Solid Solutions in the Rare-Earth Oxysulfide Series

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Investigations on the pseudobinary systems Ln_2O_2S–La_2O_2S (Ln = Nd, Sm, Eu, Gd, Dy, Yb, Lu, and Y) indicate complete solid solubility only for the systems Nd_2O_2S–La_2O_2S and Sm_2O_2S–La_2O_2S; a two-phase region is found for all other systems. The solid solubility in the isostructural oxysulfide series is discussed in terms of the differences in ionic radii of the two rare-earth components. Powder diffraction studies on two further systems (Y_2O_2S–Nd_2O_2S and Y_2O_2S–Eu_2O_2S) are consistent with such radii differences.

Introduction

Several rare-earth oxysulfides have been reported in the literature as suitable phosphor materials. The oxysulfide phosphors contain a host material (e.g., Y_2O_2S, La_2O_2S) and an activator (e.g., Eu_2O_2S, Tb_2O_2S) which together form a solid solution. In seeking new phosphors, it would therefore be advantageous to know the subsolidus phase relations in the isostructural RE oxysulfide series. However reports on solid solution formation in oxysulfide systems are few in number and partially contradictory. For instance, Sallavuard and Pâris (1) report a complete solid solubility for the system Yb_2O_2S–La_2O_2S, whereas Laud et al. (2) report a two-phase region for the system Y_2O_2S–La_2O_2S, where the difference between the ionic radii of the RE ions is smaller than in the case of lanthanum and ytterbium (3, 4).

The present investigation was undertaken in order to study systematically the solid solution formation between La_2O_2S and other rare-earth oxysulfides up to lutetium and the relationship of solid solution formation to the differences in ionic radii.

Experimental

The oxysulfides were prepared by reduction of the corresponding, homogenously dis-
persed (coprecipitated) sulfites in carbon monoxide atmosphere at 800°C in a quartz vessel, followed by 1-hr firing in nitrogen at 900°C. This relatively simple synthesis gives satisfactory results for all rare earths except cerium and scandium; it has been described and discussed in more detail previously (5). As starting materials, RE oxides (Kemira Oy, Oulu, Finland) of 99.9–99.99% purity were used. No sulfur losses were found to occur in the oxysulfides at the relatively low temperatures employed in the syntheses.

X-ray powder photographs were obtained at ambient temperature (approx 25°C) with a Guinier camera (Enraf–Nonius FR 552) of 114.6 mm diameter and monochromatized $CuK\alpha_1$ radiation ($\lambda = 1.54050$ Å). KCl was used as internal standard [$a = 6.29228$ Å (6)]. The photographs were measured with a microdensitometer (Joyce–Loebl & Co, Mk III/c). The accurate unit cell parameters were calculated by a least-squares method (7).

Results and Discussion

The Single Oxysulfide Phases

The oxysulfides of rare earths from lanthanum to lutetium and also yttrium form isostructural crystals belonging to the space group $P\bar{3}m1$ (8). Scandium oxysulfide, which

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TABLE I

Unit Cell Dimensions for the Rare-Earth Oxysulfides $Ln_2O_2S^a$

Ln	a (Å)	c (Å)	V (Å^3)
La	4.0540(5)	6.949(1)	98.91
Pr	3.9773(11)	6.832(4)	93.59
Nd	3.9479(7)	6.793(3)	91.69
Sm	3.9005(9)	6.723(2)	88.59
Eu	3.8753(6)	6.690(2)	87.01
Gd	3.8558(13)	6.670(2)	85.88
Tb	3.8297(10)	6.629(3)	84.20
Dy	3.8036(6)	6.601(2)	82.70
Ho	3.7848(6)	6.575(2)	81.75
Er	3.7629(13)	6.552(4)	80.35
Tm	3.7451(19)	6.538(3)	79.42
Yb	3.7268(12)	6.504(3)	78.23
Lu	3.7065(13)	6.491(3)	77.22
Y	3.7910(7)	6.596(2)	82.09

^{a} Ce, Pm, and Sc were not included in this work.

was not included in the present study, has a superstructure with a twofold c-axis, however (9). The unit cell parameters we obtained for the isostructural oxysulfide series are listed in Table I. The present data are in good agreement with those previously reported by Eick (10), although our values for the lighter rare earths seem to be consistently somewhat higher. The agreement with the values obtained by Flahaut et al. (11) and Collin and Loriers (12) is also generally good.

The lattice parameters show a rather regular decrease with increasing atomic number, as can be seen in Fig. 1. A slight cusp at gadolinium is clearly visible in the curve for c-axis, but other deviations seem not to be significant in the present data.

The gadolinium cusp or break and other singularities in curves describing rare-earth properties can be attributed to the tetrad
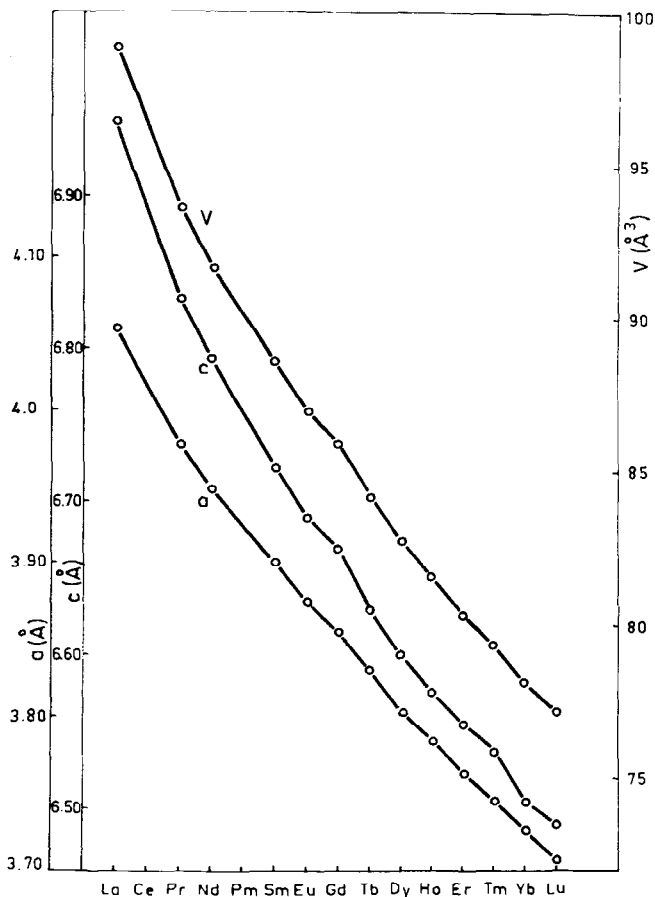

FIG. 1. Values of the unit cell parameters for the isostructural rare-earth oxysulfides.

(double–double) effect, which is apparently due to the maxima in interelectronic repulsion energies for the electronic configurations f^3–f^4, f^7, and f^{10}–f^{11} (13, 14). Siekierski (15) has previously pointed out the existence of these singularities in the unit cell volume curves of several rare-earths compounds; the curves include the rare-earth oxysulfides where he used Eick's accurate data (10).

Pseudobinary Solid Solutions

The solid solubility of lanthanum oxysulfide with other rare earths was studied in
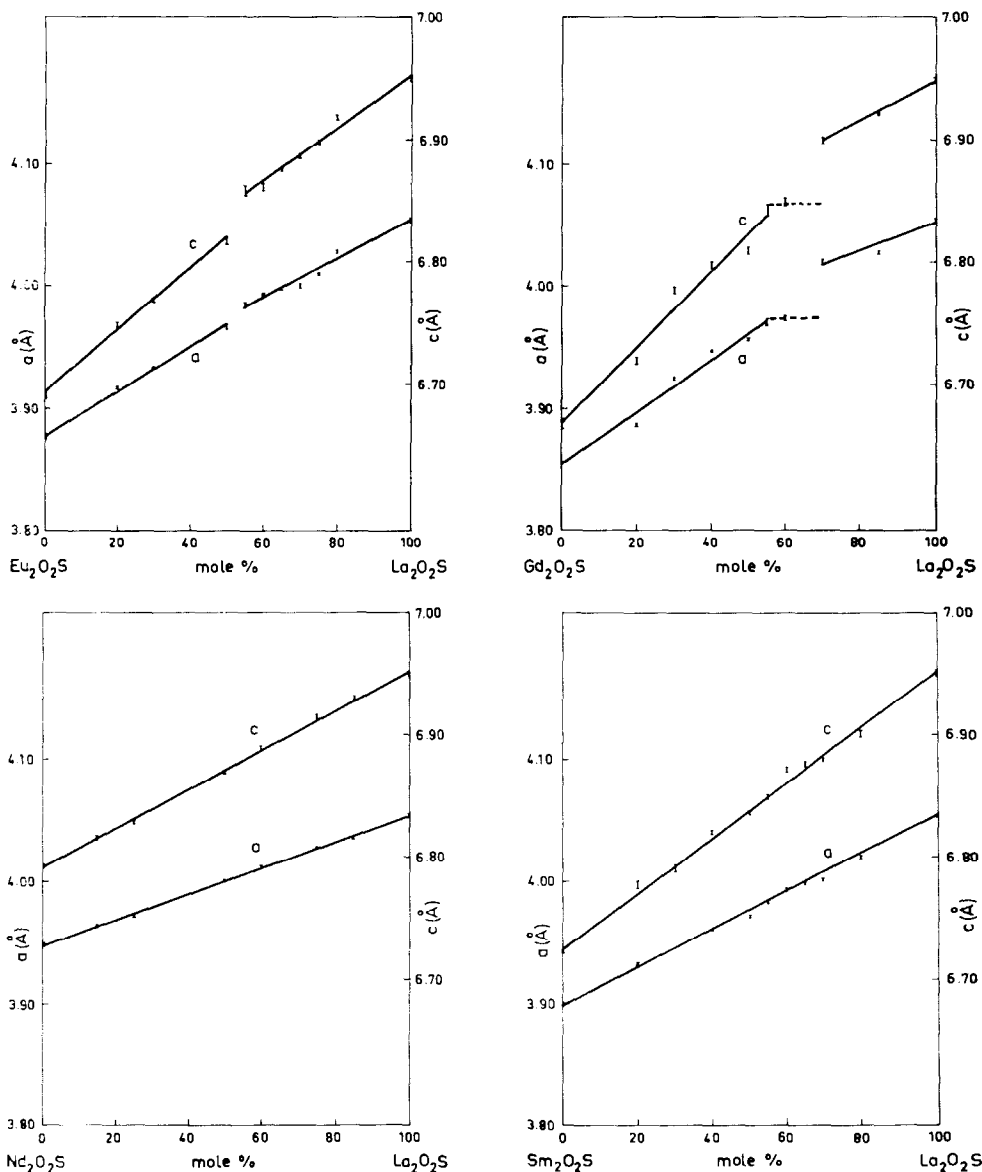

FIG. 2. Unit cell parameters *versus* composition in the systems Nd_2O_2S–La_2O_2S, Sm_2O_2S–La_2O_2S, Eu_2O_2S–La_2O_2S, and Gd_2O_2S–La_2O_2S. In single phase region a least-squares fit solid line joins the unit cell values; the length of bars is twice the esd. A dashed horizontal line is used in the two-phase region.
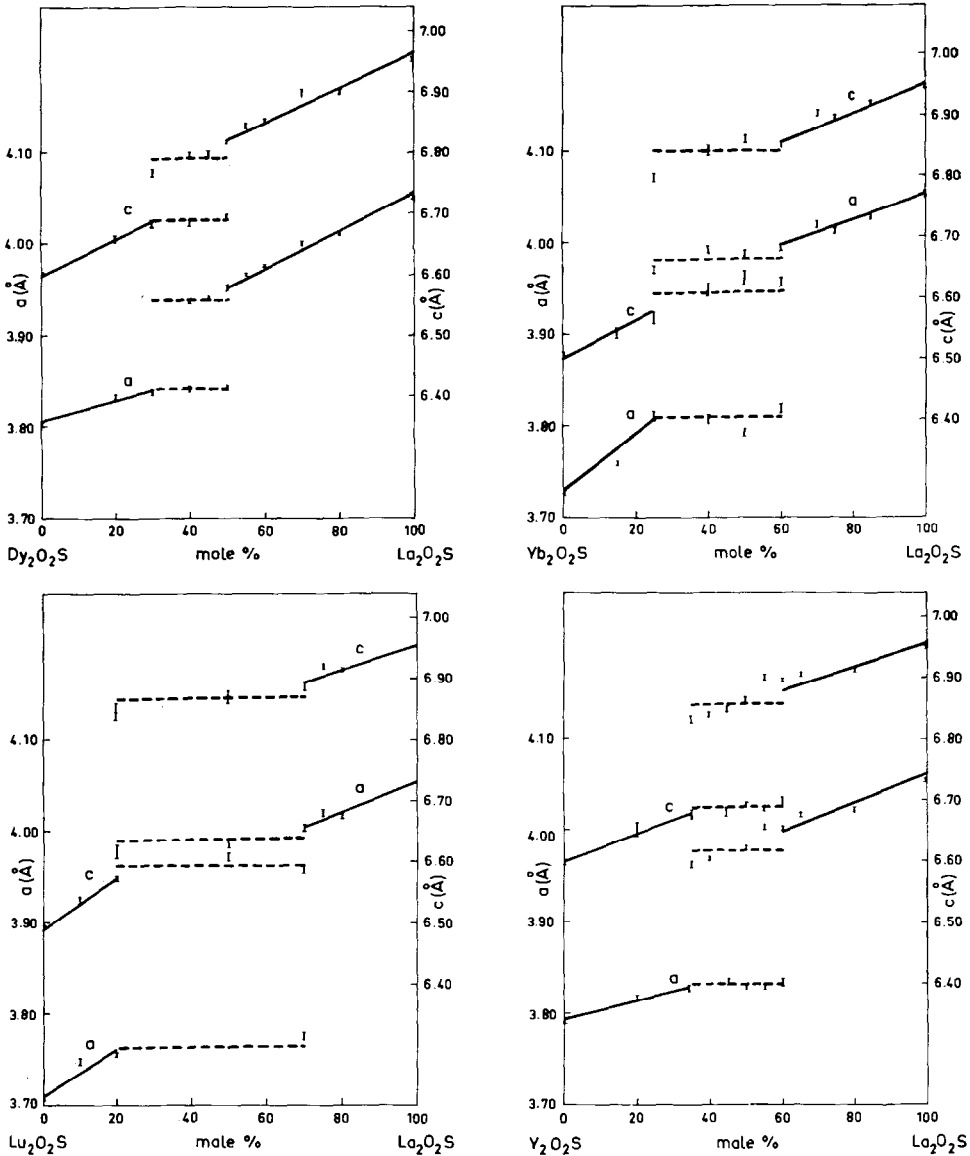
FIG. 3. Unit cell parameters versus composition in the systems $Dy_2O_2S-La_2O_2S$, $Yb_2O_2S-La_2O_2S$, $Lu_2O_2S-La_2O_2S$, and $Y_2O_2S-La_2O_2S$. For explanations, see caption for Fig. 2.

the systems $Ln_2O_2S-La_2O_2S$ where Ln is Nd, Sm, Eu, Gd, Dy, Yb, Lu, and Y. Figures 2 and 3 show least-squares fit unit cell parameters for these systems plotted against composition. It can be seen that complete solid solubility exists only up to samarium; the next rare earth, europium, shows a narrow two-phase region. As the ionic radius differ-

ence increases, the two-phase region broadens as expected. In accordance with the ionic radii (3, 4), the yttrium behaves much like dysprosium.

The general validity of the results obtained with lanthanum were checked in two other systems ($Y_2O_2S-Eu_2O_2S$ and $Y_2O_2S-Nd_2O_2S$), both involving Y_2O_2S, also an
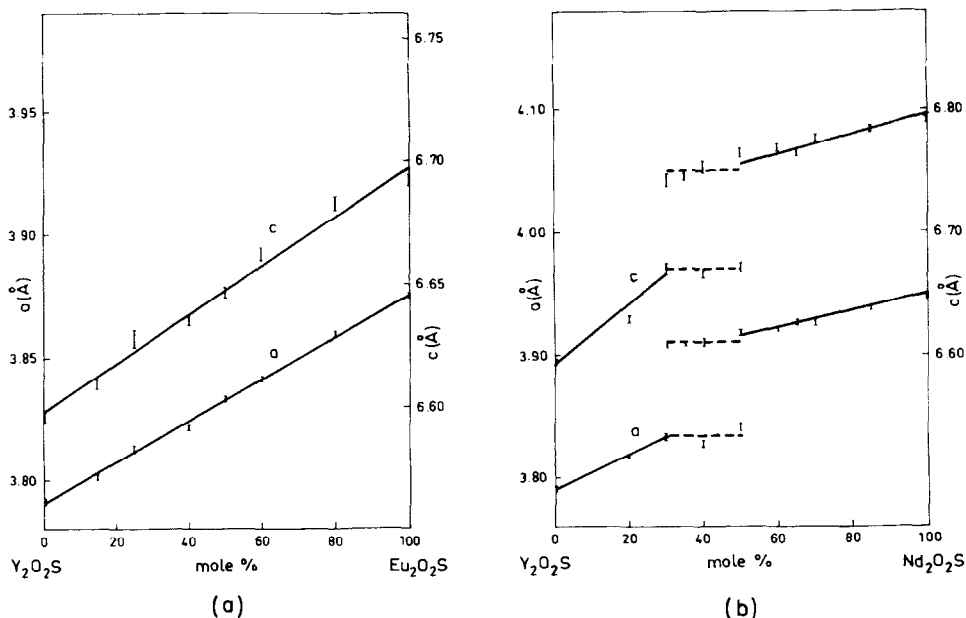
FIG. 4. Unit cell parameters versus composition in the systems $Y_2O_2S-Eu_2O_2S$ and $Y_2O_2S-Nd_2O_2S$. For explanations, see caption for Fig. 2.

important host material in phosphors. The relative difference in ionic radii in the $Y_2O_2S-Eu_2O_2S$ system $[(r_{Eu^{3+}}-r_{Y^{3+}})/r_{Y^{3+}} = 5.2\%]$ is smaller than in the $Sm_2O_2S-La_2O_2S$ system $[(r_{La^{3+}}-r_{Sm^{3+}})/r_{Sm^{3+}} = 9.1\%]$ and therefore complete solid solubility was anticipated. The results obtained are in agreement with this; cf. Fig. 4.

It should be noted that in RE oxysulfides the rare-earth ions are seven-coordinated by oxygen and sulfur atoms. The differences above were calculated from the radii of six-coordinated ions, because no complete set of ionic radii for seven-coordination is available. It can be assumed, however, that the change from six to seven coordination causes fairly regular increases in the ionic radii, as is the case between six and eight coordination (3, 4).

Similar reasoning leads to the prediction of complete solid solubility for the system $Y_2O_2S-Nd_2O_2S$ (difference 9.2%), for the difference in ionic radii is only slightly greater than in the case of the $Sm_2O_2S-La_2O_2S$ system. The results, however, show the existence of a two-phase region (Fig. 4b), indicating a behavior more like that found

in the $Eu_2O_2S-La_2O_2S$ system (difference, 10.2%). Thus, in borderline cases (difference in ionic radii 9–10%) predictions concerning the solid solubility region obviously must be checked experimentally.

The existence of complete solid solubility for all possible pseudobinary systems suitable as phosphor host materials (i.e., systems involving two of the following, white-light emitting oxysulfides: La_2O_2S, Gd_2O_2S, Lu_2O_2S or Y_2O_2S) can be postulated for all combinations except those involving La_2O_2S.

The present results are in agreement with the results published by Laud *et al.* (2) but not with the complete solid solubility suggested by Sallavuard and Pâris (1) for the system $Yb_2O_2S-La_2O_2S$ (ionic radius difference 20.4%), where probably the limited number of measurements in the two-phase region led to misinterpretation.

Acknowledgment

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