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BRIEF COMMUNICATIONS

Solid Solubility of the Oxisulfides of Y, La, and Gd

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The solid solubility in the systems Y_2O_2S–La_2O_2S, Y_2O_2S–Gd_2O_2S, and Gd_2O_2S–La_2O_2S has been investigated. Solid solutions of all compounds, throughout the whole composition range, were readily obtained, using coprecipitated oxalates and a polysulfide flux. © 1989 Academic Press, Inc.

1. Introduction

The oxisulfides of Y, La, and Gd crystallize in the hexagonal space group $P\bar{3}m1$. In this structure, the metal ions are 7-coordinated.

In this communication we present the results of an investigation of the solid solubility of the oxisulfides of Y, La, and Gd. The present study finds its origin in an investigation of the diffusion of electron–hole pairs, generated by cathode-ray excitation, in the oxisulfides of Y, La, and Gd and the corresponding mixed compounds, the results of which will be published elsewhere (*1*). Unlike Leskelä *et al.* (*2, 3*) and Laud *et al.* (*4*), who failed to prepare solid solutions of the systems La_2O_2S–Y_2O_2S and Gd_2O_2S–La_2O_2S, we found that complete solubility of all investigated oxisulfides is possible over the whole concentration range. In this paper our preparation method and the characterization of the solid solutions of the oxisulfides of Y, La, and Gd in terms of the cell axes of these compounds is described.

2. Experimental Methods

The oxides of Y (Rare Earth Products, 6 *N*), La (Rhone Poulenc, 5 *N*), and Gd (Rare Earth Products, 5 *N*) were dissolved in hot diluted nitric acid (about 4 *M*) (Merck selectipur). Oxalic acid dihydrate (Merck p.a.) was dissolved in hot water. By adding an excess of dissolved oxalic acid to the appropriate mixture of the dissolved oxides of Y, La, and Gd (about 2 to 1), the oxalates of the corresponding oxides were coprecipitated. The oxalates were converted into the oxides by heating at 800°C for a few hours. The resulting oxide mixture was mixed with excess S (U.C.B., highest purity) (6 to 1) and a stoichiometric amount of Na_2CO_3 (Merck selectipur). This mixture was heated at 1100°C in air for a few hours in a quartz vessel using a well closing lid. The sodium carbonate and the sulfur reacted to form a polysulfide flux,

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leading to a very efficient conversion of the mixed oxides into the corresponding oxisulfide. Finally the product was washed in water in order to remove the residual flux, dried, and characterized using X-ray diffraction.

We point out that this procedure differs considerably from the one used by Leskelä *et al.* (*3*), who tried to prepare solid solutions of several oxisulfides by reduction of a corresponding mixture of the coprecipitated sulfites at 800°C in a (reducing) CO atmosphere. Laud *et al.* also used coprecipitated oxalates as the starting mixture, but instead of using a polysulfide flux they converted the oxides into the oxisulfides by applying a constant flow of 20% H_2S in 80% N_2 (by volume) (*4*) at a temperature of 1250°C. A method similar to the one used by us was already described in the literature by Royce *et al.* (*5*).

For the determination of the cell axes a Philips modular diffractometer system was used. The cell parameters and the standard deviations in the cell parameters were calculated using linear regression procedures.

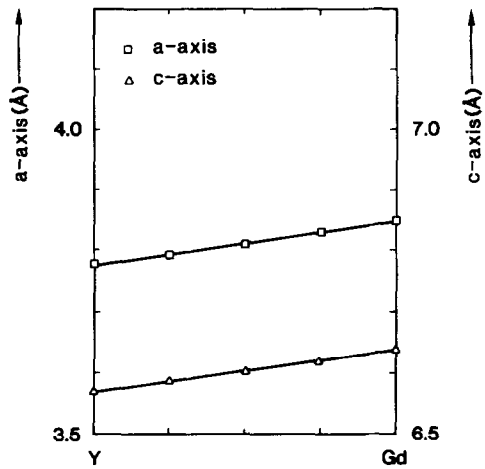

FIG. 2. Cell axes of the system Y_2O_2S–Gd_2O_2S as a function of the composition. The *a*-axes of the compositions are indicated by the squares and the *c*-axes by the triangles.

3. Experimental Results

The *a*-axes and the *c*-axes of the systems Y_2O_2S–La_2O_2S, Y_2O_2S–Gd_2O_2S, and Gd_2O_2S–La_2O_2S are given in Figs. 1, 2, and 3, respectively. We observe a continuous

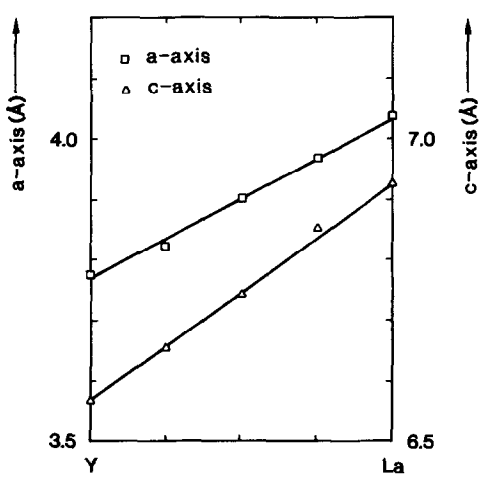

FIG. 1. Cell axes of the system Y_2O_2S–La_2O_2S as a function of the composition. The *a*-axes of the compositions are indicated by the squares and the *c*-axes by the triangles.

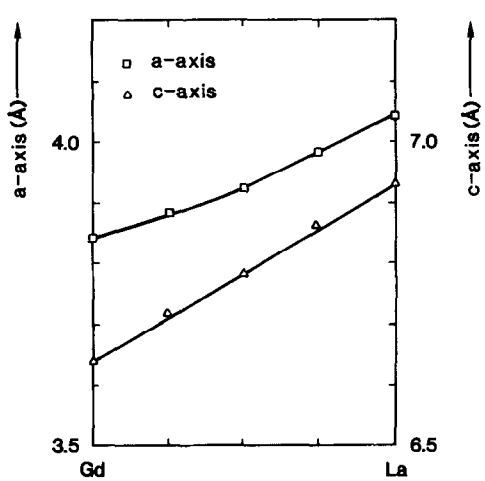

FIG. 3. Cell axes of the system Gd_2O_2S–La_2O_2S as a function of the composition. The *a*-axes of the compositions are indicated by the squares and the *c*-axes by the triangles.

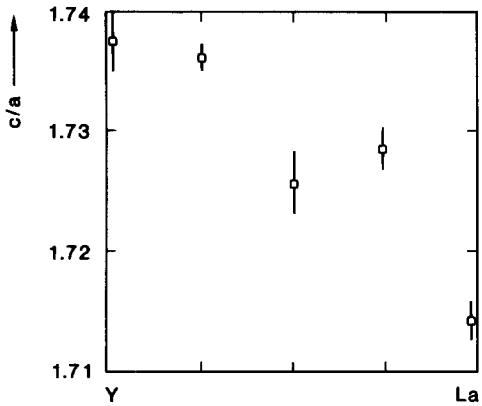

FIG. 4. The c/a ratio of the system Y_2O_2S–La_2O_2S as a function of the composition.

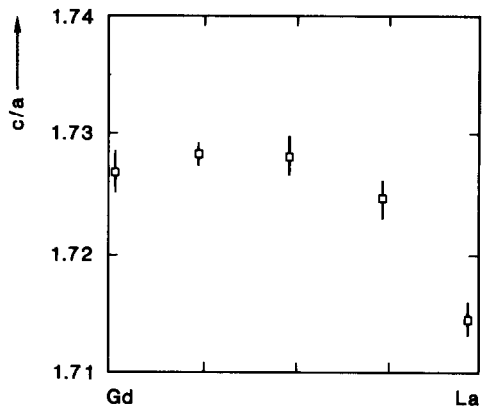

FIG. 6. The c/a ratio of the system Gd_2O_2S–La_2O_2S as a function of the composition.

change in the cell axes of these systems as a function of the composition. The reproducibility was checked on three parallel samples.

The standard deviation in the value of the cell axes is in the order of 0.05%. The standard deviation in the value of the c-axes is in some cases somewhat larger but never exceeds 0.1%. The length of the c-axis divided by the length of the a-axis (c/a ratio) of the three systems as a function of the composition is given in Figs. 4–6.

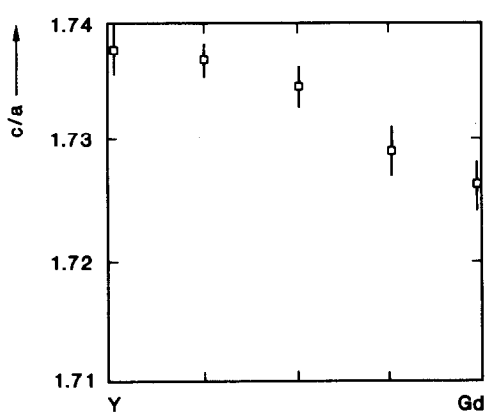

FIG. 5. The c/a ratio of the system Y_2O_2S–Gd_2O_2S as a function of the composition.

4. Discussion

Figures 1–3 clearly show that these systems form solid solutions throughout the whole composition range. The behavior of the c-axes of these systems as a function of the composition is in close agreement with the behavior predicted by Vegards' law. The same applies for the a-axes of these systems except for the system Gd_2O_2S–La_2O_2S. In this system we observe smaller values for the a-axes of the solid solutions than expected from Vegards' law. This presumably indicates a stronger interaction between Gd and La ions than between ions of the same kind (see (*7*)) and is no indication for the existence of a two-phase region.

Within the accuracy of the experiments, the c/a ratio of the systems varies smoothly with composition. This again indicates that all investigated systems form solid solutions.

Leskelä *et al.* did fail to prepare solid solutions over the whole composition range when the difference between the radii of the metal ions is too large (*2, 3*). It is of interest that the reaction rate of the sulfites with CO decreases from La to Dy (decreasing metal ion radii) (*6*)). This probably reduces the effect of coprecipitation.

The method used by Laud *et al.* is inappropriate for preparing La_2O_2S (*6*) because of the low yield. This, presumably, is the reason that Laud *et al.* did not obtain solid solutions throughout the whole composition range in the systems Y_2O_2S–La_2O_2S and Gd_2O_2S–La_2O_2S.

Finally, we remark that the use of ionic radii in order to explain the existence of or possibility of preparing solid solutions as done in (*2–4*) has a limited value. First, the statement that the metal ion radii should not differ more than 10% is rather arbitrary. Second, the values of the ionic radii depend critically on the way in which they are determined.

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