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Stabilization of the γ-Ce_2S_3 phase

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Abstract

The γ-Ce_2S_3 phase is used as a safe red pigment for plastics. Therefore, its stabilization, at low temperatures (around 800°C), has been particularly studied during the last decade. This can be realized in different ways: (1) the presence of alkali metals leading to $A_{0.5}Ce_{2.5}S_4$ (A=Li, Na and K). (2) The presence of an important carbon or silicon concentration enhances the γ-phase formation. However the γ-phases so obtained are dark or brown due to the presence of traces of these two elements. (3) The use of phosphate precursors (or phosphate dopant) also leads to the γ-phase. However during the thermal treatment under CS_2, some phosphorus is lost from the solid phase resulting in a progressive transformation of the γ-phase into the α-one. The residual monazite ($CePO_4$) does not much affect the red color of γ-Ce_2S_3. The γ-phase is also obtained by using borate precursors and to a lesser extent by vanadate and arseniate precursors or by treating some ceria associated with SiO_2. (4) γ-Ce_2S_3, as a major phase, is also obtained by treating some specific ceria under CS_2 and its color is red.

Keywords: Chemical synthesis; X-ray diffraction; Phase transitions; Optical properties

1. Introduction

The stabilization, at low temperature, of the γ-Ce_2S_3 phase has been the object of numerous studies because this phase is a safe red pigment used for plastics [1–6]. The light lanthanide sesquisulfides have three polymorphic modifications ([7,8] and references therein)

$$\alpha\text{-}Ln_2S_3 \underset{900°C}{\rightarrow} \beta\text{-}Ln_2S_3 \underset{1200°C}{\rightarrow} \gamma\text{-}Ln_2S_3$$

and the γ-phase is difficult to synthesize. This phase presents a cubic structure of the Th_3P_4 type [9–11], with metal vacancies $Ln_{2.67}\square_{0.33}S_4$. Solid solutions were known to exist from this phase to Ce_3S_4 [7,8]. Independently of metal vacancies, this phase also presents some distorted empty tetrahedral cavities, S_4.

The present paper is a small review of the different methods used to stabilize the γ-phase at low temperatures (around 800°C). The experimental methods have been described previously [12–17].

2. Results

2.1. Effect of some metal elements

Numerous studies have shown that the stabilization, at low temperature, of the γ-Ln_2S_3 can be realized by alkaline earth elements (in particular Ca^{2+}) ([18] and references therein). Small quantities of univalent cations (A=Li, Na and K) can have the same effect under temperature conditions which would otherwise give rise to the α-, β-varieties or even the disulfide. All the metallic sites of the lattice can be filled up, leading to the maximum formula $A_{0.5}Ce_{2.5}S_4$ [5,6,10,11,19]. In this formula, the additional metal randomly replaces the cerium atom. For Na:Ce=0.2, the Na-doped γ-phase is largely preponderant versus CeS_2 at 500°C [17]. This observation shows that sodium prevents, to a great extent, the formation of the cerium disulfide which is normally stable up to 750°C [20–22]. The heavy lanthanide elements, such Dy, Ho, Er and Tb, used as dopants allow the stabilization of the γ-Ce_2S_3 at low temperatures (600–800°C). However, in this case, the stabilization is only transitory, heating above 800°C yields the β-form [12,16].

2.2. Role of carbon and silicon

Carbon has been known, for a long time, to be efficient in the prevention of the formation of lanthanide oxysulfides. Even at high temperatures (>1000°C), the use of a graphite boat is recommended [7,8]. The effect of carbon was also underlined for the sulfurization treatment of

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lanthanide molecular complexes, at low temperatures [23–25], but its effect remained controversial (stabilization of the γ-phase [26,27]). Thus, we have studied again the sulfurization of lanthanide molecular complexes [16,17].

The nature of the observed sulfide greatly depends on many factors: the process conditions (sulfurization reagent, temperature and heating rate) the nature of the precursor and of the lanthanide element itself [13]. CS_2 is known to be a more efficient reagent than H_2S [28] and will be used during this study. The temperature treatment will be as low as possible. For example, the treatment of the lanthanide oxalates, at 800°C and 5°C/min for 1 h, yields pure β-phase for lanthanum and cerium while a mixture of β- and γ-phases or pure γ-phase is obtained for the other elements (Table 1) [13]. In fact, the β-phase is an oxosulfide poor in oxygen, $Ln_{10}S_{14+x}O_x$ with $0 \leq x \leq 1$ [29,30] and the lightest lanthanide elements (La, Ce) have a stronger attraction for oxygen than the others [31]. γ-Ce_2S_3, as a major phase, can be obtained either by decreasing the heating rate (1°C/min, 0.3°C/min) for the cerium oxalate or by increasing the C:Ce ratio of precursor (malonate, acetate . . . , heating rate 5°C/min) [15]. In the same way, the presence of a significant amount of carbon mixed with cerium nitrate favors the γ-phase instead of the α-one (Fig. 1). Elemental silicon presents the same properties as carbon (Table 2), it prevents the formation of α-Ce_2S_3 [15]. However, silicon is more efficient than carbon at enhancing the formation of γ-Ce_2S_3: a Si:Ce ratio of 0.5 is sufficient to prevent the formation of the α-Ce_2S_3 while a C:Ce of 10 is needed to do so. However, the so-obtained γ-phase are dark or brown due to residual traces of carbon or silicon [17].

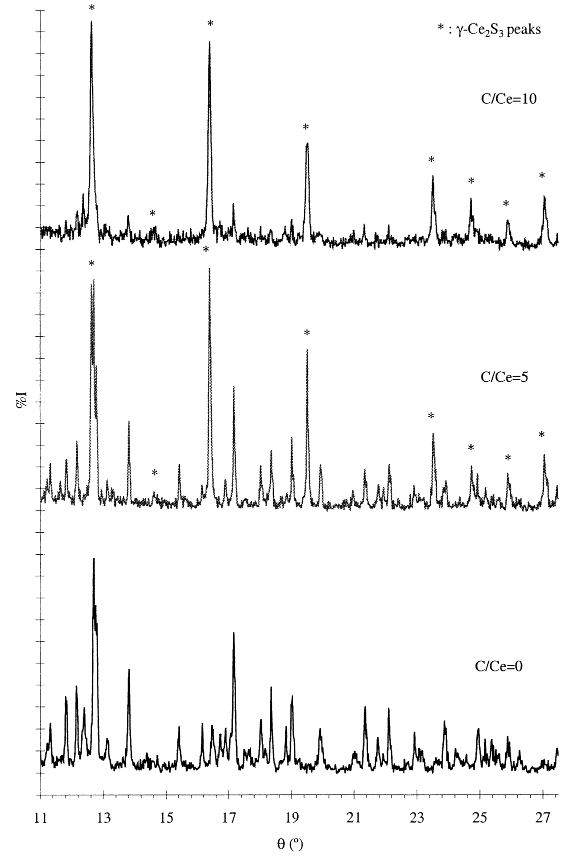

Fig. 1. X-ray powder diffraction patterns of the phases obtained by treating a mixture of cerium nitrate and carbon as a function of the C:Ce ratio, at 800°C and 5°C/min for 1 h: C:Ce = 0 α-phase; C:Ce = 5 γ- and α-phases; C:Ce = 10 mainly γ-phase.

2.3. Effect of phosphate or some oxygenated dopants

The treatment of cerium phosphate under CS_2 favors the γ-phase instead of the α- or β-phases (Table 3) [15]. Similar observations can be made by decreasing the P:Ce ratio until 0.1. Depending on the starting P:Ce ratio and of the treatment conditions, the additional phases are the monazite [32,33] and sometimes the cerium thiophosphate [34], which occurs in a small quantities. During this treatment, some phosphorus (P_2S_5, boiling point 514°C [35]) is lost from the solid phase resulting in a progressive transformation of the γ-phase into the α-one (Table 3). The γ-phase produced by this route presents an interesting color. Whereas the presence of small quantities of carbon, of silicon and of the α-phase (colored compounds) alters the color, the presence of monazite (colorless compound) does not affect the colorimetric properties of the γ-phase. Fig. 2a which corresponds to the second sample of Table 3 is brighter than that of $Na_{0.5}Ce_{2.5}S_4$ (Fig. 2c) which is used as a reference.

Some oxygenated elements (As, V and Si), which also prefer tetrahedral environment, favor the formation of the γ-phase but at a less extent than phosphate. For example, at 800°C for 1 min, the sulfidization of a mixture of ceria and amorphous SiO_2 (Si:Ce = 0.1) results in a mixture of the γ-phase and α-one (~5%). Similar observations can also be done from the borate but the process conditions must be severely controlled.

Table 1
Sulfurization of lanthanide oxalates at 800°C and 5°C/min with CS_2 ($p_{CS2} = 130$ Torr) for 1 h[a]

La	Ce	Pr	Nd	Sm	Gd	Tb	Dy	Y	Ho
β	β	γ>β	γ>β	γ	γ	γ	γ	γ	γ

[a] β-phase: $Ln_{10}S_{14+x}O_x$ with $0 \leq x \leq 1$; γ-phase: Ln_2S_3.

Table 2
Sulfurization at 800°C for 1 h and 5°C/min with CS_2 of a mixture of $Ce(NO_3)_3 \cdot 6H_2O$ and silicon as a function of the Si:Ce ratio

	Si:Ce			
	0	0.1	0.2	0.5
Observed phases	α-Ce_2S_3	α-Ce_2S_3 γ-Ce_2S_3 (~20%)	α-Ce_2S_3 γ-Ce_2S_3 (~30%)	γ-Ce_2S_3 Si (~20%)

Table 3
Sulfurization of cerium phosphate (P:Ce=1) or of a mixture of $Ce(NO_3)_3 \cdot 6H_2O$ and $(NH_4)_2HPO_4$ (P:Ce<1) with CS_2 as a function of temperature, heating rate and time[a]

	P:Ce						
	1	1	1	0.25	0.25	0.1	0.1
T (°C)	800	800	1000	800	800	750	750
V (°C/min)	5	1	5	5	5	1	5
Time (min)	1	60	1	1	60	1	90
Observed phases	$CePO_4^*$ γ-Ce_2S_3 (~30%)	γ-Ce_2S_3 $CePO_4^*$ (~30%)	γ-Ce_2S_3 $CePO_4^*$ (~45%)	γ-Ce_2S_3 $CePO_4^*$ (~15%) $CePS_4$ (traces)	γ-Ce_2S_3 α-Ce_2S_3 (~15%)	γ-Ce_2S_3 $CePS_4$ (traces)	γ-Ce_2S_3 α-Ce_2S_3 (~10%)

[a] $CePO_4^*$, monoclinic-type, monazite.

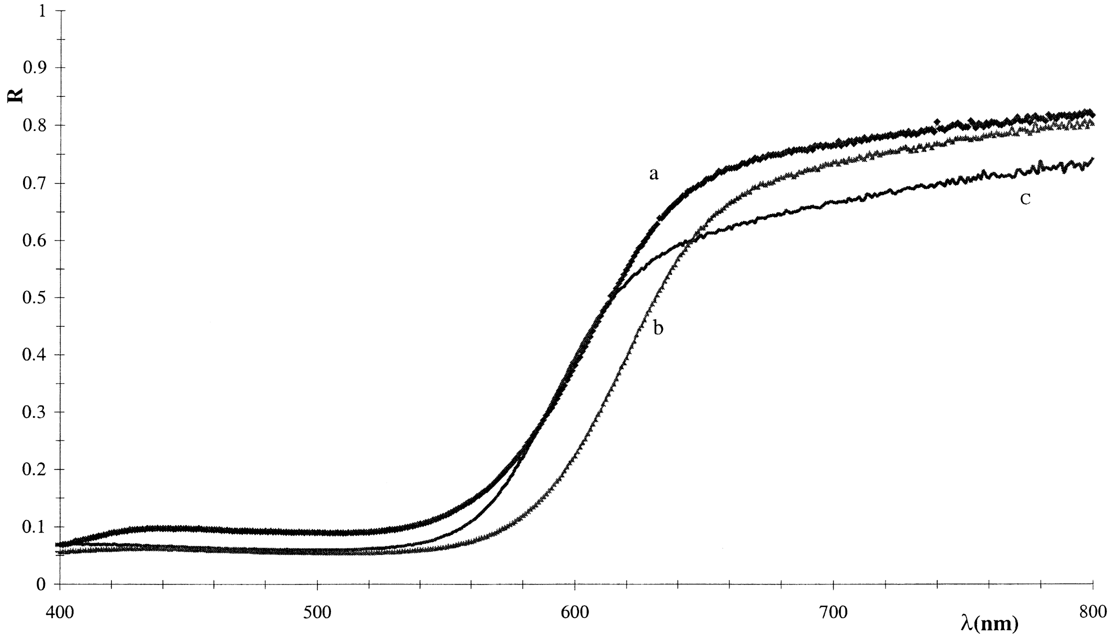

Fig. 2. Spectral reflectance curves: (a) of the second sample of Table 3; (b) of the second of Table 4; (c) of the $Na_{0.5}Ce_{2.5}S_4$ considered as a reference sample.

2.4. Direct sulfidization of the ceria with CS_2 without any dopant

At 750–1000°C and whatever the treatment time, most of the commercial ceria used, yields α-Ce_2S_3. Only one leads to a mixture of γ- and α-phases, at 800°C for a few minutes. In the same way, most of the self-prepared ceria, obtained by pyrolysis of the cerium nitrate and ancylite ($Ce(CO_3)OH$), leads to the α-phase. We have found recently that the sulfidization treatment of some specific ceria favors the γ-phase instead of the α-phase, in the temperature range 750–800°C (Table 4). However, the process conditions must be very well adapted: at 800°C, increasing the time of treatment results in the progressive transformation of the γ-phase into the α-one and, at 900°C, the α-variety is the only one. The reflectance curve of the second sample of Table 4 is presented in Fig. 1b. Compared to curves a and c, this curve presents a slight shift towards the higher wavelengths resulting in a red color instead of red-orange one [36].

Table 4
Sulfurization of some ceria with CS_2 as a function of temperature and time (heating rate 5°C/min)

T (°C)	750	800	800	800	900
Time (min)	70	1	30	60	90
Observed phases	γ-Ce_2S_3	γ-Ce_2S_3	γ-Ce_2S_3	γ-Ce_2S_3 α-Ce_2S_3 (traces)	α-Ce_2S_3

3. Conclusions

With the application in mind (pigment), the stabilization of γ-Ce_2S_3, at low temperature, whether pure or mixed with some phases that do not alter significantly the colorimetric properties of this pigment, has been successfully realized.

Many fundamental questions remain. Carbon and silicon are known for their strong ability to trap oxygen atoms. What about the phosphate which is actually the more interesting dopant? At one time, we supposed that the phosphorus can be inserted in small quantities, in the form of PS_4^{3-}species, into the empty tetrahedral sites of the γ-variety. But there are no convincing proofs to strengthen this hypothesis. Moreover, this hypothesis does not accord with the direct sulfidization of some ceria, without any dopant, which leads directly to the γ-phase, at low temperature. Such a γ-phase formation, remains for the moment unknown and it will be our main preoccupation in the near future.

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