JOURNAL OF MATERIALS SCIENCE **28** (1993) 2304–2310

Investigation of $CaLa_2S_4$ powder prepared by sulphurization of coprecipitated carbonates

LI HSING WANG, MIN HSIUNG HON
Department of Materials Engineering, National Cheng Kung University, Tainan, Taiwan

Factors, including pH, coprecipitating medium, and temperature, for preparing $CaLa_2S_4$ powder were investigated. The precursors obtained by rapid precipitation in an aqueous solution at 25 °C had a homogeneous morphology of minute dentrites, and showed little or no CaS in the X-ray diffraction (XRD) patterns after sulphurization at 950 °C for 24 h. The particle size of the precursors or sulphides obtained in the vicinity of isoelectric point of $pH = 7.8$ had a broad distribution, while that obtained at $pH > 9.24$ had a narrow distribution. The precursors obtained in hydrous ethanol were a mixture of spherical, flaky and acicular particles in morphology, but all showed calcium deficiency. Interconnected particles were obtained in anhydrous ethanol at $pH = 6.81$ and 25 °C with a highly homogeneous composition. No CaS phase was determined by XRD after sulphurization at 950 °C for 24 h. The $CaLa_2S_4$ powders obtained in both aqueous and anhydrous ethanol solutions were sintered, and a translucent pellet was obtained.

1. Introduction

The morphology of calcium and lanthanum carbonates obtained through precipitation has been little investigated. Depending on the water content, the normal carbonate $La_2(CO_3)_3 \cdot 8H_2O$ [1] is formed in aqueous solution which hydrates to basic carbonate $La(OH)CO_3 \cdot xH_2O$ [2–4]. The precursor particles of the basic carbonate of lanthanum, were prepared by homogeneous precipitation, and was prismatic and crystalline [2]. The three lanthanum carbonates differ in thermal behaviour and physical properties. The calcium carbonate exhibits many crystal forms, according to the preparation conditions, and the morphology of these crystals was spherical, dendritic, chain-like, or colloidal in appearance [5–7].

The aims of this work were to investigate the phase and chemical compositions, particle shape and size distribution of the coprecipitates and sulphides. Powders were characterized with respect to size, shape, crystal structure, and thermal decomposition behaviour.

2. Experimental procedure

As starting materials, commercial reagents $La(NO_3)_3 \cdot 6H_2O$ and $Ca(NO_3)_2$ solution were chosen for $CaLa_2S_4$ formation. The calcium and lanthanum solutions prepared were mixed in a ratio of $La/Ca = 2.10$.

Ammonium carbonate and ammonium hydroxide solutions were fabricated in different media. They were dissolved in water, and hydrous ethanol or anhydrous ethanol, respectively. The ammonium carbonate was added as 50% excess over the stoichiometric amount required to produce a coprecipitate at temperatures from 25–65 °C. After the setting temperature was reached, the solution was quickly titrated to the ammonium carbonate solution and stirred vigorously. The precipitates obtained in aqueous and hydrous ethanol solutions were filtered and washed more than twice, and then ultrasonically dispersed in ethanol for 30 min, while the precipitate obtained in anhydrous ethanol was sedimented and centrifuged in order to separate the supernatant with a high concentation of nitrates by the decantation method. The pH of the aqueous and hydrous ethanol solution was adjusted by adding ammonium carbonate, while that of the anhydrous ethanol solution was kept at $pH = 6.81$ after precipitation. These coprecipitates were dried in an oven at 80 °C overnight and then decomposed in vacuum at 600 °C for 1.5 h and sulphurized at 950 °C in an H_2S atmosphere for 24 h. After grinding by mortar and pestle, the resultant light-green powders were isostatically compacted at 250 MPa in a rubber mould into discs 15 mm diameter and 2.6 mm thick. Samples were packed in $CaLa_2S_4$ powder in a graphite crucible and sintered in pure H_2S at 1400 °C for 8 h.

The dried carbonates, sulphurized powders and pellets, were examined by X-ray diffractometry and X-ray fluorescence (XRD/XRF), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), and differential thermal analysis (DTA).

3. Results and discussion

The homogeneity of the precipitates was significantly influenced by the fabrication parameters of the precursor. The rate of crystallization of the lanthanum

0022–2461

carbonate was promoted by the addition of water, while that of calcium carbonate seemed to be indifferent to water, because the affinity of water was weak. Typical morphologies of the sulphides obtained

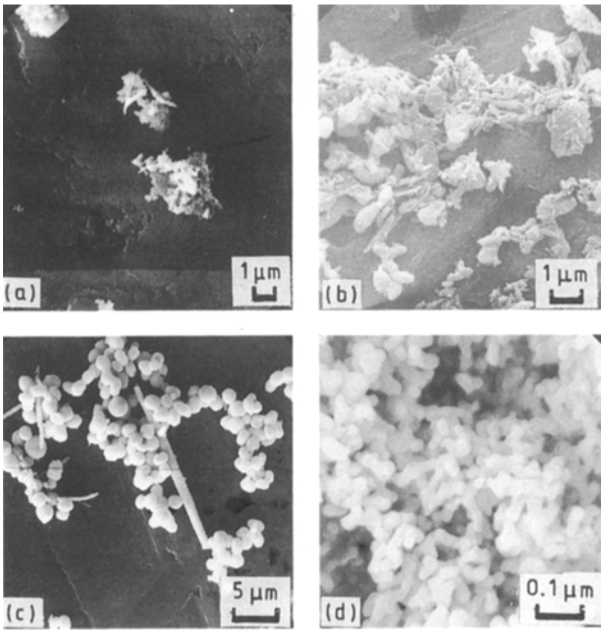

Figure 1 Scanning electron micrographs of sulphides obtained by sulphurization of the carbonates in (a) aqueous solution at 25 °C, (b) aqueous solution at 65 °C, (c) hydrous ethanol at 25 °C and (d) anhydrous ethanol at 25 °C.

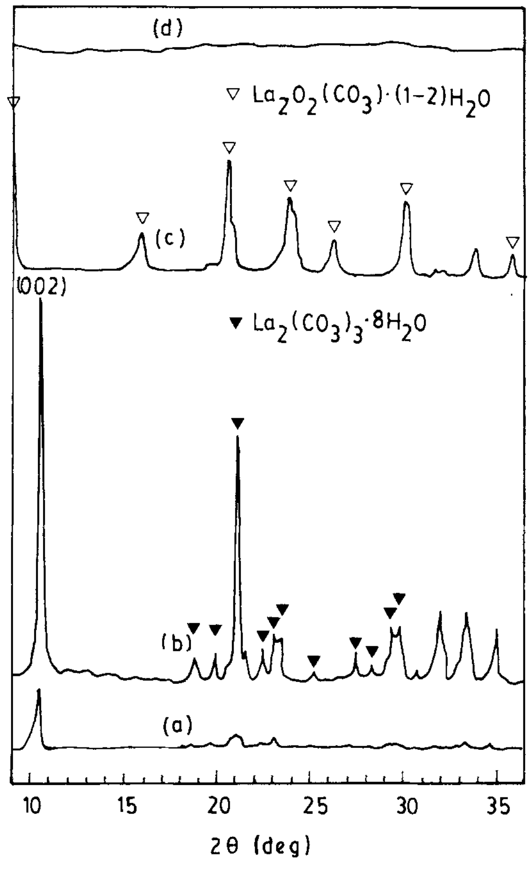

Figure 2 XRD patterns of (a) coprecipitated carbonates obtained in aqueous solution at 25 °C; (b) $La_2(CO_3)_3 \cdot 8H_2O$ obtained in aqueous solution at 65 °C, the intensity of (0 0 2) was reduced by four times, (c) $La_2O_2(CO_3)_3 \cdot$ (1–2) H_2O obtained at pH = 6.14–9.29 and (d) amorphous phase obtained at pH = 10.52 in hydrous ethanol.

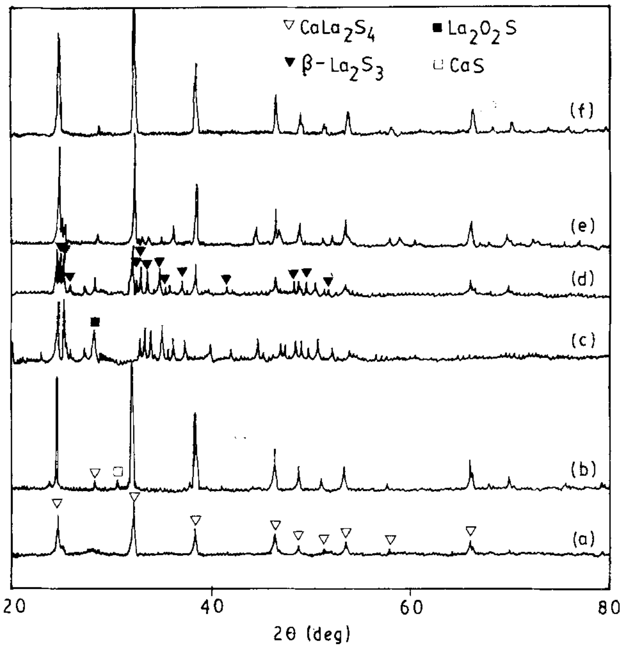

Figure 3 XRD patterns of the sulphide powder obtained by sulphurization of the coprecipitated carbonates in Fig. 1 (a, b), and hydrous ethanol with (c) pH = 6.14, (d) pH = 8.18, (e) pH = 10.52, and (f) anhydrous ethanol.

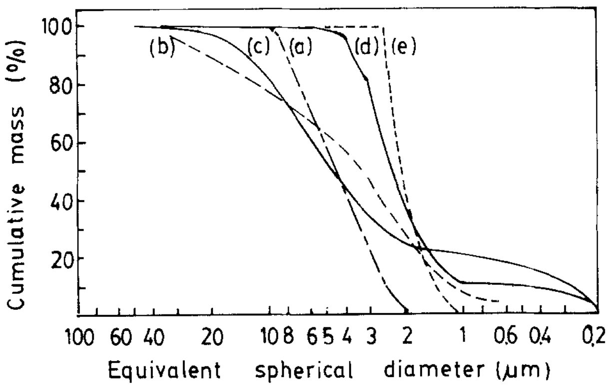

Figure 4 Particle-size distribution of the sulphides obtained by sulphurization of the coprecipitated carbonates formed at 25 °C in aqueous solution with pH (a) 7.91, (b) 7.98, (c) 8.62, (d) 8.88 and (e) 9.24.

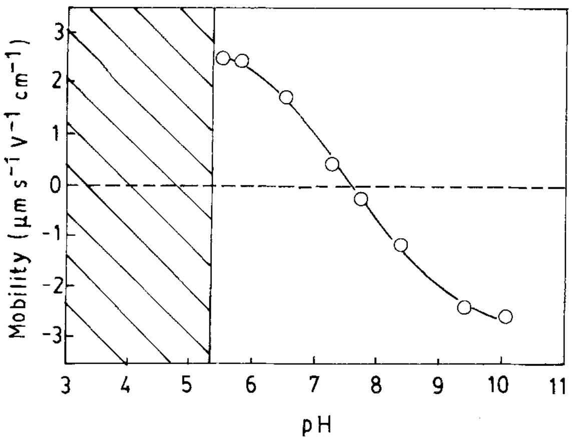

Figure 5 Electrokinetic mobilities of the dispersion of $La_2(CO_3)_3 \cdot 8H_2O$ particles obtained in aqueous solution as a function of pH in 0.001 mol dm^{-1} KNO_3.

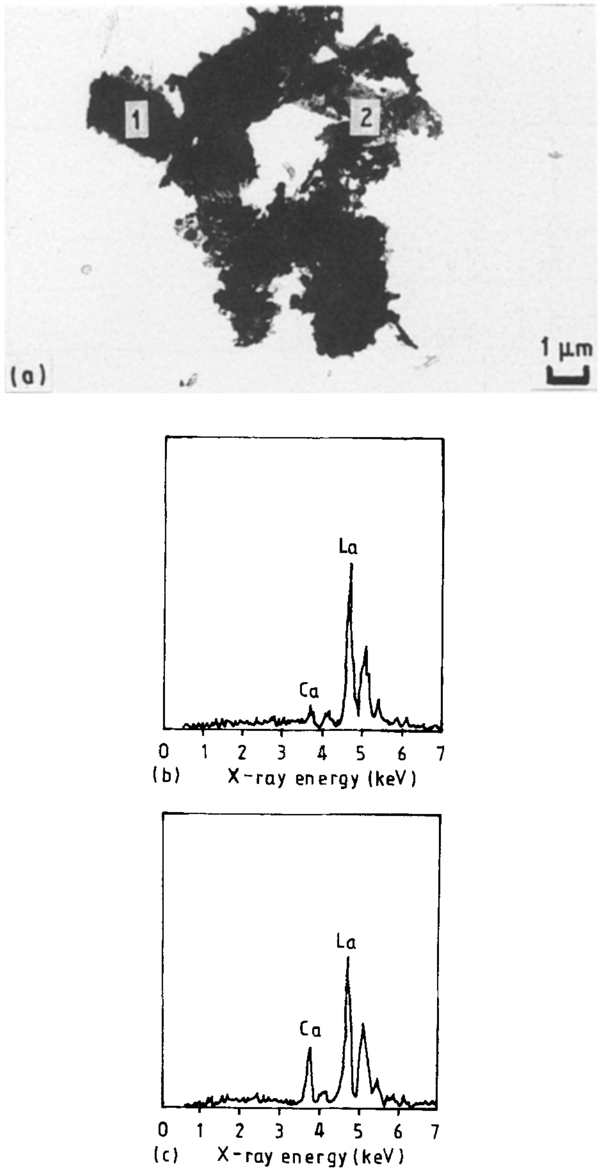

Figure 6 (a) Transmission electron micrograph precursors obtained in aqueous solution at pH = 7.98 and EDX of (b) a round powder and (c) a whisker powder, found at 1 and 2 in (a) respectively.

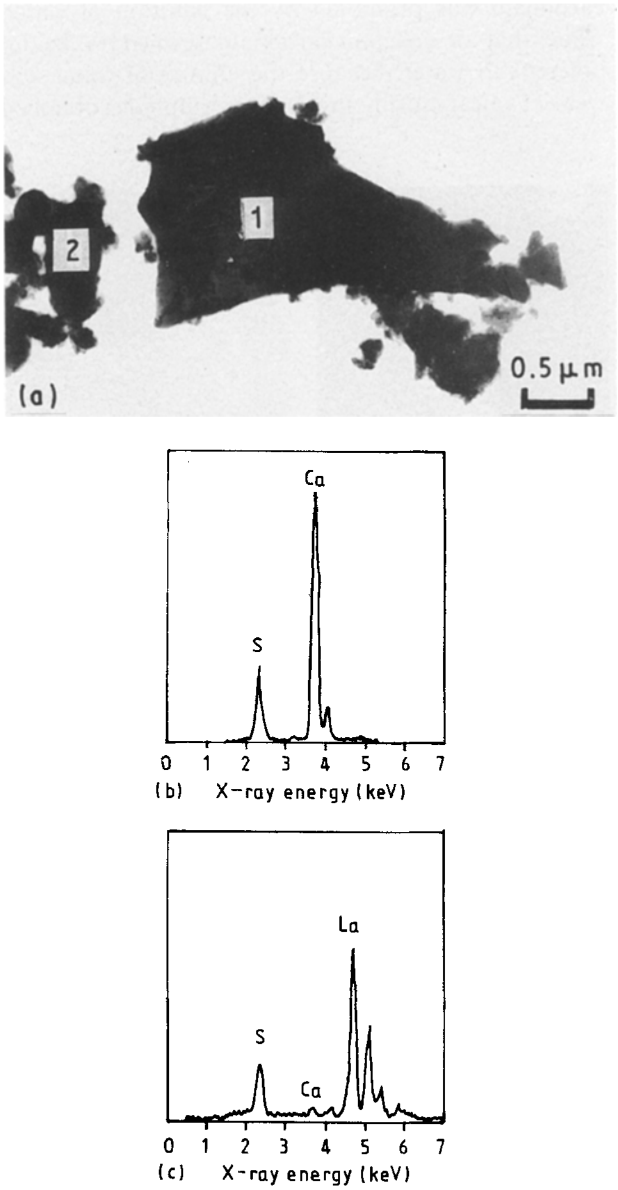

Figure 7 (a) Transmission electron micrographs of sulphides obtained in aqueous precursors at pH = 7.98 and (b, c) EDX of the plate powder for sites (1) and (2).

by sulphurization of the coprecipitates which was formed in aqueous solution at 25 and 65 °C, are shown in Fig. 1a and b, respectively, while those obtained in hydrous and anhydrous ethanol are shown in Fig. 1c and d, respectively. It is seen that the morphologies of these powders in Fig. 1a–c are inhomogeneous.

The powder coprecipitated at 25 °C was poorly crystallized (Fig. 2a), while that coprecipitated and washed with water at 65 °C was identified as $La_2(CO_3)_3 \cdot 8H_2O$ by XRD (Fig. 2b). The sulphide powder obtained by sulphiding the coprecipitates from aqueous solution at 25 °C were homogeneous in composition, and no detectable CaS was found by XRD (Fig. 3a), while coprecipitates obtained at 65 °C had detectable CaS in the sulphide powder (Fig. 3b).

The pH played a minor role in the phase formation of dried carbonates obtained in aqueous solution at 25 °C and the subsequent sulphides, but it played an important role in the determination of particle-size distribution of these powders, as shown in Fig. 4. It broadened at pH = 7.8, due to agglomeration in the vicinity of the isoelectric point, according to the graph of electrokinetic mobility of $La_2(CO_3)_3 \cdot 8H_2O$ particles in an aqueous solution (Fig. 5). From the TEM analyses, the broad particle-size distribution at pH = 7.98 was not only due to agglomeration but also to the different sizes and shapes of particles of carbonates and sulphides existing in the powder. Those powders with a large round shape were lanthanum-rich (Fig. 6a), while those with ultrafine whisker shape were homogeneous in composition, as identified by EDX (Fig. 6b). After mild sulphurization, the powder with plate shape, produced from precursors made in an aqueous solution, showed an inhomogeneous composition with both lanthanum- and calcium-rich particles, as determined by EDX (Fig. 7a, b). Those precursors were sulphurized at 950 °C for 24 h and showed Th_3P_4-type phase and a minor peak of CaS by XRD. Traces of CaS were not easily detected by XRD but had an adverse influence on the transmittance of

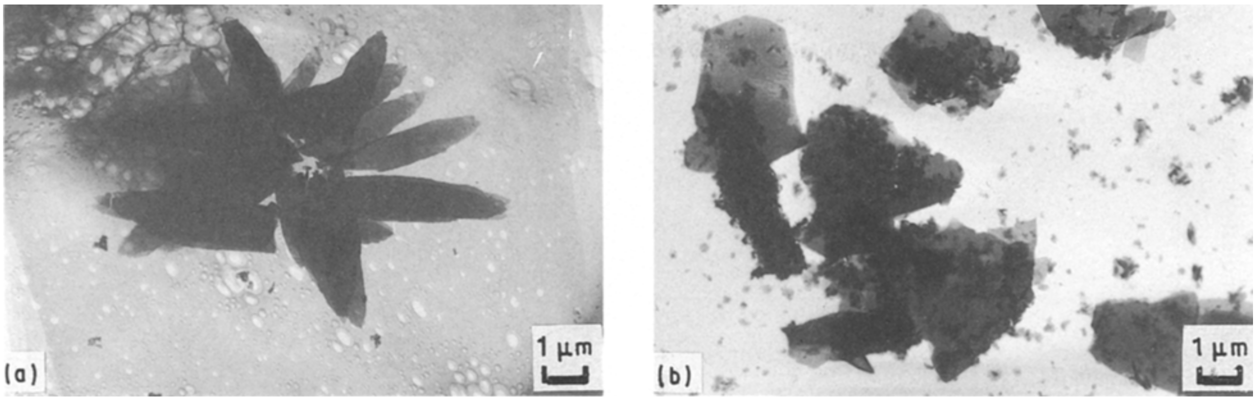

Figure 8 Transmission electron micrographs of (a) carbonates obtained in aqueous solution at pH = 9.24, and (b) a powder stored in air for 10 days.

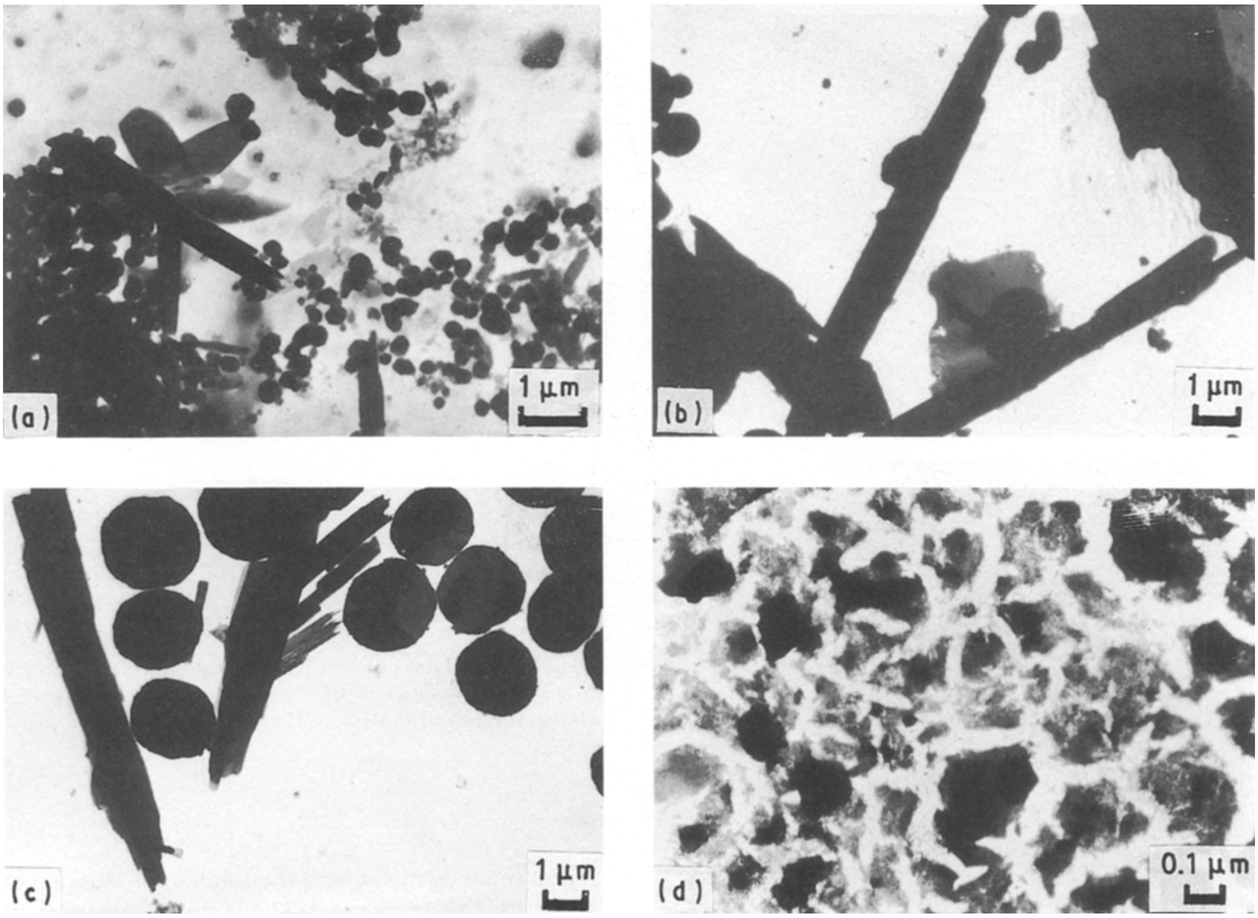

Figure 9 Transmission electron micrographs of carbonates obtained in hydrous ethanol at pH (a) 6.14, (b) 7.63, (c) 9.29 and (d) 10.52.

the $CaLa_2S_4$ pellet due to scattering in the two sulphides with different structure, thus the lanthanum should be present in excess of the stoichiometric amount in the preparation to inhibit CaS formation during precipitation and sulphidization [3, 4]. The powder obtained at pH > 9.24 had a narrow particle-size distribution with only one particle shape (Fig. 8a), but it changed from the worm-like shape to plate shape on absorption of moisture in the air, and hydrated to the basic carbonate (Fig. 8b). The powder with whisker shape in the precipitated carbonates obtained at 25 °C was much more homogeneous in composition than that of the worm-like powder obtained at 65 °C. The inhomogeneity of the composition became serious for the precursor obtained at 65 °C, in that CaS was formed, as identified by XRD (Fig. 3b).

To eliminate agglomeration, pure ethanol was chosen as the washing medium [8–10], and ethanol also can substitute the coprecipitation medium to obtain the coprecipitated carbonates. If water was

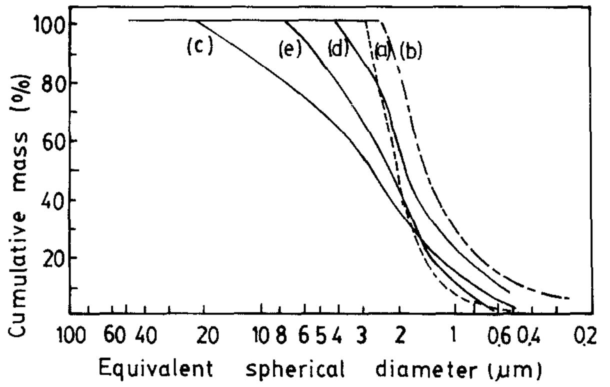

Figure 10 Particle-size distribution of the sulphides obtained by sulphurization of the coprecipitated carbonates formed at 25 °C in hydrous ethanol with pH (a) 6.14, (b) 7.63, (c) 8.18, (d) 9.29 and (e) 10.52.

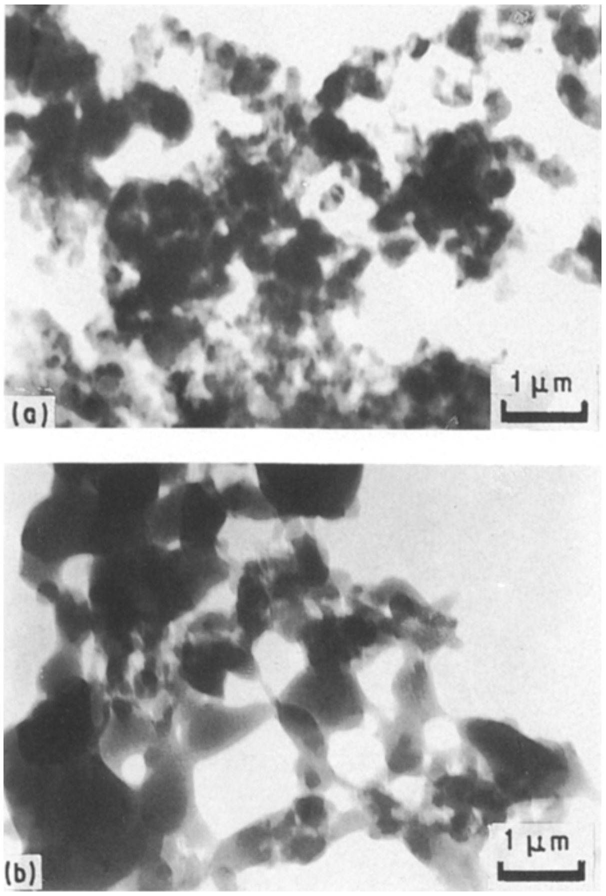

Figure 11 Transmission electron micrographs of (a) carbonates obtained in anhydrous ethanol solution, and (b) sulphide from (a).

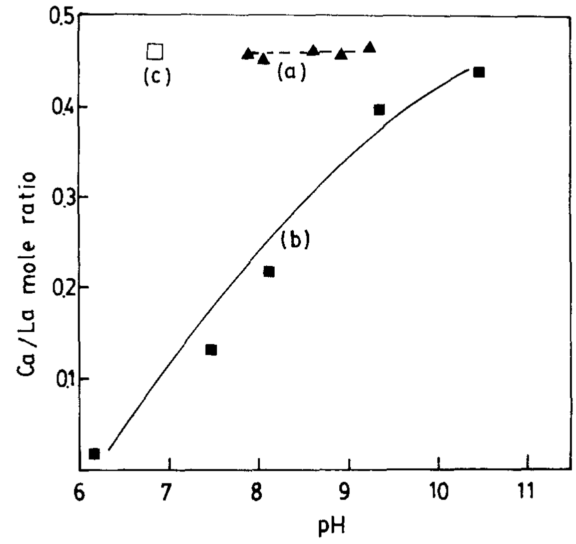

Figure 12 The pH dependence of the cation molar ratio of the coprecipitated carbonates obtained in (a) aqueous, (b) hydrous ethanol and (c) anhydrous ethanol solutions.

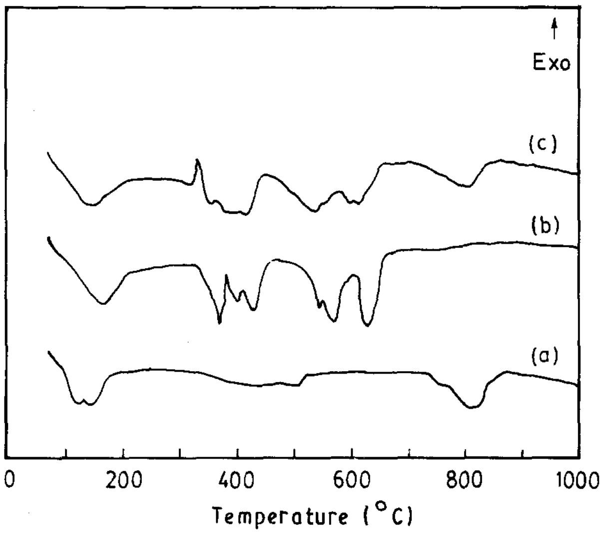

Figure 13 DTA curve of coprecipitated carbonates formed at 25 °C in (a) aqueous solution with pH = 7.98, (b) hydrous ethanol solution with pH = 6.14, and (c) pH = 10.52 at a heating rate of 10 °C min^{-1} in air.

carefully expelled from the coprecipitation system, the carbonates obtained were amorphous, while a small amount of water induced the crystallization of $La_2O_2(CO_3)_3 \cdot (1\text{–}2)H_2O$ as identified by XRD (Fig. 2c). During filtration, the amorphous calcium carbonates dissolved in solution, and the stoichiometry was changed. The morphologies of the carbonates obtained in hydrous ethanol were spherical, flaky and acicular, as shown in Fig. 9a–c. The carbonates obtained at pH = 7.63 had a larger aspect ratio for flaky and acicular particles, and the fraction of these kinds of particles also increased. The lanthanum carbonate particle grew on drying in the oven at 70 °C, while the gelatinous calcium carbonate melted for the coprecipitates obtained at pH $<$ 8.18. As with the precursors obtained at pH $>$ 10.52, the precipitated carbonates became amorphous and the particles were too fine to be detected by TEM, as shown in Fig. 9d. These precursors contained no hydroxyl groups, as analysed from the infrared spectra, and thus it was assumed that no $Ca(OH)_2$ or $La(OH)_3$ existed in it. The particle-size distribution of the sulphide obtained from hydrous ethanol precursors in Fig. 10 showed a similar result to that obtained in aqueous solution (Fig. 4).

If the coprecipitated carbonates were processed carefully in anhydrous ethanol, the precursor was

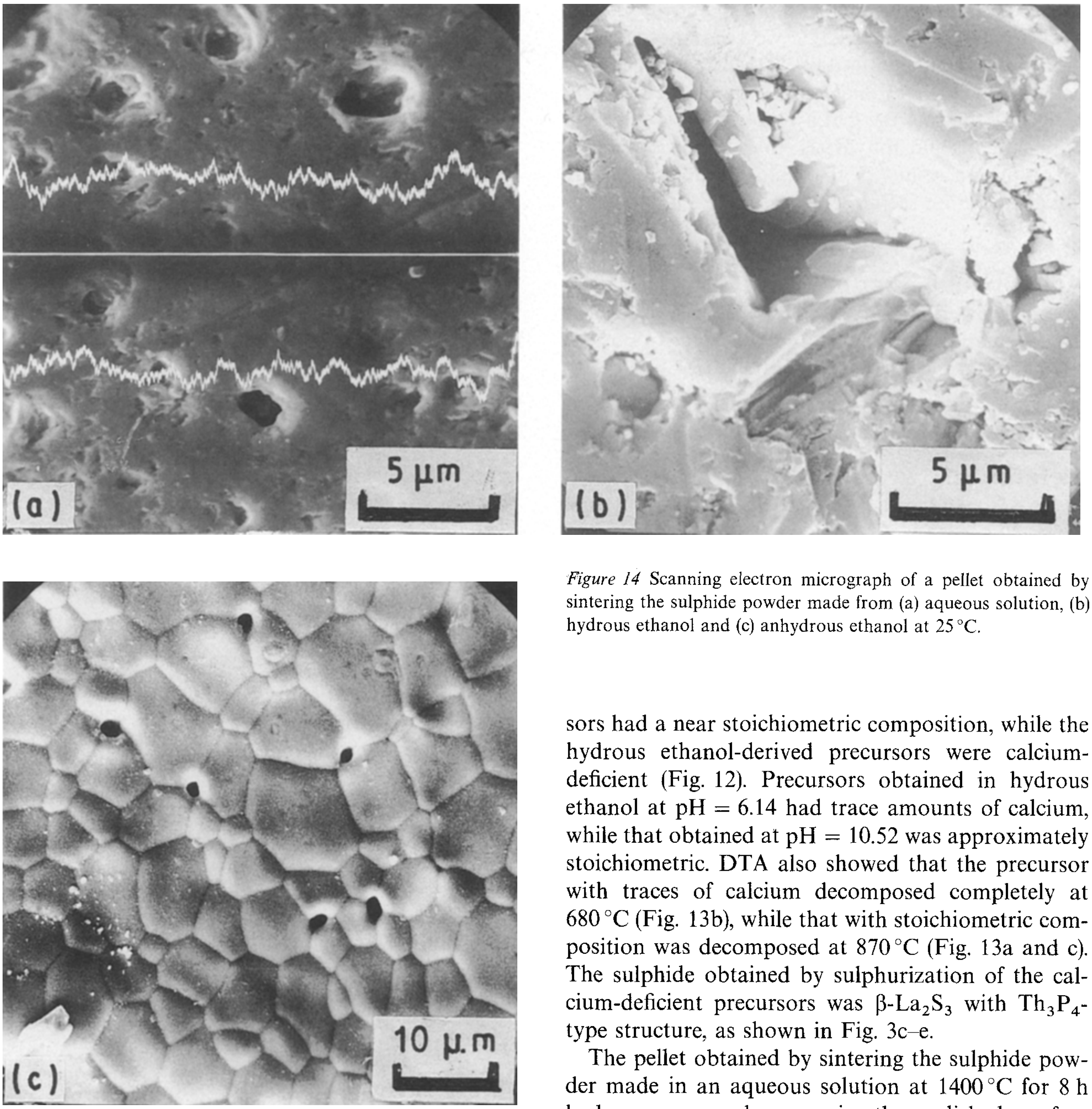

Figure 14 Scanning electron micrograph of a pellet obtained by sintering the sulphide powder made from (a) aqueous solution, (b) hydrous ethanol and (c) anhydrous ethanol at 25 °C.

amorphous and the sulphide obtained was the Th_3P_4-type phase without impurity (especially CaS), as determined by XRD (Fig. 3f). However, if the precursor powders were stored in air, they would absorb water and catalyse crystallization of the lanthanum carbonates. The resultant sulphide powders from these stored precursors also showed a CaS impurity formation. Sulphide powders obtained by immediate sulphidizing of the amorphous precursor showed single-phase $CaLa_2S_4$. A spherical particle interconnected by an amorphous gel was obtained in the precursors, as shown in Fig. 11a, b. The sulphide obtained by sulphidizing this precursor was still spherical and, after grinding, the powder was homogeneous and pseudo-spherical in appearance.

The pH had a significant influence on the composition of these precipitates. XRF analysis indicated that the aqueous and anhydrous ethanol-derived precursors had a near stoichiometric composition, while the hydrous ethanol-derived precursors were calcium-deficient (Fig. 12). Precursors obtained in hydrous ethanol at pH = 6.14 had trace amounts of calcium, while that obtained at pH = 10.52 was approximately stoichiometric. DTA also showed that the precursor with traces of calcium decomposed completely at 680 °C (Fig. 13b), while that with stoichiometric composition was decomposed at 870 °C (Fig. 13a and c). The sulphide obtained by sulphurization of the calcium-deficient precursors was β-La_2S_3 with Th_3P_4-type structure, as shown in Fig. 3c–e.

The pellet obtained by sintering the sulphide powder made in an aqueous solution at 1400 °C for 8 h had many round pores in the polished surface (Fig. 14a), while that obtained in hydrous ethanol with acicular or flaky morphology, had many triangular pores (Fig. 14b). However, the pellet obtained by sintering the sulphide made in anhydrous ethanol had pores distributed at the intersections of grain boundaries (Fig. 14c). Pellets obtained by sulphiding and sintering the precursors precipitated in both aqueous and anhydrous ethanol solutions at 25 °C showed translucency in thin sections.

4. Conclusions

The precursors obtained by rapid precipitation in aqueous solution at 25 °C were homogeneous in morphology with minute dentrites, and showed little or no CaS from XRD after being sulphurized at 950 °C for 24 h. The precursors obtained in hydrous ethanol were spherical, flaky and acicular in shape, but showed a calcium-deficiency. The particle size of the precursors or sulphide obtained in the vicinity of the isoelectric point of pH = 7.8, was broadly distributed, while that obtained at pH > 9.24 had a narrow distribution. The powders obtained in anhydrous ethanol at pH = 6.81 and 25 °C were homogeneous in morphology and composition, and showed no CaS, as determined by XRD, after being sulphurized at 950 °C for 24 h. Sintering the $CaLa_2S_4$ powders obtained in both aqueous and anhydrous ethanol solutions showed promising results in that translucent pellets were obtained in thin sections.

Acknowledgements

The support from Chung Shan Institute of Science and Technology and the National Science Council of the Republic of China under contract no. CS-79-0210-D006-12 is appreciated.

References

1. J. A. K. TAREEN and T. R. N. KUTTY, *J. Crystal Growth* **50** (1980) 527.
2. M. L. SALUTSKY and L. L. QUILL, *J. Amer. Chem. Soc.* **72** (1950) 3306.
3. M. AKINC and D. SORDELET, *Adv. Ceram. Mater.* **2** (1987) 232.
4. H. YAGI, A. IWAZAWA, R. SONOBE, T. MATSUBARA and H. HIKITA, *Ind. Engng Chem. Fundam.* **23** (1984) 153.
5. T. HIROICHI, *Gypsum and Lime* **216** (1988) 314.
6. D. B. VANDSERHEIDEN, US Pat. 4367 207 (1983).
7. H. YAMADA and N. HARA, in "Synthesis of Calcium Carbonate by Electrical Conductivity Monitoring", Ceramic Transactions Vol. 1, edited by G. L. Messing, (American Ceramic Society, OH, 1988).
8. R. E. JAEGER, T. J. MILLER and J. C. WILLIAMS, *Amer. Ceram. Soc. Bull.* **53** (1974) 850.
9. K. R. RESZKA and J. RESZKA, "High Tech. Ceramics", edited by P. Vincenzini (Elsevier, Amsterdam, 1988) pp. 707–15.
10. M. S. KALISZEWSKI and A. H. HEUER, *J. Amer. Ceram. Soc.* **73** (1990) 1504.

Received 15 October 1991
and accepted 14 August 1992