Sulphurization of coprecipitated carbonates for formation of CaLa$_2$S$_4$

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Factors including BET surface area and La/Ca mole ratio of the coprecipitated carbonates, pH value of the solvent and decomposition atmosphere before sulphurization for fabrication of ultrafine CaLa$_2$S$_4$ powder were investigated. The CaLa$_2$S$_4$ powder was formed through decomposition of coprecipitated carbonates in vacuum and sulphurization with hydrogen sulphide at low temperature. The resultant powder was determined to be a pure CaLa$_2$S$_4$ without oxysulphide phase, as analysed by X-ray diffraction. It consisted of fine particles of size $\sim 1.6\,\mu$m and showed translucency after sintering at 1400 °C under an H$_2$S atmosphere.

1. Introduction

CaLa$_2$S$_4$ is a candidate for optical application, because it transmits at longer infrared wavelength (14 μm cut-off) than other dome materials, and possesses good mechanical properties [1]. For the optical grade CaLa$_2$S$_4$ ceramic, a low-porosity sintered body was difficult to achieve; this was attributed to aggregation and a broad particle size distribution from the long soaking time and high temperature for sulphurization of the mixed oxides [2].

La/Ca mole ratios of the coprecipitated carbonates played a significant role in sulphurization due to the different reaction rate of sulphurization of calcium oxide and lanthanum oxide [3], while the BET surface area of the carbonate precursor which was an indication of nucleation and growth rate during coprecipitation [4].

Highly reactive oxide powder could be obtained by decomposing the carbonates in vacuum, and the sulphurization temperature or time could be reduced for the formation of sulphide powders. Studies [5–9] have been performed on the relations between thermodynamics, kinetics and microstructure of these oxides that can be produced with some endothermic decomposition reactions. The oxides obtained by decomposition in vacuum at low temperature (< 620 °C) having the highest BET surface area must not come into contact with air or water vapour before subsequent sulphurization.

The chemisorption and degree of dissociation of the sulphurization agent were other factors which influenced the sulphurization rate [10]. Some investigations on the preparation of lanthanum sulphides from lanthanum oxide using carbon disulphide as a sulphurizing agent, were made by Toide [9], while Kumta [12] prepared the lanthanum sulphides from metal alkoxides using hydrogen sulphide as a sulphurization agent.

The purpose of the present paper is to report a method of preparing highly sinterable CaLa$_2$S$_4$ powders. The coprecipitation rate, temperature and solvent were optimized to obtain little or no composition fluctuation of the carbonate precursors with high BET surface area. The precursor powder was decomposed in vacuum, then sulphurized to obtain high-purity single-phase CaLa$_2$S$_4$ powders for further densification.

2. Experimental procedure

As starting materials, commercial reagents La(NO$_3$)$_3$·6H$_2$O and Ca(NO$_3$)$_2$ solution were chosen to supply lanthanum and calcium components, respectively, for CaLa$_2$S$_4$ fabrication. The calcium and lanthanum solutions prepared were mixed in a mole ratio of La/Ca = 1.6–2.4. On the other hand, ammonium carbonate and ammonium hydroxide were dissolved in ethanol. It should be noted that the quantity of ammonium carbonate was 50% excess over the stoichiometric amount required to produce coprecipitation, and the volume of ethanol was two to six times greater than that in the calcium and lanthanum mixed solution. Both of solutions were cooled to about 20 °C. The cation solution was quickly titrated to the ammonium carbonate solution and stirred vigorously. The pH of the solution before and after precipitation was about 9.5 and 7.5, respectively. The precipitate was filtered, washed free from nitrates, and ultrasonically dispersed in ethanol for 0.5 h. These coprecipitates were dried at 80 °C in air overnight. The dried powder was decomposed in vacuum at 500 °C for 2 h and sulphurized at 650 °C for more than 3 days in an H$_2$S atmosphere. Before pressing, the sulphide powder was washed with distilled deionized water until the conductivity of the supernatant dropped below 5 μS. The resulting light green powders were

compacted at 400 MPa in a tungsten carbide-lined die into discs of 15 mm diameter and 3 mm thickness. Samples were packed in $CaLa_2S_4$ powder in an alumina crucible and sintered in pure H_2S at 1400 °C for 4–16 h.

The dried carbonates and the sulphurized powders were examined by X-ray diffractometry and X-ray fluorescence (XRD/XRF), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The powders were also characterized by measurements of surface area by the BET method and particle size distribution using the sedimentation technique (micromerities) and a coulter particle analyser (model N4SD). The homogeneity of the powders and the pellets was analysed by energy dispersive microanalysis (EDX).

3. Results and discussion

It was found in this study that the sulphurization and transformation temperature changed with the BET surface area and the La/Ca mole ratios of the coprecipitated carbonates and the decomposition atmosphere.

The BET surface area of the coprecipitated carbonates varied with coprecipitation temperature, titration rate, concentration of the precipitation agent and solvent used in the coprecipitation.

Carbonates, formed at higher precipitation temperature, had a greater particle size and lower surface area due to the low supersaturation and fewer nuclei [13], as shown in Fig. 1, but the ammonium carbonate began to crystallize itself below 15 °C and made the composition of the coprecipitated powder fluctuate seriously and the phase of La_2S_3 [14], CaS [15], La_2O_2S [16], and $La_2O_2S_2$ could be detected by X-ray diffraction after these precursor powders sulphurized.

The titration rate influenced the BET surface area and composition homogeneity of the carbonates. Rapid coprecipitation can cause the simultaneous precipitation of all unlike cations in a mixed aqueous solution [17] and produced carbonates with the highest BET surface area and uniform composition distribution. The homogeneity of Pellet R-1 (50 ml min^{-1}) was better than that of pellet R-2 (5 ml min^{-1}) as shown in Table I. The precipitation medium, ethanol, had some effect on the BET surface area of the coprecipitated carbonates, as shown in Fig. 3. On coprecipitating the carbonates at 20 °C in ethanol solution, the smallest particle size with maximum BET surface area and narrow size distribution could be obtained (Fig. 2a).
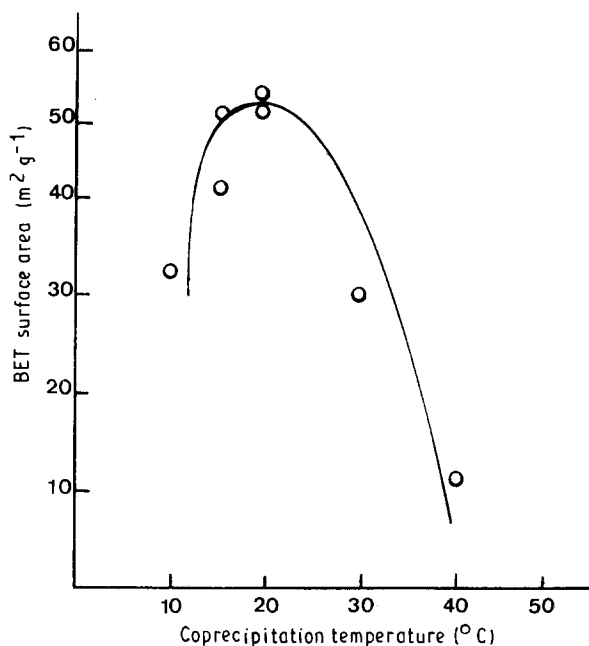

Figure 1 BET surface area of coprecipitated powders as a function of coprecipitation temperature.

Fig. 4 shows the XRD of the coprecipitated carbonates with La/Ca mole ratios from 1.6–2.4. The ratio of $CaLa_2S_4$ phase (1 3 0) to La_2O_2S phase (1 0 1) was changed with the La/Ca mole ratio of the carbonates as shown in Table II, because the phases formed in the powder during firing at 650 °C were La_2O_2S and CaS initially, then $CaLa_2S_4$ and La_2S_3, as shown in Fig. 5, as determined by XRD. The nucleation rate of $CaLa_2S_4$ could be enhanced by the presence of CaS: this can be washed out with water, while part of the $CaLa_2S_4$ could decompose to La_2O_2S and $Ca(OH)_2$ depending on the water temperature.

The pH value of the coprecipitated carbonate solution had little influence on the powder characteristics for dried carbonates, but had a great influence on the sulphide powders. The sulphide powder with a broad particle size distribution had an agglomerate size varying from 0.1 μm spheres up to 35 μm flakes. The solution with the lower pH value produced a smaller average particle size (as shown in Fig. 6) and needed the shortest time for completion of the final powder with Th_3P_4 structure during firing.

Decomposition temperature, CO_2 partial pressure and soaking time controlled the microstructure and the BET surface area of the decomposed powder. The thermal decomposition of the coprecipitated carbonates was studied by thermogravimetric analyses in air, as shown in Fig. 7. The process was completed at

TABLE I EDX of sintered pellets of $CaLa_2S_4$ coprecipitated

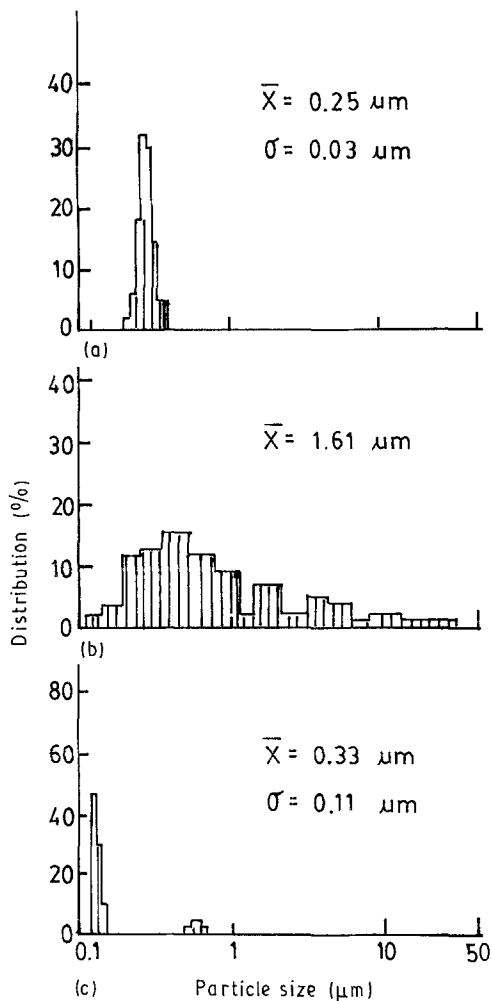|	Pellet R-1, 50 ml min^{-1}						Pellet R-2, 5 ml min^{-1}					
Element	1	2	3	4	5	6	1	2	3	4	5	6
Ca (mol %)	11.5	11.5	11.7	11.9	12.2	11.8	13.8	9.3	3.8	4.5	6.4	5.3
S (mol %)	54.2	53.7	54.7	52.2	53.9	51.5	53.2	54.6	53.5	52.1	46.8	55.2
La (mol %)	34.2	34.7	33.6	35.8	34.0	36.7	33.0	36.1	42.7	43.4	46.8	39.5

Figure 2 Particle size distributions for (a) carbonate powders coprecipitated at 20 °C in ethanol solution, $\bar{x}$ = 0.25 μm, (b) $CaLa_2S_4$ powder sulphurized at 650 °C for 72 h, $\bar{x}$ = 1.61 μm, (c) powder obtained from (b) after grinding for 60 h, $\bar{x}$ = 0.33 μm, σ = 0.11.

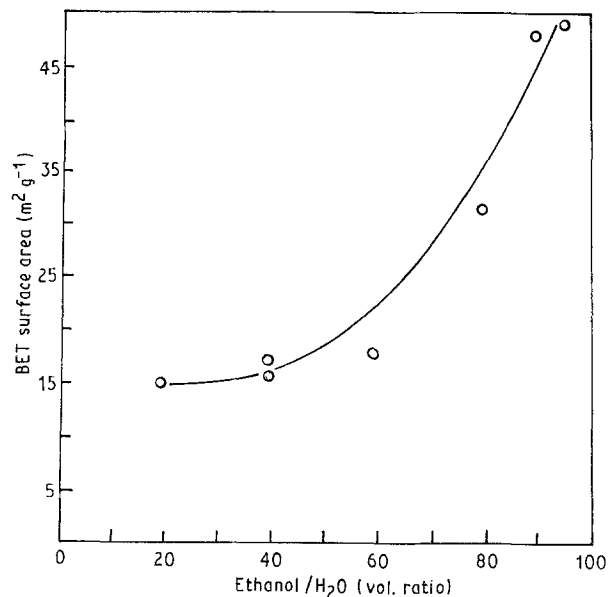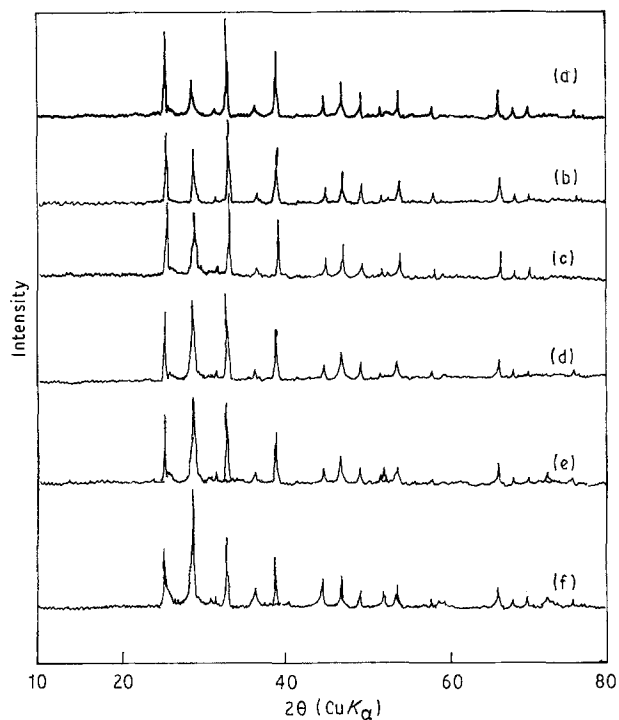*Figure 4* XRD of the $CaLa_2S_4$ powders changed with the La/Ca mole ratios: (a) 1.60; (b) 1.80; (c) 2.00; (d) 2.10; (e) 2.20; (f) 2.40.

TABLE II The ratio of the $CaLa_2S_4$ phase (1 3 0) with the La_2O_2S phase (1 0 1) changed with La/Ca mole ratios: (A) raw nitrate, (B) Coprecipitated carbonates analysed by XRF

La/Ca (mol %)		$I_{1\,3\,0}/I_{(1\,0\,1)}$
A	B	
1.60	1.64	2.89
1.80	1.87	1.57
2.00	2.06	1.29
2.10	2.11	1.05
2.20	2.26	0.91
2.40	2.61	0.61

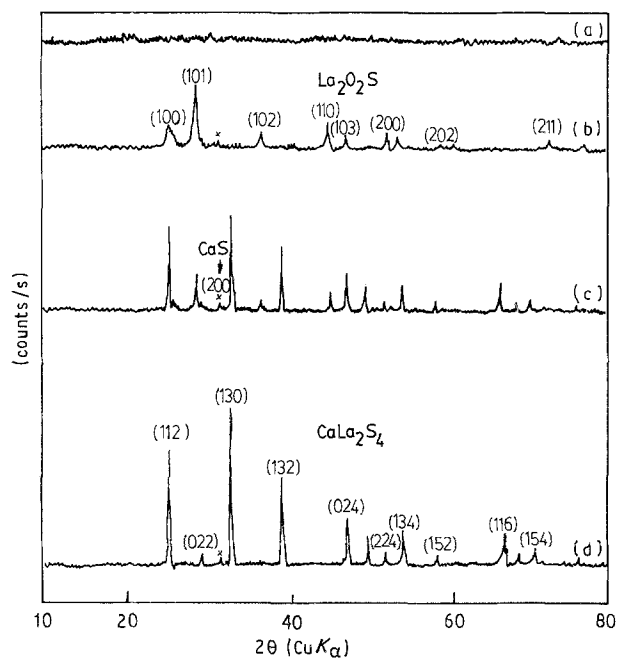*Figure 3* BET surface area of coprecipitated carbonates as a function of volume per cent ethanol in water.

Figure 5 X-ray diffraction patterns of (a) coprecipitated carbonates, and powder fired in pure H_2S at 650 °C for (b) 24 h, (c) 48 h, (d) 72 h.
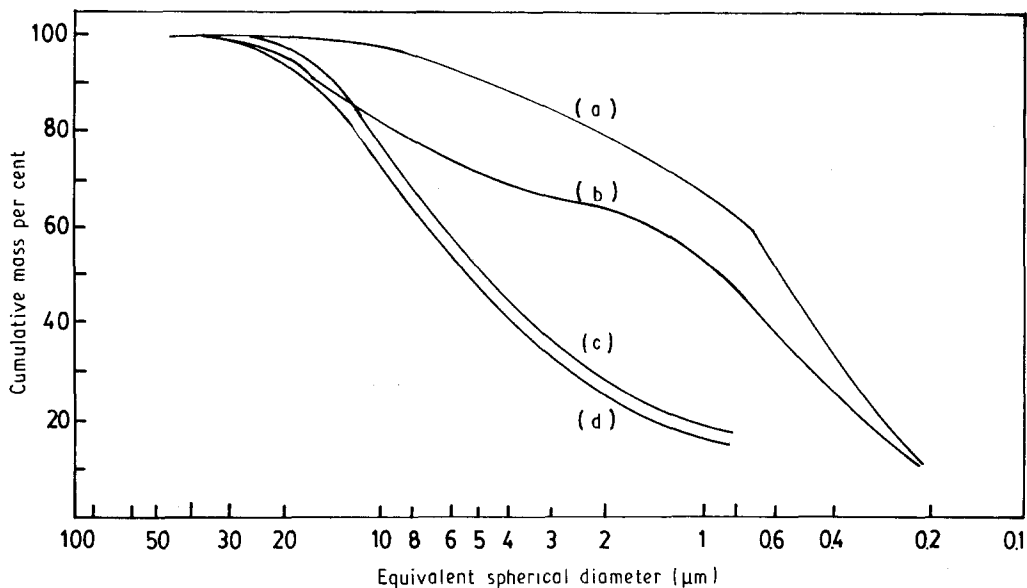
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Figure 6 Particle size distribution of $CaLa_2S_4$ changed with final pH values of the coprecipitation solution for precursor formation with the same sulphurization condition: (a) 7.91, (b) 8.92, (c) 9.62, (d) 9.94.
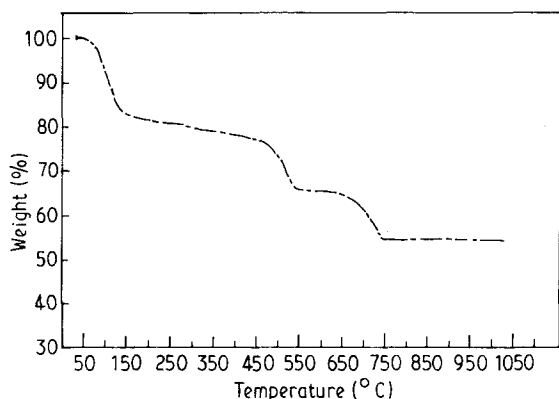

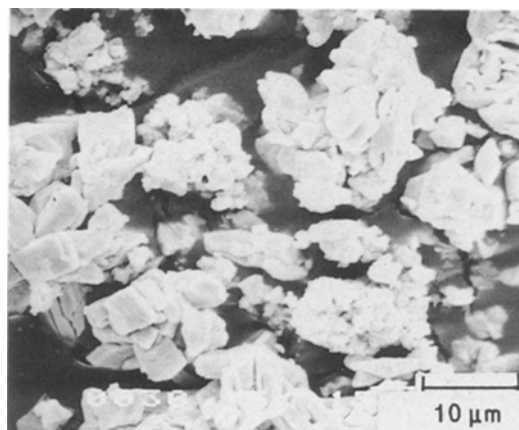*Figure 7* TGA curve of precipitated carbonates measured at a heating rate of $10\,^\circ C\,min^{-1}$ in air.

Figure 8 Scanning electron micrograph of oxide produced by decomposition of coprecipitated carbonates at $550\,^\circ C$ for 3 h.

$745\,^\circ C$ by the evolution of CO_2, and the formation of oxides. If the powder was decomposed in air, the sulphurization must proceed at a temperature higher than $745\,^\circ C$ and a continuous flow must carry CO_2 to the outside. Below $550\,^\circ C$ the oxides obtained from decomposition in vacuum were amorphous or poorly crystallized. The surface area of these oxides was initially relatively high but decreased as decomposition proceeded due to sintering. All the samples decomposed in vacuum below $650\,^\circ C$ had a similar morphology, as shown Fig. 8. The characteristic features of the cracks, holes and a smooth surface often existed in the parent coprecipitated carbonates. From the relationship of the BET surface area with the decomposition temperature in vacuum (Fig. 9), it was found that the most highly reactive oxides can be obtained at about $550\,^\circ C$ within 4 h in a 3 cm thick powder bed.

As a sulphurization agent, CS_2 was faster than H_2S for the formation of La_2S_3 [10], but the degree of dissociation of H_2S could be enhanced with adding a catalyst such as sulphided platinum and cobalt molybate [17]. Mullite refractory is a kind of lewis, and
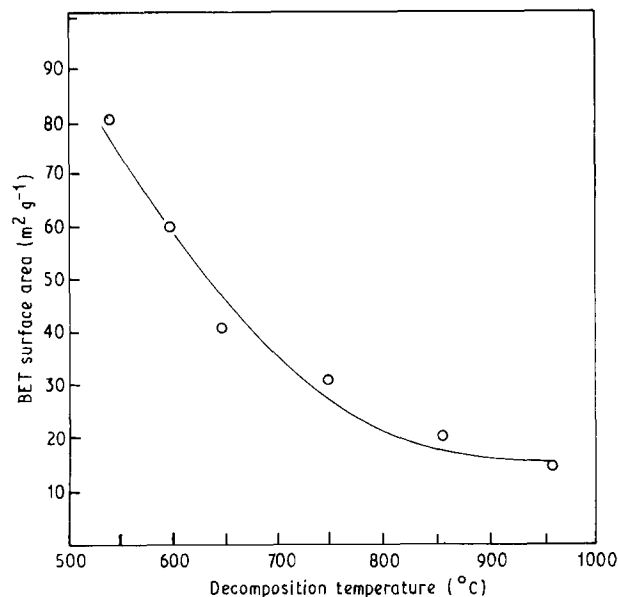

Figure 9 BET surface area of decomposed carbonates as a function of decomposition temperature.

bronsted acids also catalysed the dissociation potential of H_2S [18]. La_2S_3 and $CaLa_2S_4$ that were formed by a sulphurization agent such as CS_2 and catalysed H_2S with a deep rust colour, were not suitable for sintering due to their excessive sulphur content. The excessive sulphur in the sample will melt and vaporize from the green compact and leave some holes in the surface of the pellet.

The sulphurization temperatures and soaking time were varied to optimize $CaLa_2S_4$ powder formation with minimum aggregation. In the sulphurization process, the particles obtained at higher firing temperature (950 °C) underwent some initial sintering, or necking (Fig. 10a), while for those obtained from a lower firing temperature (650 °C), the agglomeration can be reduced by grinding in a nylon jug with zirconia as grinding medium (Fig. 10b). The powder which coprecipitated at 20 °C with a high titration rate and vacuum decomposed at 550 °C and sulphurized at 650 °C in pure H_2S without grinding, had a surface area of $11.8 \pm 2.5 \, m^2 g^{-1}$ (Fig. 11) with a mean particle size of 1.6 μm (Fig. 2b).

$CaLa_2S_4$ powders prepared at low temperature (650 °C) were compacted and sintered in an H_2S atmosphere. In comparison with the sintered ceramics prepared from coprecipitation in aqueous solution and calcined at high temperature, the low-temperature ethanol solution-made powders could be sintered to denser ceramics with lesser porosity. Figs 12a and 13a

Figure 12 Scanning electron micrographs showing $CaLa_2S_4$ sintered ceramics (a) sulphurized at 950 °C and sintered at 1400 °C, (b) sulphurized at 650 °C and sintered at 1400 °C.

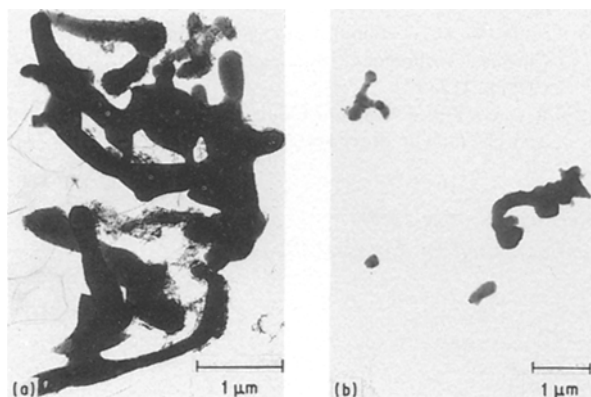

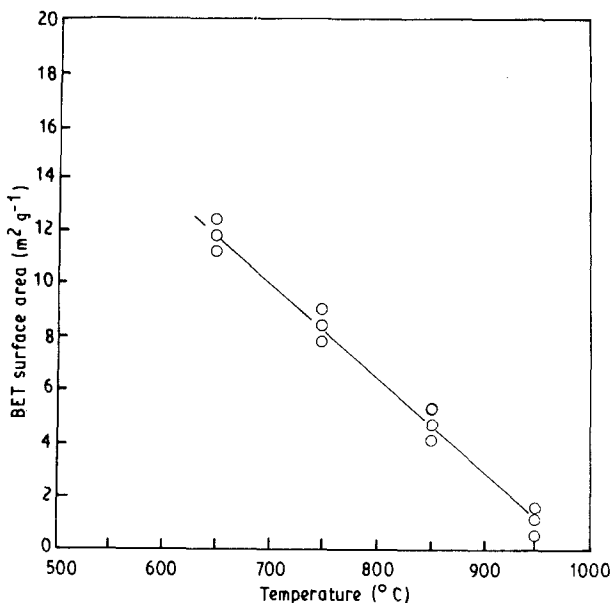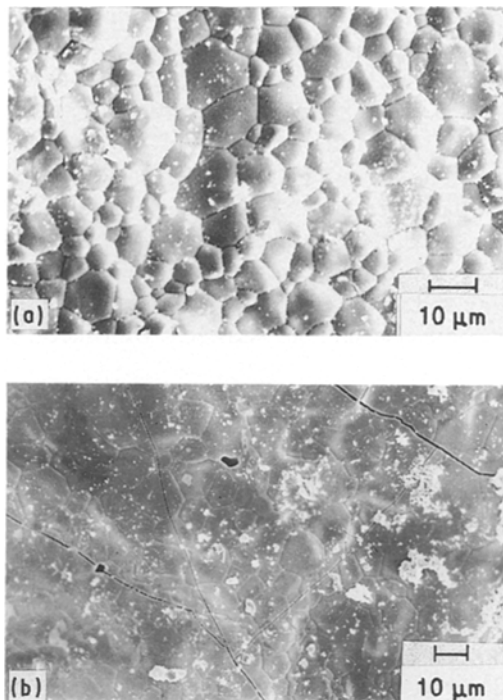Figure 10 Transmision electron micrographs showing $CaLa_2S_4$ ceramic powders sulphurized at (a) 950 °C (b) 650 °C.

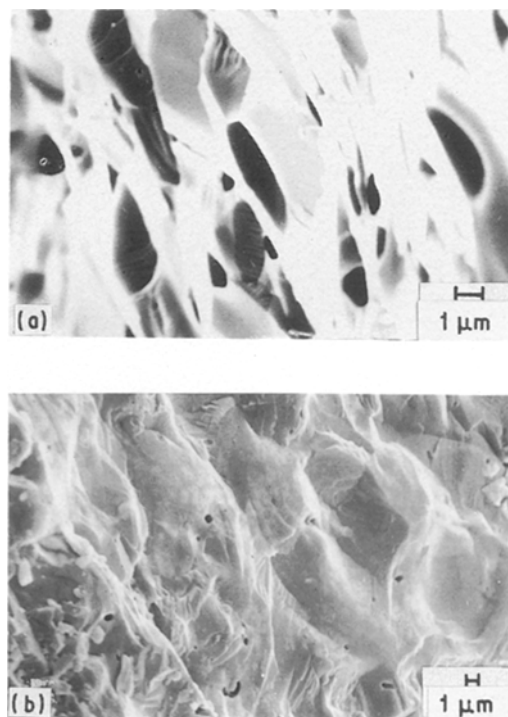Figure 11 BET surface area of $CaLa_2S_4$ powders as a function of sulphurization temperature.

Figure 13 Fracture surface of the sintered ceramics of samples which were sulphurized at (a) 950 °C, and (b) 650 °C.

show the microstructure and fracture surface of $CaLa_2S_4$ ceramics fired at 1400 °C for 8 h. The reduction in grain size and the decrease of pore density (Figs 12b, 13b) in ceramics prepared at lower temperatures (650 °C sulphurization) were apparent.

4. Conclusion

The coprecipitated carbonates obtained in ethanol solution at 20 °C with a titration rate of 50 ml min^{-1} had a narrow particle size distribution with a BET surface area of 55 ± 8.0 m^2 g^{-1} and an average grain size of 0.1–0.3 µm without agglomeration. The sulphide powder from decomposition in vacuum at 500 °C for 2 h and sulphurized at 650 °C for more than 2 days, had a broad particle size distribution with a BET surface area of 11.8 ± 2.5 m^2 g^{-1} and an average grain size of 0.8–1.8 µm with agglomeration which can be reduced by grinding. After 400 MPa uniaxial pressing and sintering at 1400 °C for 8 h under an H_2S atmosphere, the samples showed a translucency.

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