### GROWTH OF EuO, EuS, EuSe AND EuTe SINGLE CRYSTALS\*

T. B. REED and R. E. FAHEY

Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02173, U.S.A.

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Single crystals of the europium monochalcogenides weighing up to 60 g have been grown from Eu-rich solutions and from stoichiometric melts by using a gradient cooling technique. Since all four compounds have high Eu partial pressures near their melting points, the crystals were grown in weld-sealed tungsten crucibles 1.25 or 2.5 cm in diameter.

The oxide was synthesized and grown in the same run. Dried  $Eu_2O_3$  was heated with an excess of Eu metal to about 2200 °C, and the solution obtained was directionally frozen from the bottom by cooling to room temperature at 5–50 °C/hr. The resulting boules were single crystals with total impurities ranging from 250 to 5000 ppm. These crystals were then remelted, either with or without additional Eu metal, and directionally frozen

#### 1. Introduction

The divalent europium chalcogenides, which have the rock salt cubic structure, are of considerable current interest as magnetic semiconductors which are transparent in the infrared<sup>1</sup>). Some of their characteristic physical properties are summarized in table  $1^2$ ).

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Com-	Color in reflection	Melting point*	Lattice param- eter	Room temperatur abs. edge	Critical e tempera- ture
pound	reneetton	( <sup>∞</sup> C)	(Å)	(eV)	(°K)
EuO	Magenta	2016 8	5.143	1.122	$T_{\rm c} = 69$
EuS	Gold	2320-2450	5.968	1.690	$T_{\rm c} = 16.5$
EuSe	Green	2320-2450	6.104	1.879	$T_{\rm n} = -4.6$
EuTe	Dark green	2320-2450	6.598	1.959	$T_n = -9.6$

TABLE 1

Physical properties of the divalent europium chalcogenides

\* Determined in this study.

The growth of EuO crystals from metal-rich solution was first described by Guerci and Shafer<sup>3</sup>). We have grown crystals of all four compounds up to 2 cm on a

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337

to obtain crystals containing total impurities of about 200 ppm primarily C and Ca. The crystals were also used subsequently for growing crystals doped with Gd or La.

The other compounds were synthesized in sealed quartz ampoules by the reaction of Eu metal at about 600  $^{\circ}$ C with vapor of the other element supplied by a reservoir at a lower temperature. Single crystals similar in size and purity to those of the oxide were then grown by the gradient cooling technique. The effect of deviations from stoichiometry on optical and electrical properties are discussed.

The melting point of EuO, measured with an optical pyrometer and a W-(W, 26% Re) thermocouple, was  $1980\pm20$  °C. EuS, EuSe and EuTe all melt between 2250 and 2500 °C.

side by slowly cooling either metal-rich solutions or stoichiometric melts sealed in tungsten crucibles. The synthesis and growth of EuO will be described in detail, and variations in technique used for EuS, EuSe and EuTe will then be noted.

#### 2. EuO crystals

At the melting point of EuO, the partial pressure of Eu vapor over the compound is probably about 1 atm. [This estimate<sup>4</sup>) is based on an extrapolation of partial pressure data for EuO-Eu mixtures<sup>5</sup>) and EuO- $Eu_3O_4$  mixtures<sup>6</sup>).] Therefore synthesis and crystal growth must be performed in a sealed system. Tungsten crucibles 3 in. long and either 0.5 in. in diameter  $\times$  0.020 in. wall (total charge about 25 g) or 1 in. in diameter  $\times$  0.060 in. wall (total charge about 85 g) were used for growing most of the crystals. They are supplied with "insertion" lids, which are welded in an argon atmosphere by means of a laboratory arc melter<sup>7</sup>) at a current of about 100 A. During welding the crucible is held in a water-cooled cylindrical graphite anode, as shown in fig. 1, which restricts melting to a narrow zone and keeps the charge cool. A few

INSERTION CAP TUNGSTEN CATHODE O ARC WELD INSERT - Cu ANODE WATER-COOLED SLEEVE GRAPHITE INSERT

Fig. 1. Apparatus for welding insertion caps to tungsten crucibles.

crystals were also grown in molybdenum crucibles with similar results.

Synthesis and growth from solution are accomplished by sealing  $Eu_2O_3$  (dried at 1000 °C in vacuum and pressed into pellets) together with an excess of Eu metal into a crucible in the ratio of one mole of  $Eu_2O_3$ to two moles of Eu (100% excess Eu). One or two crucibles are mounted in a cylindrical molybdenum block (with a small sighting hole drilled through one wall) inside a resistance furnace with tantalum or tungsten heating elements<sup>8</sup>) as shown in fig. 2. With argon at atmospheric pressure flowing through the furnace at 30 cm<sup>3</sup>/min, the temperature is slowly raised to about 2300 °C. (It is estimated that the europium pressure at this temperature reaches at least



Fig. 2. Apparatus for growth of Eu chalcogenide crystals from solution and melt.

twenty atmospheres; the tungsten lids and bottoms of the crucibles frequently bulge but have never broken.) The furnace is then cooled at about 10  $^{\circ}$ C/hr to 1200  $^{\circ}$ C and at 20  $^{\circ}$ C/hr to room temperature. The temperature gradient is such that the solution freezes from the bottom to the top.

After cooling the crucible is very brittle and can be removed by gently cracking and peeling it from the ingot to which it adheres because of the excess metal. The lower two-thirds of the ingot is generally a single crystal with marked cubic cleavage perpendicular to the  $\langle 100 \rangle$  axis. Although it is difficult to remove the crystal from the crucible without some cracking, cubes up to 2 cm on an edge and weighing over 30 g have been recovered. Above the crystal there is a two-phase tegion of leathery texture, and above this is a layer of excess Eu metal.

The EuO crystals are moderately stable in air but tarnish noticeably in a few weeks. A typical mass spectrographic analysis of the first portion of the crystal to freeze shows C = 100, K = 50, Ca = 35, N = 20, Sr = 12, Te = 12, Na = 8, As = 4, Mg = 2, all others less than 1 atomic p.p.m. (crystal 95).

Doped or undoped crystals have been grown from the synthesized compound by adding 10% excess Eu metal (by weight) and a dopant if required, and repeating the above procedure. The concentrations of impurities in the first to freeze and last to freeze portions of crystal 48, grown from a solution doped with 8000 p.p.m. Gd are shown in fig. 3.

The sealed crucible method has also been employed to grow single crystals of EuO from nominally stoichiometric melts, by using the synthesized compound without adding excess Eu metal. The crystals obtained in this manner, which do not adhere to the crucible, do not contain a second phase of either Eu metal or higher oxides. The formation of single phase material in this manner shows that EuO melts congruently. The melting point was determined by melting a single crystal in a sealed molybdenum crucible and measuring the temperature of the thermal arrest observed on cooling. Consistent results were obtained with a W– (W, 26% Re) thermocouple and with an optical pyrometer. The average value obtained for 57 cooling runs on the same sample was  $1980 \pm 20$  °C.

An attempt was made to grow crystals by slow cooling of melts containing excess oxygen. In all cases the crystals contained small amounts of  $Eu_3O_4$  as a second phase.

The results of mass spectrographic analysis of a single crystal grown from a nominally stoichiometric melt doped with 0.8 at % Gd are shown in fig. 4. It can be seen that the degree of purification due to segregation of impurities is much less than that observed in growth from Eu-rich solution (fig. 3).

In general undoped crystals grown from Eu-rich solution are highly transparent in the infrated from 2–10  $\mu$ m, with absorption coefficients in this region of less than 1 cm<sup>-1</sup>, while crystals grown from a stoichiometric melt have much larger absorption coefficients<sup>1</sup>). The room temperature electrical resistivity of the last-to-freeze portions of doped and undoped crystals grown from solution is as low as 10<sup>-1</sup> ohm-cm, while that of crystals grown from the melt is about 50 ohm-cm. The first-to-freeze portions of both solution and melt-grown crystals have resistivities above 10<sup>6</sup> ohm-cm, the limit of our measurement.

The homogeneity range of EuO is quite narrow and difficult to measure. Weight change on combustion of EuO<sub>x</sub> to Eu<sub>2</sub>O<sub>3</sub> gives values of  $x = 1.000 \pm 0.005$  for typical single crystal samples, but there is sufficient scatter in the results so that it has not yet been possible to correlate them with other properties. The variation of the unit cell across the homogeneity range is also small and difficult to measure reliably. Shafer<sup>9</sup>) reports a lattice parameter of 5.142 Å for a number of annealed samples containing excess metal and 5.143 Å for samples equilibrated with Eu<sub>3</sub>O<sub>4</sub>. Other values in the literature range from 5.142–5.145 Å, as do all those measured for EuO crystals in this laboratory, the higher values being associated with excess oxygen.

The optical and electrical properties of EuO are extremely sensitive to the small variations in composition occurring during crystal growth or in subsequent annealing. The effects of composition were demonstrated by an annealing experiment on a high-resistivity crystal of EuO. One part of the crystal was annealed at 1400 °C for 60 hr in a sealed crucible in the vapor over a mixture of Eu and EuO and another part was similarly annealed in the vapor over a mixture of EuO and  $Eu_3O_4$ . After annealing, these samples had lattice parameters of 5.1422 and 5.1438  $\pm 0.005$  Å respectively, compared with the initial value of 5.1432 Å.

The resistivity of the O-saturated sample is about



Fig. 3. Impurity segregation in EuO crystal grown from Eurich solution, doped with 0.5 at% Gd. (Diagonal lines connect points for the same element and do not imply a linear distribution.)

 $5 \times 10^3$  ohm-cm at room temperature and increases slowly and smoothly with decreasing temperature to about  $5 \times 10^4$  ohm-cm at 50 °K, passing smoothly through the Curie point. The resistivity of the Eusaturated sample is about  $10^2$  ohm-cm at room temperature, rises to a maximum of about  $10^3$  ohm-cm at 80 °K and then drops to about  $10^{-3}$  ohm-cm at 50 °K. This behavior, which is associated with the ferromagnetic transition in EuO, has also been observed in some as-grown samples taken from the last-to-freeze portions of solution-grown ingots<sup>2</sup>). These striking differences between the Eu-saturated, as-grown, and Osaturated crystals show that deviations from stoichiometry are of great importance in determining the properties of EuO.



Fig. 4. Impurity segregation in EuO crystal grown from nominally stoichiometric melt doped with 0.8 at% Gd.

## 3. EuS, EuSe, and EuTe crystals

The other three Eu chalcogenides were synthesized by reacting Eu metal with chalcogen vapor, using the method of Miller<sup>10</sup>) and Holtzberg<sup>11</sup>). Chunks of Eu metal were placed at one end of a fused quartz tube 20 cm long, and the stoichiometric amount of the chalcogen at the other end. After being evacuated and sealed, the tube was placed in a horizontal muffle furnace 50 cm long with the metal kept below 600 °C and the chalcogen in a cooler region near one end of the furnace, in order to prevent too rapid reaction. After the reaction was essentially complete, usually in a day or two, the temperature was raised to 900 °C for 16 hr. There was no evidence of reaction with the quartz.

Crystals of all three compounds were grown from solution by adding 20 wt $^{0/}_{-0}$  excess of Eu metal to the synthesized material, heating to 2300 °C, and cooling in sealed tungsten crucibles at the same rate used for EuO. As in the case of EuO, no special precautions were necessary to obtain single crystals. The as-grown crystals are almost opaque in the infrared, and their electrical resistivity at room temperature is of the order of 1 ohm-cm. These properties suggest the presence of excess Eu metal. Therefore EuS and EuSe crystals have been subjected to two annealing procedures designed to increase the ratio of chalcogenide to metal. After being annealed in a dynamic vacuum  $(10^{-2} \text{ torr})$ at 1600 °C for 48 hr, the crystals became insulating (resistivity greater than 10<sup>6</sup> ohm-cm) and quite transparent in the infrared and red. Annealing as-grown crystals at 1000 °C for 64 hr in 1 atm of sulfur or selenium vapor also increased the resistivity. The weight changes accompanying the addition of chalcogenide or evaporation of europium suggest that the homogeneity ranges of the sulfide and selenide are several atom percent wide.

In cooling experiments on the three compounds unmelted material was observed in crucibles heated to 2250 °C, measured in a blackbody hole with an optical pyrometer. Crystals of all three compounds have been grown from the melt by cooling from 2500 °C, indicating that their melting points all lie between 2250 and 2500 °C.

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