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THERMAL STABILITY OF Ce_2O_2S. DOES $Ce_2O_2SO_4$ EXIST?

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ABSTRACT

Ce_2O_2S oxidizes between 300 and 600 °C when heated in air. The weight gain observed upon heating is 17 %. The oxidized phase is stable up to 700 °C after which the decomposition to CeO_2 begins. According to the X-ray powder diffraction and IR spectroscopical studies the oxidized phase seems to be $Ce_2O_2SO_4$ analogous to other rare earth oxysulfates.

INTRODUCTION

The rare earth oxysulfides, RE_2O_2S (RE = La, Gd, Y, Lu) activated with selected rare earths, form the most efficient class of cathodoluminescent phosphors (1). The preparation and the luminescent properties of these compounds have been extensively investigated (2 and references therein).

The rare earth oxysulfides decompose to oxysulfate, $RE_2O_2SO_4$, when heated in air. The oxidation temperature decreases with increasing atomic number and similarly the stability range of the oxysulfate diminishes along the lanthanoid series (3). The oxidation reaction is incomplete with the heavier rare earths and pure $RE_2O_2SO_4$ is not therefore obtained, but a mixture of oxysulfide, oxysulfate and oxide.

Though the thermal stability of Ce_2O_2S has not earlier been investigated there are several thermoanalytical studies on the rare earth(III) sulfate hydrates. Cerium has been reported to behave exceptionally in not forming an oxysulfate intermediate phase when the sulfate decomposes to an oxide (4,5). Rather cerium oxidizes to form highly stable CeO_2. Kay _et_ _al_. have studied thermal equilibrium in the RE_2O_2S-$RE_2O_2SO_4$ system and presented the Ce-O-S phase diagram (6). According to them cerium does not form any oxysulfate.

EXPERIMENTAL

The preparation of cerium oxysulfide is more difficult than that of the other rare earths. In general, the reduction of sulfate or sulfite provides a simple way of producting oxysulfides on a laboratory scale (2), but this seems not to be true for cerium. Possible preparation methods for Ce_2O_2S are: (1) heating of Ce_2O_3 in H_2S atmosphere, (2) reaction between Ce_2O_3 and Ce_2S_3 and (3) the use of sulfurizing fluxes with trivalent cerium compounds (7-9). The last method was employed in the present work. Ce(III) oxalate was mixed with

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the flux of Na_2CO_3, K_2CO_3 and S and heated in reducing atmosphere at 1100 °C for several hours.

Cerium oxysulfide crystallizes in hexagonal symmetry. The lattice parameters observed, $\underline{a}$ = 4.009 (2) and $\underline{c}$ = 6.869 (3) Å, are in good agreement with the earlier determinations (7).

In thermoanalytical measurements a Mettler Thermoanalyzer TA-1 with simultaneous TG and DTA recording were employed. The isothermal firings were carried out under static air atmosphere in a standard laboratory furnace.

The products were studied with a Philips X-ray powder diffraction apparatus as well as with an Enraf-Nonius Guinier-Hägg powder camera. In IR spectroscopical studies a Perkin-Elmer 521 spectrometer was employed with KBr-pellet techniques.

RESULTS AND DISCUSSION

The TG curve shows the oxidation of cerium oxysulfide to start slowly above 300 °C. The highest oxidation rate is reached between 500 and 600 °C (Fig. 1). The DTG and DTA curves show that the process has three stages. The maxima in the DTA curve are at 360, 460 and 530 °C and those in the DTG curve at 360, 530 and 560 °C. The existence of several maxima indicates that the particle size in the sample may have been inhomogeneous. The oxidized phase is stable up to 700 °C, after which endothermic decomposition begins. This reaction is rapid up to 800 °C and slow between 800 and 1100 °C. The experimental conditions, especially the particle size, affect the actual reaction temperatures (3), however, The weight increase observed in the oxidation is about 17 %, while that calculated for the oxysulfate, $Ce_2O_2SO_4$, is 18.6 %.

The oxidation of Ce_2O_2S occurs at lower temperature than would be expected from the position of cerium in the lanthanoid series; for La_2O_2S and Pr_2O_2S oxidize above 700 °C (3). The stability range of the oxidized phase of lanthanum and praseodymium is greater than 350 °C, whereas that of cerium is only 150 °C. Cerium oxysulfide oxidizes easily in air but the oxidized phase is unstable and CeO_2 is formed above 700 °C.

Earlier investigations have suggested that cerium(III) does not form an oxysulfate. The weight gain upon heating nevertheless indicates the formation of sulfate, whether $Ce_2O_2SO_4$, $Ce_2(SO_4)_3$, $CeOSO_4$ or $Ce(SO_4)_2$ (10).

The X-ray diffraction patterns of the samples fired at 500 - 700 °C show peaks from several phases. In addition to the peaks from Ce_2O_2S ($\underline{d}$ = 3.05, 3.40, 2.41, 1.90, 1.99, 2.25 Å) and CeO_2 ($\underline{d}$ = 3.12, 1.91, 1.63, 2.71 Å), small diffuse peaks at about $\underline{d}$ = 3.1 - 2.9 and 1.75 - 1.65 Å can be observed. The strongest reflections in orthorhombic $La_2O_2SO_4$ are $\underline{103}$, $\underline{013}$ and $\underline{110}$, having the $\underline{d}$-spacings of 3.13, 3.09 and 3.00 Å, respectively. Comparison indicates that

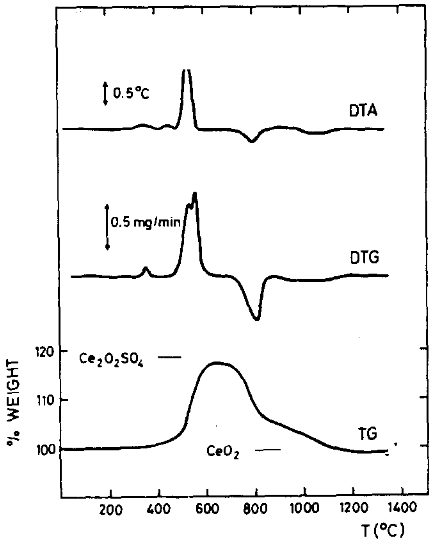

Fig. 1. The TG, DTG and DTA curves for Ce_2O_2S heated in dynamic air atmosphere. Heating rate 6 °C/min, sample size 32.9 mg.

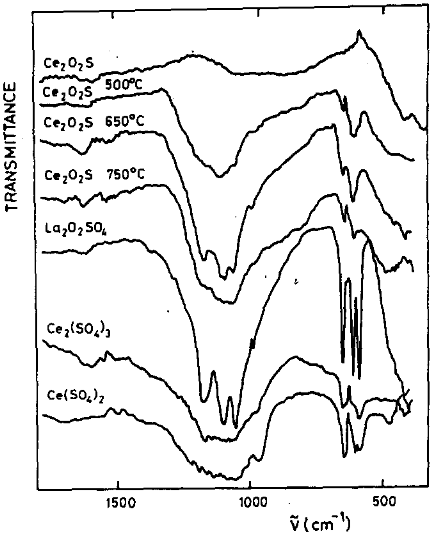

Fig. 2. IR spectra of Ce_2O_2S heated in air at 500, 650 and 750 °C, and the spectra of $Ce_2(SO_4)_3$, $Ce(SO_4)_2$ and $La_2O_2SO_4$ in the region 1800 - 400 cm^{-1}.

the oxidized phase of Ce_2O_2S contains an oxysulfate isomorphous with the other rare earth oxysulfates. Though the number of reflections observed was small, rough lattice parameters for $Ce_2O_2SO_4$ could be calculated as follows: $\underline{a}$ = 4.27, $\underline{b}$ = 4.24 and $\underline{c}$ = 13.63 Å.

The rare earth oxysulfides show IR absorption at about 500 and 400 cm^{-1} due to the RE-O and RE-S stretching vibrations. $La_2O_2SO_4$ shows strong absorption at 1000 - 1200 and 550 - 650 cm^{-1}, with three sharp peaks in both regions (1175, 1095, 1050, and 645, 605, 585 cm^{-1}) (Fig. 2). These wave numbers are typical for S-O vibrations in sulfate. The isothermally decomposed Ce_2O_2S samples have IR absorptions in these same regions, though the bands are broad and not completely resolved. The IR-spectra of $Ce_2(SO_4)_3$ and $Ce(SO_4)_3$ differ clearly from those of fired Ce_2O_2S samples. It seems probable therefore that upon heating under air atmosphere cerium oxysulfide forms an oxysulfate in an analogous manner to lanthanum oxysulfide.

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