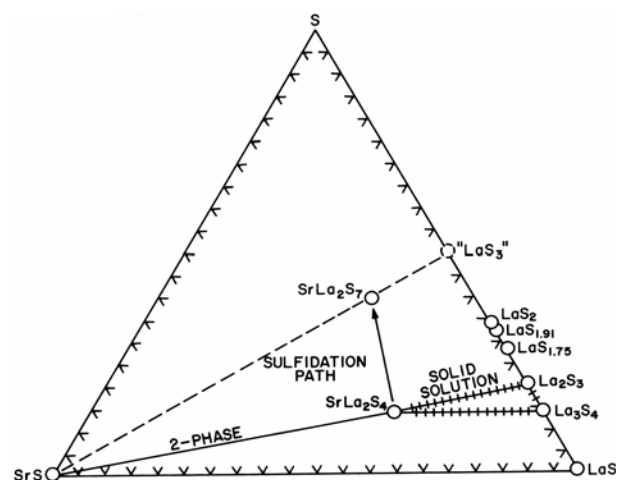


Fig. 1. Composition diagram for the ternary system SrS - LaS - S showing known compounds within the system. From Provenzano and White [13].

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has the halite structure but is metallic. La_2S_3 occurs in two crystallographic forms, the orthorhombic $\alpha\text{-La}_2\text{S}_3$ and the cubic $\gamma\text{-La}_2\text{S}_3$. Both are insulators with band gaps of 2.73 and 2.70 eV respectively [12]. La_3S_4 has the cubic Th_3P_4 structure but is black and metallic. In addition, there are a series of higher sulfides, $\text{LaS}_{1.75}$, $\text{LaS}_{1.91}$ and LaS_2 . Discovery of a family of compounds [13] of which SrLa_2S_7 is a member, also implies the possible existence of LaS_3 .

It is likely that the $\text{CaS-La}_2\text{S}_3$ join will be similar to the $\text{SrS-La}_2\text{S}_3$ join. A continuous solid solution is expected between CaLa_2S_4 and La_2S_3 . There is also continuous solid solution between CaLa_2S_4 and La_3S_4 . In addition there is the unknown influence of the higher sulfides.

Two approaches were used to determine the phase diagram along the $\text{CaLa}_2\text{S}_4\text{-La}_2\text{S}_3$ join: a closed system and an open system. Because the materials were processed in flowing H_2S , open system phase equilibria were appropriate. It is also helpful to know the condensed phase equilibria along the join.

Closed system equilibria

To obtain closed system equilibria, experiments were conducted with mixtures of CaLa_2S_4 and La_2S_3 of specified compositions in evacuated sealed silica glass tubes. The starting materials were CaLa_2S_4 synthesized from CaCO_3 and La_2O_3 fired in flowing H_2S as described previously [1] and commercial La_2S_3 . The tubes were fired from one to three days, quenched in water, and the contents analyzed by X-ray powder diffraction. The results of this matrix of experiments are shown in Fig. 2.

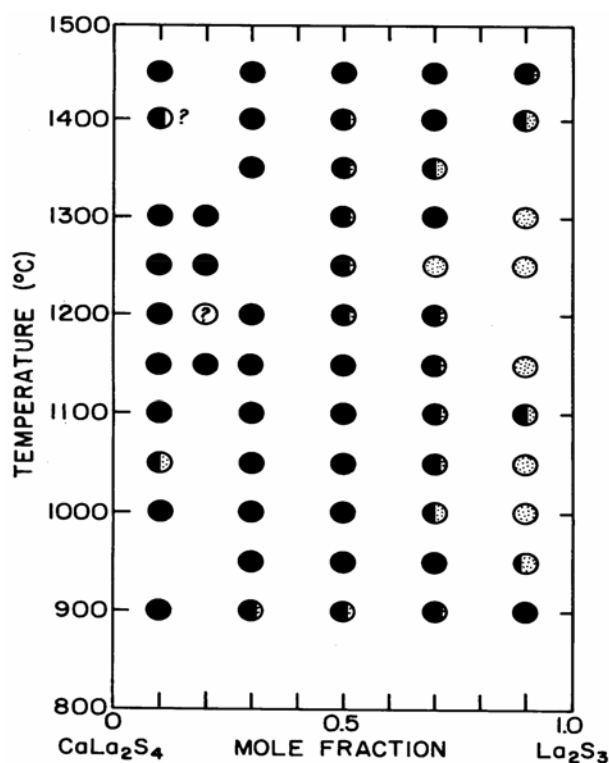


Fig. 2. Results of closed system experiments along the join $\text{CaS-La}_2\text{S}_3$. Closed circles: Th_3P_4 structure solid solutions (γ -phases). Dotted circles: $\beta\text{-La}_2\text{S}_3$ structure.

It can be seen that the cubic gamma structure persists over the entire experimental range. There is a low temperature kinetic threshold between 800 and 900 °C, below which the mixtures do not react under the experimental conditions in a reasonable period of time. The effective upper limit is dictated by the silica glass tubes used as containers. By accepting a certain failure rate, it was possible to extend the silica tube technique to 1450 °C, although at this temperature there is some devitrification and considerable collapse of the tubes. In no case was there evidence for a chemical reaction between the silica and the sulfide samples.

The uptake of oxygen by the lanthanide sulfides is a serious problem. There exists an oxysulfide related to $\beta\text{-La}_2\text{S}_3$ with the end member composition of $\text{Ln}_{10}\text{S}_{14}\text{O}$. It is an ordered compound in which the 15th sulfur ion in the $\beta\text{-La}_2\text{S}_3$ structure is replaced by oxygen which occupies a distinct lattice site [14]. Introduction of further oxygen into the system produces the well known oxysulfide $\text{La}_2\text{O}_2\text{S}$. There is apparently a continuous solid solution between the oxygen-saturated compound and $\beta\text{-La}_2\text{S}_3$ which has the same structure. However, because of the difficulty in determining small quantities of oxygen in these materials, no one has established satisfactorily that the beta phase is actually a pure sulfide although Besançon et al. [15] claimed that a pure sulfide beta phase could be made for the larger rare earths La, Ce, and Pr. Some of the phase equilibria problems in the ternary La-S-O system are discussed elsewhere [16].

When compositions were fired in sealed silica tubes with no special treatment, the beta structure appeared at the lanthanum-rich end of the join but not in a very consistent fashion (Fig. 2). It was found that if the silica tubes were baked out under vacuum and a segment of graphite rod included with the pellet, that much of the beta phase disappeared. If the beta phase does indeed occur as an end-member sulfide, it cannot extend more than a few mole percent along the ternary join.

French workers [17] have claimed that the transition from the orthorhombic alpha structure to the beta structure occurs at 950 °C and that the beta La_2S_3 phase persists to 1300 °C. No evidence for this was found in the experiments described here. The commercial La_2S_3 starting material was the alpha form. It converted completely to the gamma at all temperatures above the kinetic threshold. The results presented in Fig. 2 show that in a closed system the gamma form persists over the entire temperature range.

Open system equilibria

The open system experiments were carried out with oxide and carbonate starting materials. Mixtures were prepared containing CaCO_3 and La_2O_3 in 10 mole percent increments. These were spooned into individual compartments cut into a graphite boat which was then placed in a silica walled tube furnace and fired in flowing H_2S at roughly one atmosphere pressure. Run times were five days at 50 degree temperature intervals from 950 to 1200 °C and at 1300 and 1400 °C. Run products were pulled from the hot zone

of the furnace with a silica rod and cooled rapidly while remaining in flowing H_2S . Phase identification was by X-ray powder diffraction using Al_2O_3 as an internal standard.

The results, shown in Fig. 3, were remarkably different from the sealed tube results. On the calcium-rich side there is only a two-phase region extending from CaS to CaLa_2S_4 . Some degree of solid solution cannot be ruled out on the basis of the present experiments, but the range is small, less than a few mole percent. On the lanthanum-rich side, at temperatures above 950°C , there is a complete gamma structure solid solution between CaLa_2S_4 and La_2S_3 . Oxyulfides formed below 950°C . X-ray diffraction patterns were measured on the solid solutions and the lattice parameters of the cubic cells were calculated using the Appleman refinement program (Fig. 4). Lattice parameters change in a linear fashion with composition on the lanthanum-rich side but there is a small break in slope at about 70 mole

percent that appeared in the three temperatures for which X-ray data were measured.

Additional higher temperature runs were made in a graphite tube furnace which allowed the temperature range to be extended to 1600°C . At temperatures above 1150°C , the products darkened with the darkening increasing with increasing temperature. Plots of unit cell edge as a function of composition have the same shape and the same break in slope observed at lower temperatures but the curves were offset to smaller values. The systematic decrease in cell edge may represent a change in metal/sulfur stoichiometry which could also account for the optical absorption.

At temperatures above 1400°C , pellets with intermediate compositions showed evidence of melting. The pellets at other compositions and temperatures were recovered as sintered masses with their original cylindrical shape. The pellets of intermediate composition collapsed into small rounded masses at temperatures above 1400°C . Calcium lanthanum sulfide solid solutions are typically a pale yellow color. The melted materials were solid black.

If the join remains binary, there seems to be no thermodynamically reasonable way to draw a liquidus loop between the high melting points of CaLa_2S_4 and La_2S_3 that would include a melting minimum near 1400°C . The black color also suggests that these materials do not lie on the $\text{CaS-La}_2\text{S}_3$ join. Evidence obtained from the $\text{SrS-La}_2\text{S}_3$ system [13] suggests that the H_2S gas stream is sufficiently oxidizing to push the composition off stoichiometry to the sulfur-rich side of the join. Electron microprobe analyses of the $\text{SrS-La}_2\text{S}_3$ system showed a distinct compound with a bulk composition that could be normalized to SrLa_2S_7 . This would lie on the join between SrS and a hypothetical LaS_3 and also on the join between SrLa_2S_4 and sulfur. We conclude that in the open system, the phase equilibria must be treated as ternary. The composition migrates onto a liquidus surface curving downward toward the lower melting polysulfides in the sulfur-rich part of the ternary system. The "phase diagram" shown in Fig. 3 must be taken as a projection of ternary equilibria onto the binary join rather than a true binary phase diagram.

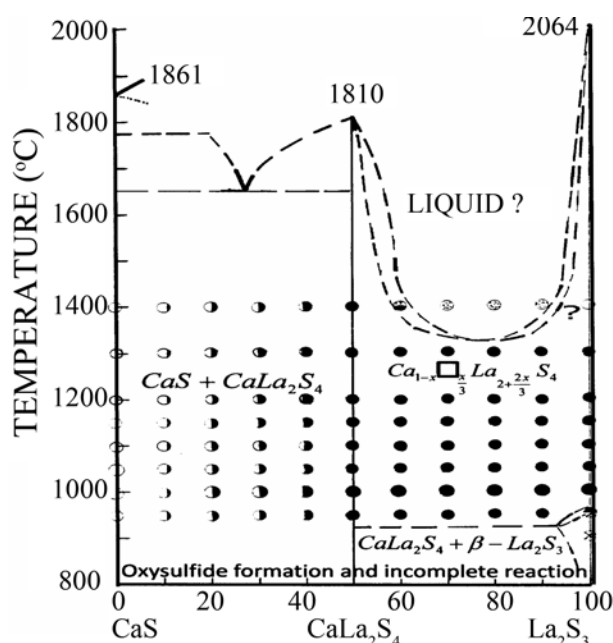


Fig. 3. Results of open system experiments along the join $\text{CaS-La}_2\text{S}_3$.

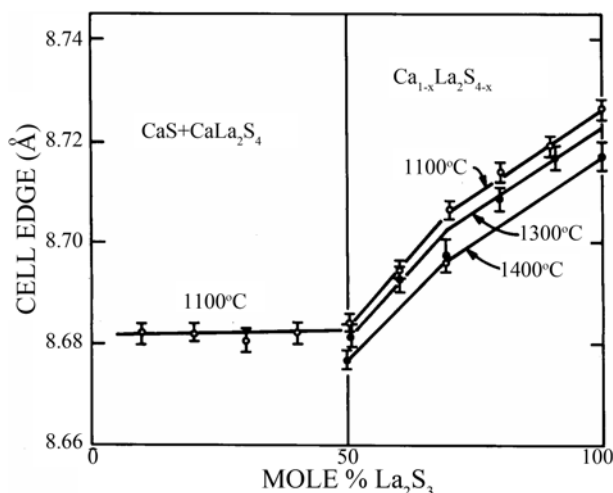


Fig. 4. Unit cell edge as a function of composition and temperature.

Ceramic Processing

Successful processing of ternary sulfides into dense ceramic compacts relies mainly on the powder morphology or physical characteristics of the starting powder. The abrasive nature of the material has made conventional size reduction techniques such as ball milling and fluid energy milling useless. Although these comminution techniques resulted in particle size reduction, contamination resulted from the grinding medium or from oxidation of the particle surfaces by exposure to the turbulent air stream. The most effective approach to preparation of fine-grained powders was the evaporative decomposition of solutions (EDS) method (also known as spray pyrolysis) as demonstrated earlier [18].

Calcium and lanthanum nitrate solutions were prepared

and mixed at 10 mole percent increments between the CaLa_2S_4 and La_2S_3 compositions to produce a 0.1 molar solution. These solutions were converted to fine-grained oxides in the EDS furnace. The oxide powders were spooned into a $5 \times 5 \times 30$ cm fused silica boat which was then placed in an 8-cm diameter horizontal tube furnace. The tube was purged with argon after which the powder was heated for 48 hours at 1000°C in a flowing atmosphere of 50% H_2S and 50% H_2 . The $\text{H}_2\text{S}/\text{H}_2$ mixture was necessary to completely strip the sample of oxygen. X-ray powder diffraction patterns showed that the oxide precursors had been completely converted to sulfide.

Two procedures were used for densification:

(i) HP-HIP. Vacuum hot press (HP) at 1400°C and 4 MPa for five minutes followed by hot isostatic pressing (HIP) at 1400°C and 20 MPa for 2 hours.

(ii) S-HIP. Sinter in flowing H_2S at 1500°C for 2 hours followed by hot isostatic pressing at 1350°C and 24 MPa for 1.5 hours.

A flow sheet shows more of the details (Fig. 5).

In series (i) the sulfide powders were densified in a vacuum hot press before a final densification by hot isostatic pressing. These samples were processed at temperatures higher than the temperatures where the open system phase equilibrium experiments had indicated melting but there was no evidence of melting. The HP-HIP samples did darken indicating some drift from stoichiometry.

The powder was formed into a green compact in a cold press at 170 MPa for 3 minutes. The compact was then transferred to an Astro 2700 evacuated tube furnace and held for one hour under vacuum at 100°C to remove superficial water and CO_2 . The furnace was then backfilled to atmospheric pressure with the $\text{H}_2\text{S}/\text{H}_2$ gas mixture which was maintained at a flow rate of $250\text{ cm}^3\text{ minute}^{-1}$. The furnace temperature was taken to 1000°C at a rate of $10\text{ K}\cdot\text{minute}^{-1}$ and held at 1000°C for 24 hours to strip any remaining hydrates or oxides. After the soak period, the hydrogen was turned off and the H_2S flow increased. The sample was heated to 1500°C and allowed to sinter for 1.5 hours. The furnace was then turned off and cooled. At 600°C , the furnace was

purged with argon and then allowed to cool to ambient.

The sintered ceramics were translucent with an amber color. The density, measured by displacement in CCl_4 , ranged near 95% of theoretical. Samples were slabbed, polished, and etched with nitric acid. SEM images (Fig. 6) revealed some grain growth and a closed pore structure.

The sulfide ceramics were brought to full density by hot isostatic pressing (HIP). The sintered compact was placed in a fused silica crucible surrounded by powder of the same composition and inserted in the hot isostatic press. The press was filled with argon and heated at $12\text{ K}\cdot\text{minute}^{-1}$ to 1100°C where the full gas pressure of 20 MPa was applied. Then the temperature was raised to 1400°C and held for 1.5 hours after which the furnace was cooled to room temperature. Polished wafers were amber-colored and transparent (Fig. 7). Measured density was 100% of theoretical; SEM images did not reveal any pores.

Characterization and Ceramic Properties

Although X-ray patterns of both the EDS sulfide powders

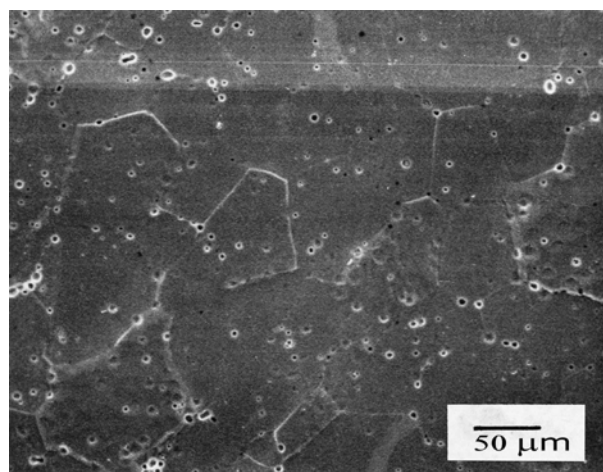


Fig. 6. SEM image of CaLa_2S_4 ceramic after sintering but before the HIP treatment.

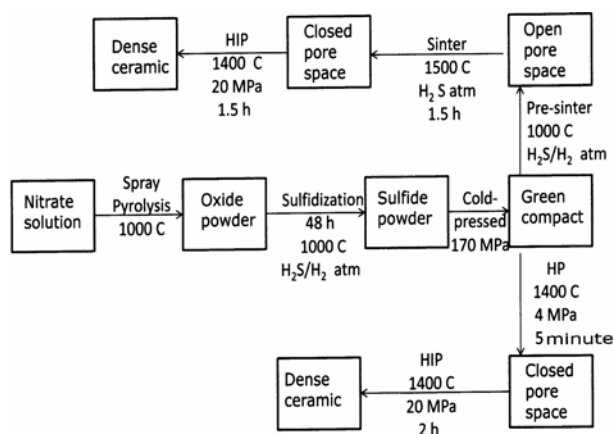


Fig. 5. Flow sheet for the processing of ternary sulfide ceramics by HP-HIP and S-HIP routes.

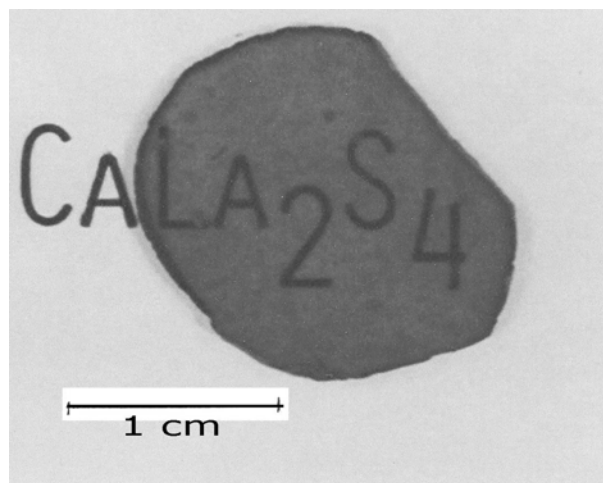


Fig. 7. Photograph of finished ceramic wafer illustrating optical transparency.

and the sintered compacts show complete solid solution between CaLa_2S_4 and $\gamma\text{-La}_2\text{S}_3$, there is a break in slope in the plot of cell edge against composition (Fig. 4). A similar break in the plot of unit cell edge in the SrNd_2S_4 - Nd_2S_3 system [15] also appeared as a break in the Raman spectra obtained at various compositions along the join. The Raman data were interpreted as a change in defect character

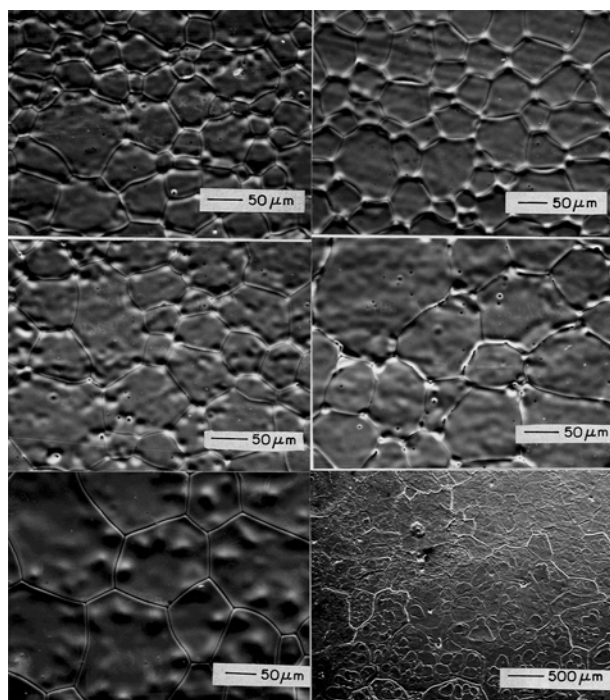


Fig. 8. SEM images of acid-etched sintered CaLa_2S_4 ceramics.

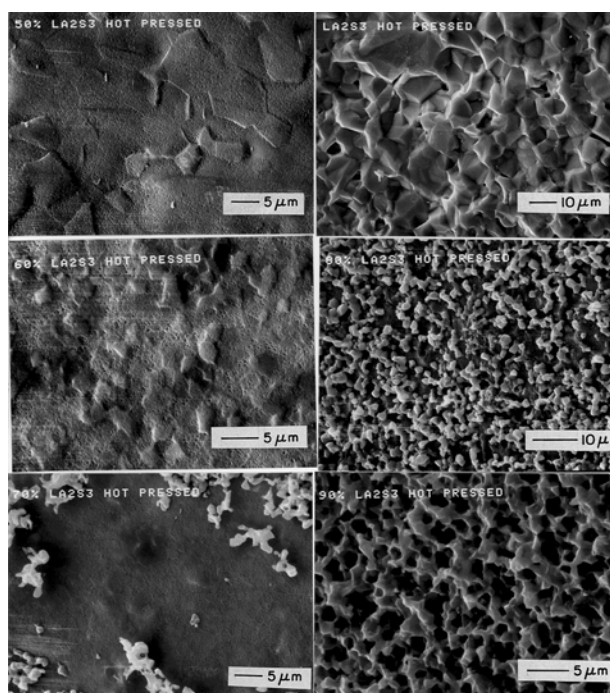


Fig. 9. SEM images of acid-etched hot-pressed (HP) CaLa_2S_4 ceramics.

along the solid solution series. Although the composition can be represented as $\text{Ca}_{1-x}\text{La}_2\text{S}_{4-x}$, the evidence is that the anion sublattice remains completely occupied so that the defect structure is confined to the cation sublattice. The composition would then be written $\text{Ca}_{1-x}\square_{x/3}\text{La}_{2+2x/3}\text{S}_4$. The break in slope in the cell edge plot indicates an even more complicated defect structure.

Ceramic wafers were prepared at 10 mole percent intervals for sintered, hot-pressed and hot pressed-hot isostatic pressed ceramics. These were polished and etched in nitric acid so that the grain boundaries and other microstructural features could be seen in SEM images (Figs. 8-10). The sintered specimens (Fig. 8) show a grain structure with a grain size of about $50\text{ }\mu\text{m}$ with pores localized on the grain boundaries and boundary intersections. Vacuum hot-pressing reduces the grain size (Fig. 9) and increases the density of the wafers. At high La_2S_3 concentrations the microstructure reveals differential etching which may be due to incipient phase separation along the solid solution series. Hot isostatic pressing the HP samples produces dense wafers but these also exhibit differential etching (Fig. 10).

Microhardness values were determined using a Leitz Miniload Hardness Tester (Fig. 11). The reported hardness for $\gamma\text{-La}_2\text{S}_3$ is around 400 kg/mm^2 (400 MPa) which was the value obtained from sintered specimens of this composition. Note that in all cases, a break in slope occurs at 70 mole percent La_2S_3 which corresponds to the break in slope observed in the cell edge data and also the onset of differential etching.

Infrared transmission spectra of five of the S-HIP polished wafers are shown in Fig. 12. The samples were 0.5 mm thick. The spectra have not been corrected for front surface

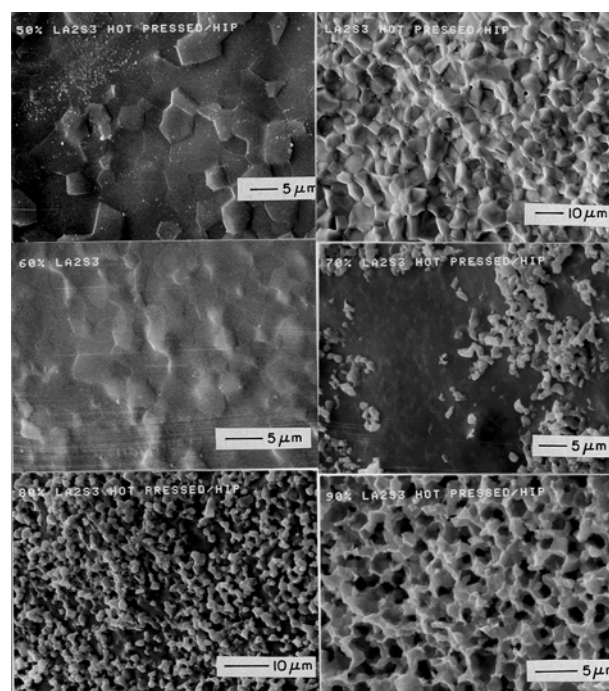


Fig. 10. SEM images of acid-etched HP-HIP CaLa_2S_4 ceramics.

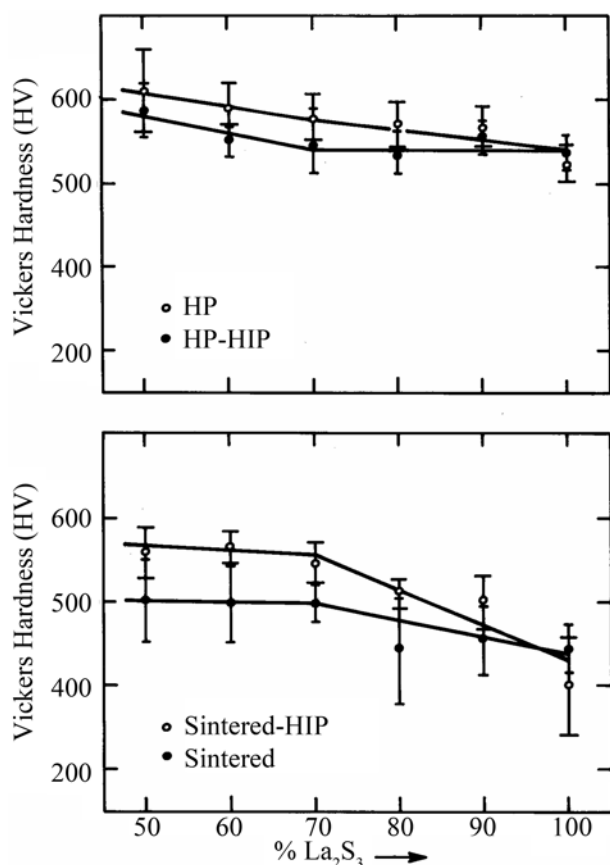


Fig. 11. Vickers hardness as a function of composition.

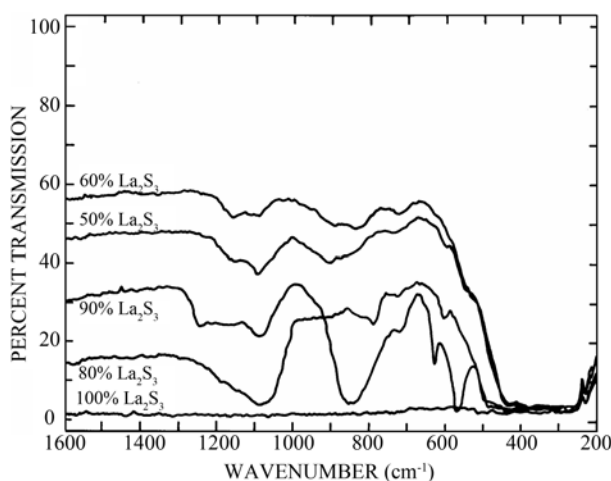


Fig. 12. Infrared spectra for a series of ceramics of different composition.

reflectance which is 23% in this wavenumber range (Merzbacher, Chess and White, unpublished data). The actual transmission in the mid-range IR would be in the range of 75-85% for the 50 and 60 mole percent compositions. As the lanthanum concentration increases, the optical transmission decreases, impurity bands appear and increase in intensity. The absorption feature near 1100 cm^{-1} matches

the spectrum of the SO_4^{2-} ion. The complex absorption spectrum of the 90% sample is of unknown origin. The very intense absorption below 550 cm^{-1} is the intrinsic lattice absorption of the compound itself.

Conclusions

$\text{CaLa}_2\text{S}_4\text{-La}_2\text{S}_3$ ceramics with good transparency in the visible and in the mid-range infrared can be fabricated by a series of steps. Key aspects of the processing are: (i) production of extremely fine-grained initial powders by spray pyrolysis; (ii) removing all oxygen during sulfidization by a flowing $\text{H}_2\text{S}/\text{H}_2$ atmosphere; (iii) sintering to a closed pore microstructure in an H_2S atmosphere; and a final densification by hot isostatic pressing.

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