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Formation and densification of $Pb_{0.1}Ca_{0.9}La_2S_4$ powders by sulfidization of modified metal alkoxides

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Abstract

The highly sinterable submicron $CaLa_2S_4$, (CLS) powders with high La/Ca ratios were prepared by sulfidizing calcium and lanthanum alkoxides under CS_2 for 8 h and then a pure H_2S atmosphere for 2 h at 500–800°C. It is for application in infrared transmitting window material of 8–14 μm wavelength. In the range of La/Ca ratios from 10 to 15, the phase obtained are LaS_2 intermediate phase at low temperature (500°C), a β-La_2S_3 minor phase at 700°C, and a pure Th_3P_4 phase after 800°C treatment. The $Pb_xCa_{1-x}La_2S_4$ (PCLS) sulfide particle sizes formed are in the range 0.2–5 μm. After HIPing and annealing in an H_2S atmosphere at 1350°C, the $Pb_{0.1}Ca_{0.9}La_2S_4$ pellet has 60% IR transmittance in the 14 μm region for the specimen with a thickness of 0.86 mm. The IR transmittance at 11 μm region for pellet of $Pb_{0.1}Ca_{0.9}La_2S_4$ with 1.6 wt% chlorine residue is 55%, while the IR transmittance at 11 μm region of it with 0.2 wt% chlorine residue is 43%. © 1999 Elsevier Science Limited and Techna S.r.l. All rights reserved.

1. Introduction

Polycrystalline $CaLa_2S_4$ (CLS) ceramic has become a novel window material lately for 8–14 μm IR range based on its mechanical property [1,2], while it was difficult to achieve a highly sinterable CLS powder due to powder aggregation and broad particle size distribution from long soaking time and high sulfidization temperature for the mixed oxides [3,4]. Recently, many new techniques [5–9] were developed for optical-grade CLS ceramic syntheses; however, uncontrolled variations in particle size homogeneity, purity and stoichiometry continued to exist, and reproducibility was difficult to obtain.

The alkoxide method for preparing ceramic powders has become a promising method recently due to its reproducibility and stoichiometry insistence [10–13] narrow particle size distribution and spherical particle shape with higher purity [14–16]. The mixed alkoxides were used as a precursor to synthesize an easily compacted and sintered CLS powder to achieve an optical ceramic [17–22]. A better CLS can be obtained by using CS_2 to sulfidize the precursor [23–25]. Another method is to dope with low melting sulfide compound to reduce the melting temperature or use the liquid phases sintering for full density [26]. The object of this study was trying to eliminate the second phase in the sulfide while lowering the sulfidization temperature and to optimize the conditions for densification.

2. Experimental procedure

The preparative work of alkoxide was carried out in a Teflon-coated stainless steel made reactor in an atmosphere of dry air. All procedures for preparation of alcohol solutions were completed in a reflux condenser with a drying tube on the top. Methanol was dried using calcium alkoxide and distilled directly into a reaction container. Compounds were handled at all times in dry air atmosphere and stored in an evacuated desiccator.

The lanthanum tris methoxide was synthesized with the method developed by Bradley et al [27–29]. A 30 g lanthanum trichloride powder (99.9%) was put into a container filled with lithium methoxide to form lanthanum methoxide. The progress of the reaction was estimated by titration of supernatant liquid with silver nitrate, and potassium chromate was as an indicator.

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After lanthanum methoxide formation was completed, the calcium metal powder (99.5%) was mixed for calcium methoxide formation. Then 30 ml carbon disulfide was mixed into the container for further reaction and a yellow complex was obtained. Methoxide mixtures for forming $Pb_xCa_{1-x}La_2S_4$ (PCLS) was obtained by synthesizing lead methoxide first, and poured lanthanum calcium mixture into it. The lead methoxides were formed by using lead chloride to react with lithium methoxide in distilled methanol. The CS_2 reacted with the lead methoxide to show the black color. The methoxide mixtures reacted with CS_2 to yield a well homogenized modified methoxide. The PCLS powder was fabricated through a direct sulfidization of the dried modified methoxides in a graphite crucible under CS_2 for 8 h and then a pure H_2S atmosphere for 2 h at 500–800°C. The PCLS obtained at 700–800°C was aggregate which can be reduced by grinding with a pestle and mortar to obtain discrete particles to improve flowability of the powder.

The PCLS powder was dry pressed to 20 MPa in a tungsten carbide lined die and was further cold isostatically pressed (CIP) to 250 MPa for 20 min to form pellets which were then heated in a pure H_2S atmosphere at 1300°C to ensure the stoichiometry of CLS and removal ofthe adsorbed gases. After cooling, the green densities of the specimens were estimated by geometric measurements. The PCLS compact packed in PCLS powder in a graphite crucible was sintered in a pure H_2S atmosphere at 1300°C for 4–8 h and further hot isostatically press (HIP) sintered at 1350°C under 200 MPa of Ar for 1 h. Annealing in a pure H_2S atmosphere at 1300°C for 2 h restored the sulfur stoichiometry and IR transmission capability of PCLS specimens.

The thermal behavior and structural changes on heating of the as prepared CLS and PCLS powder in air were examined by Differential Thermal Analysis and Thermogravimetry (DTA/TG), X-ray diffractometry (XRD) and IR spectroscopy. The gas evolved from the methoxide in the sulfidization duration was determined by gas chromatography (GC) with thermal conductivity detector. The carbon and chlorine contents in the powder were estimated by elemental analysis (Heraeus CHN-O Rapid and Tacussel Coulomax 78). The morphology and homogeneity of the powders and pellets were analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The Hitachi 270-30 Infrared Spectrophotometer used in transmission measurement from 2.5 to 25 μm gave in-line transmittance.

3. Results and discussion

The use of sol–gel techniques to prepare optical ceramics, fiber, thin film and glasses offers outstanding opportunity for breakthroughs in technology [30–34]. This field is rather rapidly developed and authors would achieve much better understanding of sol–gel process from metal alkoxides [30–34], however, the sulfide ceramics should not use the hydrolysis process because water will compete with the hydrogen sulfide to destroy sulfide compounds. Lanthanum isopropoxide is readily soluble in common solvent and have advantage to mix well with the liquid calcium alkoxide. Nevertheless, the yield is low and need purification and filtration for synthesis of lanthanum isopropoxide, and the compound is extremely moisture sensitive; the presence of $<$ 10 ppm of water is sufficient to initiate hydrolytic decomposition [16]. Considering the large reactivity of lanthanum isopropoxide, this prehydrolyzed by moisture in air would catalyzed the to different compounds [20]. As a result, hydrolysis and sulfidization reactions occur simultaneously, and the result precursor can be expected to be a mixture of lanthanum hydroxide and oxysulfide. The presence of hydroxyl ions would render the sulfur unable to complete replace them leading to a mixture phases (β-La_2S_3 and γLa_2S_3) [20].

CS_2 will react with alkoxide to form a stable compound to impede the attack of the moisture in the air [17]. The CS_2 reacted with lead methoxide to form a black compound in the methanol, and black color held until totally dried. The CS_2 reacted with lanthanum methoxide to form a yellow compound in the methanol, and the yellow color faded during drying. The reaction rate of the lead chloride is apparently higher than lanthanum chloride for methoxide formation. The lead methoxide could be formed within two days, while the lanthanum methoxide was formed after two weeks reaction. The IR curves showed adsorbed methanol, hydroxide (3646 cm^{-1}) [15] and carbonate (1380–1600 cm^{-1}) [15] were formed as shown in Fig. 1(a) and (b) showed the as prepared calcium methoxide with a similar absorption curve to that for lanthanum methoxide. Fig. 1(c) showed the as-prepared lead methoxide without hydroxide and carbonate that may be due to short reaction time compared with the lanthanum methoxide. After reacted with CS_2, the carbonate and hydroxyl absorption peaks disappeared because the methoxide had the affiliation to CS_2 [Fig. 1(e)]. Because both calcium and lanthanum alkoxides were in solid particles and the solubility were low in methanol [14], homogeneous phase can not be easily obtained by mixing. Homogeneity of the mixture was worsen by hydrolysis also [17,20]. It was found that the calcium and lanthanum methoxides and its modified methoxides were amorphous [Fig. 2(a)]. The lead methoxide with black color would form LaS_2 at 500°C in CS_2 atmosphere for 4 h (Fig. 2(b)). Usually, the LaS_2 and Th_3P_4 phase mixture were formed at 600°C [Fig. 2(c)], the Th_3P_4 and β-La_2S_3 phase mixture were formed at 750°C. [Fig. 2(d)]. The pure Th_3P_4 phase was formed higher than 800°C [Fig. 2(e)].

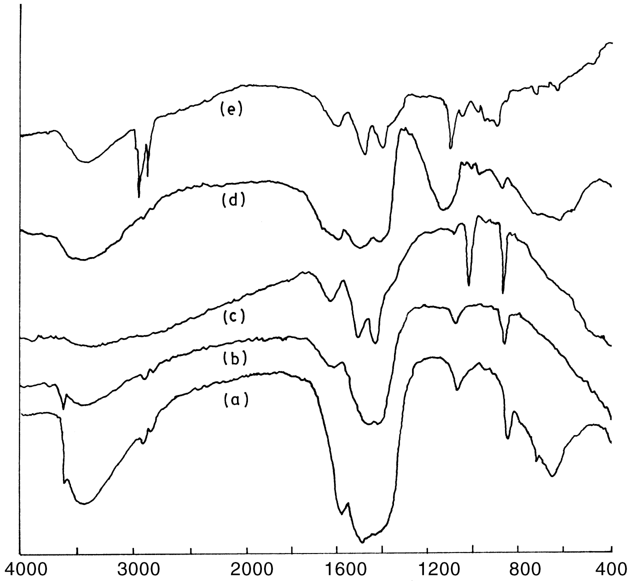

Fig. 1. IR spectra of (a) lanthanum methoxide, (b) calcium methoxide (c) lead methoxide, (d) methoxide mixtures from (a), (b) and (c); (e) modified methoxides powder prepared by drying at 62°C.

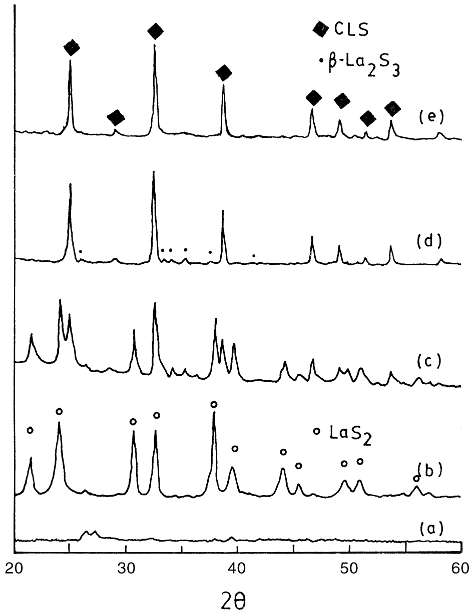

Fig. 2. XRD patterns of the powders prepared at (a) 62°C, and sulfidized at (b) 500°C (c) 600°C and (d) 700°C and (e) 800°C.

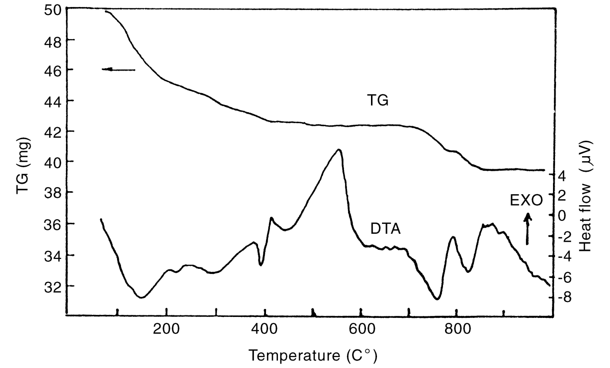

Fig. 3. DTA and TG curves of modified methoxide powder upon heating in air at a heating rate of 10°C/min.

According to TG/DTA and gas chromatography, approximately 70 wt% loss was observed in thermal decomposition of the modified methoxides in air at 70–420°C due to dehydration of adsorbed methanol and dealkoxylation. The exothermic peak in the pattern was from oxidation or combustion of the evolved methanol and other organic compounds at 500–600°C (Fig. 3). The exhaust collected at the exit of the sulfidizing system was CH_3SH as analyzed by gas chromatography. After a period of time for sulfidization at 700°C, the CH_3SH gas evolved was too low to be detected and the Th_3P_4 phase was formed as identified by XRD patterns. From these analyses, the mechanism of the sulfidization process for the Modified methoxide was proposed that the gas–solid reaction started at $\leqslant$600°C initially then solid state reaction between LaS_2 and Ca compound occurred at 700°C subsequently.

Decomposition of the PCLS powder upon heating in air was investigated by TG/DTA and; results obtained on powders heated at 10°C/min in air were presented in Figs. 4 and 5. Mild oxidation occurred below 650°C, the exothermic peaks at 730, 700 and 630°C were due to vigorous oxidation for $x = 0.1$, 0.5 and 1.0, respectively [Fig. 4(a),(c) and (d)]. For $x = 0.1$, the weight gain indicated the reaction with air to obtain oxysulfide compounds such as $La_2O_2S_2$, La_2O_2S, $La_2O_2SO_4$ and $CaSO_4$ [24,34]. For $x = 0.5$, the vigorous oxidation peak shifted to 700°C, while the weight gain was levelled by weight loss due to lead oxide evaporation. The lead oxide obtained by oxiding the sulfide powder can be identified by the endothermic peak at 902°C and the weight began to lose quickly at the onset of 902°C for $x = 0.5$ and 1.0 [Fig. 5(c) and (d)].

The PCLS powders sulfidized at 800°C for 8 h from the modified methoxides were aggregates in appearance as shown in Fig. 6. The primary average size is 0.2–0.3 μm for $x = 0.2$ [Fig. 6(a)], while it is 2-5 μm for $x = 0.8$ [Fig. 6(d)]. The more lead the sulfide particles had, the more metallic character it behaved; moreover, the worse powder shape [Fig. 6(d)] it had for further densification. The green compact of $Pb_{0.1}Ca_{0.9}La_2S_4$ was formed by grinding for 12 h in CS_2 medium. The green density of the sample was about 60% theoretical density after CIP at 300 MPa for 10 min and the sintered density was about 97% theoretical density after sintering at 1300°C for 8 h in H_2S atmosphere. The polished and thermal etched surface of the sintered specimen was shown in Fig. 7(a), while the fracture surface of it after HIPing and annealing was shown in Fig. 7(b) in which very few pores could be found.

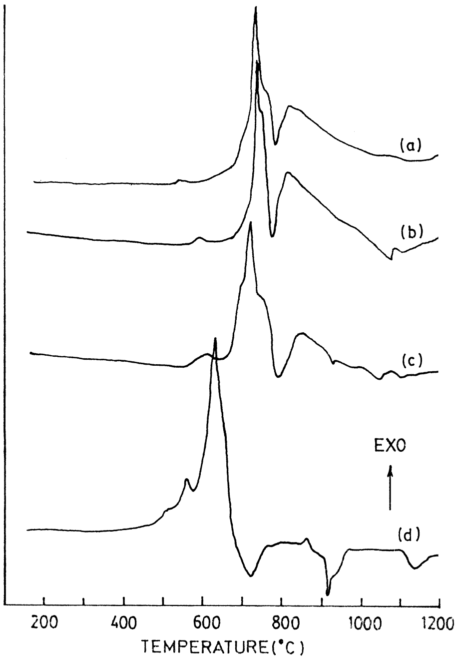

Fig. 4. DTA curve of PCLS powder upon heating in air at a heating rate of 10°C/min for (a) $x=0.0$ (b) $x=1.0$ (c) $x=5.0$ (d) $x=1.0$.

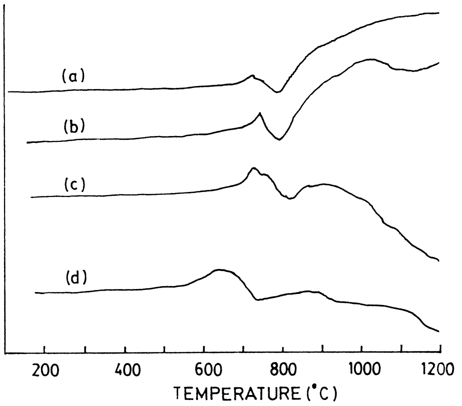

Fig. 5. TG curve of PCLS powder upon heating in air at a heating rate of 10°C/min for (a) $x=0.0$ (b) $x=1.0$, (c) $x=5.0$ (d) $x=1.0$.

Fig. 8 showed that the carbon and chlorine contents varied with sulfidizing temperature for $Pb_{0.1}Ca_{0.9}La_2S_4$ powders. The carbon and chlorine were less than 5.0 wt% after sulfidizing at 500°C for 8 h. Comparing with other methoxide powders, the R1 had 4.9 wt% chlorine and the R2 had 1.2 wt% chlorine. After sulfidizing, the sulfide powder (PCLS1) from R1 had 1.6 wt% chlorine and sulfide powder (PCLS2) from R2 had 0.2 wt%.

Fig. 9(a) showed the dependence of IR transmittance of the annealed pellet derived from $Pb_{0.1}Ca_{0.9}La_2S_4$ (PCLS1) powders on the sulfidization temperature. The characteristic absorption bands of sulfite and sulfate at

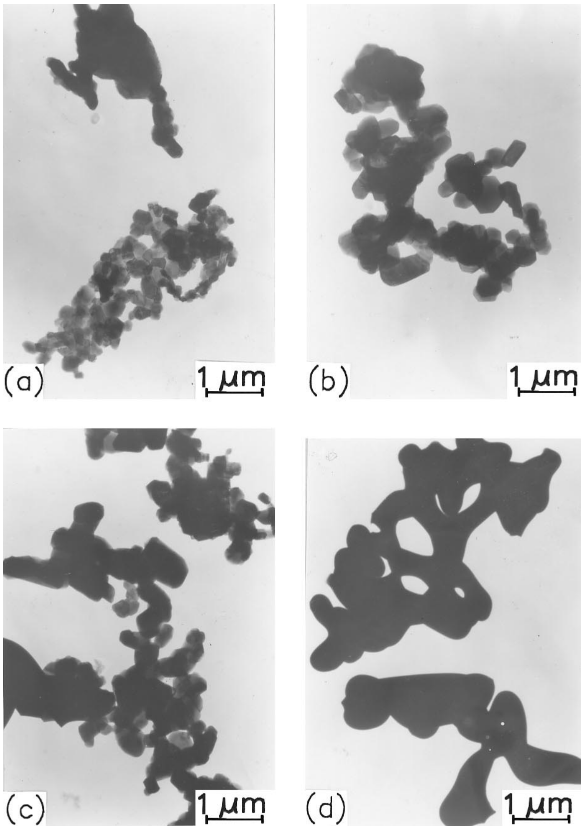

Fig. 6. TEM micrographs of PCLS powders prepared by sulfidizing at 800°C for (a) $x=0.2$ (b) x 0.4 (c) $x=0.6$ and (d) $x=0.8$.

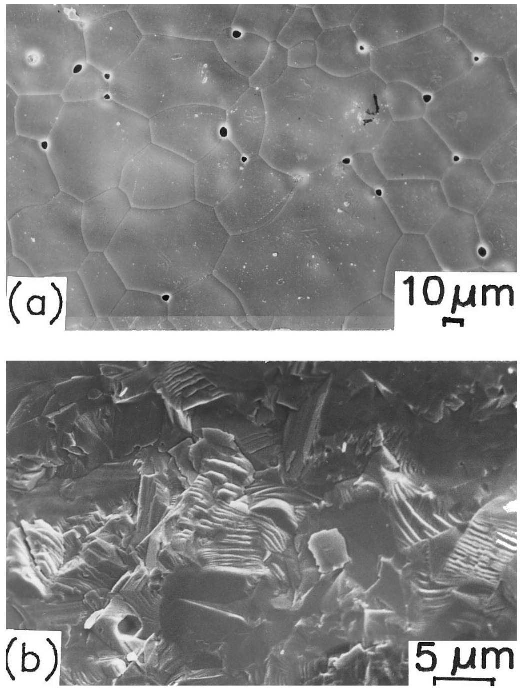

Fig. 7. SEM micrographs of (a) polished and thermal etched surface of the sintered specimen and (b) fracture surface of the pellet after HIPing and annealing by using the 800°C sulfidized powder as a precursor.

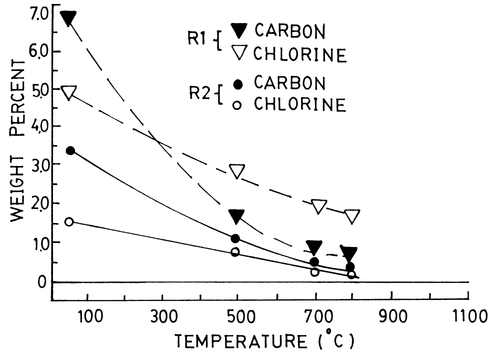

Fig. 8. The dependence of C, Cl residue contents in R1, R2, PCLS1 and PCLS2 powders on the sulfidization temperature.

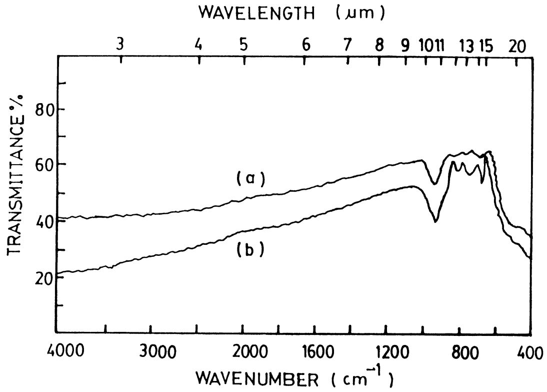

Fig. 9. Infrared transmission spectra of sintered and HIPed $Pb_{0.1}Ca_{0.9}La_2S_4$ pellets with a thickness of 0.86 mm from (a) PCLSI with 1.6 wt.% residue chlorine (2) PCLS2 with 0.2 wt% residue chlorine.

9.2 and 11 μm were reduced by using PCLS1 powder. The transmittance of pellet from PCLS1 at 11 μm was 55% [Fig. 9(a)], while the transmittance of PCLS2 at 11 μm was 43% [Fig. 9(b)]. Therefore, it may deduce that the minor chloride residue in methoxide and sulfide from $LaCl_3$ had the advantage to eliminate the hydroxyl group in the sulfidization process and to eliminate the sulfite or sulfate group in the sintering process. After HIPing and annealing in an H_2S atmosphere at 1350°C, the pellet from PCLS2 had 60% IR transmittance in the 14 μm region for the specimen with a thickness of 0.86 mm.

4. Conclusion

For high La/Ca ratios and the calcium replaced by lead to have Pb:Ca:La = 0.1:0.9:12, the phase obtained were the LaS_2 intermediate phase at low temperature (500°C), a β-La_2S_3 minor phase at 700°C, and a pure Th_3P_4 phase after 800°C treatment. The PCLS sulfide particle sizes were in the range 0.2–5 μm when treated in CS_2 at 800°C for 8 h. The $Pb_{0.1}Ca_{0.9}La_2S_4$ decomposed initially at 730°C to $La_2O_2S_2$, La_2O_2S, $La_2O_2SO_4$ and $CaSO_4$ and the weight gained by heating in air. The $Pb_{0.5}Ca_{0.5}La_2S_4$ decomposed initially at 700°C to PbO and other oxides and the weight lost by vaporization of lead compound as heated in air. After HIPing and annealing in an H_2S atmosphere at 1350°C, the $Pb_{0.1}Ca_{0.9}La_2S_4$ pellet had 60% IR transmittance in the 14 μm region for the specimen with a thickness of 0.86 mm. The sulfide powder with high chorine residue had low sulfite or sulfate absorption due to elimination of the residue of oxide during densification. The IR transmittance at 11 μm region of pellet from PCLS with 1.6 wt% chlorine residue was 55%, while the IR transmittance at 11 μm region of PCLS2 with 0.2 wt% chlorine residue was 43%.

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