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# HIGH TEMPERATURE VAPOUR PHASE GROWTH OF EUROPIUM SULPHIDE, SELENIDE AND TELLURIDE

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Preliminary results are reported for the synthesis, crystal growth and characterisation of EuTe, EuSe and EuS. The crystals were grown by chemical transport (EuTe, EuSe) and sublimation (EuTe, EuS) in evacuated and sealed molybdenum crucibles. The temperature of the iodine transport was 1700 °C and that of sublimation 2050 °C. Reaction between iodine and molybdenum was avoided by working at temperatures where the molybdenum iodides are not stable ($T > 1500$ °C). Optical measurements show that the absorption edge of the iodine grown crystals agrees with the values given in the literature. The rest absorption and the refractive index of EuTe and EuSe is lower for transported crystals and the lowest reported up to now in the literature. The magnetic properties of EuTe grown by iodine transport have been measured and found comparable to the ones reported in the literature.

## 1. Introduction

Physical and chemical investigations on high temperature materials have been seriously hindered up to now due to the difficulties of growing crystals at high temperatures. High melting points, non-compatibility of the wall materials, high degree of imperfection and non-stoichiometry are some difficulties frequently met when high temperature crystal growth is tried. However, it could be expected that if vapor phase methods in closed systems and particularly chemical transport could be used, some of these difficulties could be solved.

We have used the sealed molybdenum crucible method[1]), which has been successfully used up to now in our laboratory[2]), for crystal growth both by chemical transport and sublimation. Single crystals of EuTe and EuSe have been grown by chemical transport at 1700 °C and those of EuTe and EuS by sublimation at 2000 °C. In the following the synthesis, crystal growth and characterisation of these compounds are reported.

## 2. Synthesis and sublimation of EuTe and EuS

The difficulties of synthesising bivalent europium compounds arise from the high reactivity of europium metal and the sensitivity of $Eu^{2+}$ to oxidation. The handling, therefore, of the europium metal and the compounds in powder form took place in an argon filled dry box. A 30% Na–70% K liquid alloy has been used as getter.

The compounds have been synthesised by direct reaction of the elements in evacuated and sealed silica ampoules. The reaction with tellurium begins at much higher temperatures and is not completed even by heating for many days at 880 °C, as can be seen by the faint yellow vapour in the ampoule (table 1). Heating at higher temperatures in silica ampoules is not possible because of the reaction with silica.

The reaction of europium with sulfur is almost completed between 90 and 180 °C in 48 hours. The temperature of 90 °C is critical. When it is reached, the heating rate must be slowed down to 2 °C/hr in order to avoid explosions. To ensure complete reaction, the ampoule is heated for one day at 880 °C. At this temperature no reaction with the silica wall can be seen.

The contents of the silica ampoules were used as starting material for sublimation experiments. The powder was transferred into a degassed molybdenum

TABLE 1

Characteristic temperatures of the synthesis of europium chalcogenides

| | Temperature of reaction of Eu with $I_2$ (°C) | Temperature of reaction of the elements (°C) | Max heating temperature (°C) |
|---|---|---|---|
| EuTe | — | 600–730 | 880 |
| $EuTe+I_2$ | 175–270 | 600–730 | 880 |
| $EuSe+I_2$ | 175–210 | 185–210 | 750 |
| EuS | — | 90–180 | 880 |

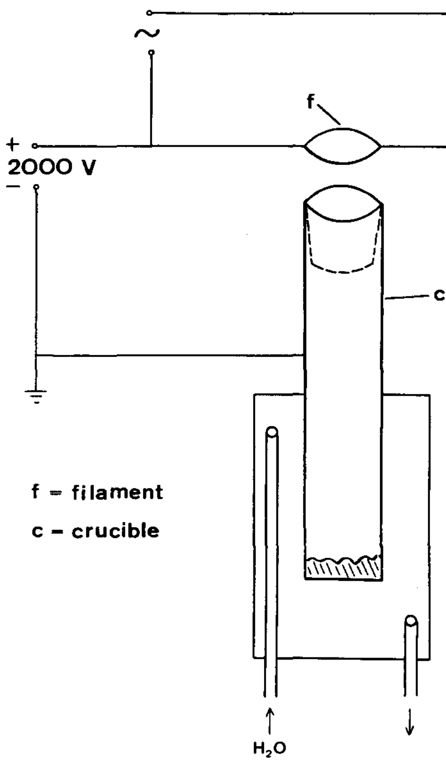

Fig. 1. Principle of the apparatus used for sealing molybdenum crucibles under high vacuum.

crucible (30 mm diameter and 120 mm length) and the crucible was put in the sealing apparatus. To seal the molybdenum crucibles, any commercial electron beam welding apparatus can be used. In our work, we have used a simple apparatus based on the same principle (fig. 1). A dc voltage of 2000 V is applied between the hot filament and the crucible. Part of the emitted electrons heat the thin edge of the lid and seal it with the crucible. To avoid decomposition of the starting material, effective cooling must be used. Before the sealing starts, the vacuum in the sealing chamber is $10^{-6}$ Torr; during the sealing, the vacuum falls to $10^{-4}$ Torr. At pressures higher than $10^{-3}$ Torr, discharges in the chamber make sealing impossible.

The sealed crucible is put in a high temperature furnace for the crystal growth. We have used both HF-high vacuum, silica double-walled, water cooled furnaces and resistance heated, high vacuum, graphite furnaces. In these furnaces temperature profiles have been measured with tungsten–rhenium (97% W–3% Re versus 75% W–25% Re) thermocouples. From these profiles apparent undercoolings, $\Delta T$, can be calculated[3]). Though they are different from the actual undercoolings in the crucible, they can be used in order to increase the reproducibility of the experiments.

## 3. Synthesis and chemical transport of EuTe and EuSe

For chemical transport the same molybdenum crucibles were used. To avoid any reaction of the iodine with the crucible walls the experiments were performed at temperatures where the molybdenum iodides are not stable[4]) ($T > 1500$ °C). The high temperatures during the sealing of the crucible make difficult the selection of the transporting agent. Even with intensive cooling, the temperature of the charge reaches a few hundred degrees Celsius. This temperature makes impossible the use of most conventional transporting agents, under high vacuum, due to their high vapour pressure. Therefore, to keep high vacuum during the sealing of the crucibles, $EuI_2$ has been used as a source of iodine and the synthesis procedure was modified. Stoichiometrical amounts of the elements together with the necessary quantity of iodine were sealed and heated in the ampoule, where the following reaction takes place:

$$\mathrm{Eu} + \tfrac{1}{2}\,\mathrm{X}_2 + n\,\mathrm{I}_2 \rightleftharpoons (1-n)\,\mathrm{EuX} + n\,\mathrm{EuI}_2 + \tfrac{1}{2}n\,\mathrm{X}_2$$
$$(\mathrm{X} = \mathrm{Te,Se}).$$

Details about the way to introduce the iodine in the evacuated silica ampoule have been given earlier[3]).

As it can be seen from table 1 for EuSe, the reaction of europium with iodine and selenium takes place in the same temperature range (175–210 °C). To ensure completion of the reaction, the ampoule is heated at 750 °C. However, the temperature of the reaction of europium with tellurium is not influenced by the presence of iodine.

The contents of the silica ampoules were transferred, under argon atmosphere, in the molybdenum crucible, evacuated and sealed as above.

It was assumed that chemical transport will take place according to the equilibrium

$$\mathrm{EuX}_{(s)} + \mathrm{I}_{2(g)} \rightleftharpoons \mathrm{EuI}_{2(g)} + \tfrac{1}{2}\mathrm{X}_{2(g)} \qquad (\mathrm{X} = \mathrm{Te,\ Se}). \tag{1}$$

The $EuI_2$ and chalcogen necessary to start the transport are provided by the synthesis reaction.

A problem of the synthesis of the bivalent europium chalcogenides has been the $Eu^{3+}$ content. Investigations with Mössbauer-effect[5]) have shown that some of the first synthesised powders of EuTe[6]) contained up to 25% $Eu^{3+}$. With recrystallisation at higher temperatures, it was possible to suppress the $Eu^{3+}$ content.

An advantage of the use of equilibrium (1) for the crystal growth of bivalent europium compounds is that in the gas phase only $Eu^{2+}$ is stable. $EuI_3$ decomposes at temperatures lower than 1000 °C. Any $Eu^{3+}$ content of crystals grown under these conditions would probably result from a secondary reaction of defects or from subsequent oxidation.

## 4. Results of the crystal growth

At this first stage of our investigations, with which this paper is dealing, it was tried primarily to improve, as far as possible, the quality of the crystals and not their size. The crystals grew as rather thin layers (2 to 3 mm thick) on the lid of the crucible because for the first experiments only small amounts of starting materials were used. It is clear that if greater amounts of starting material are used, the crystals can be much thicker. The conditions of the crystal growth experiments together with some properties of the crystals are summarised in table 2.

TABLE 2

Crystal growth data for europium chalcogenides

| | $T_1$ (°C) | $T_2$ (°C) | $\Delta T$ (°C) | $I_2$ (mg/cm³) | (mg/h) | Dimensions of the crystals (mm) |
|---|---|---|---|---|---|---|
| $EuTe+I_2$ | 1722 | 1627 | 95 | 1.35 | 18.6 | 9×8×3 |
| EuTe | 2000 | 1857 | 143 | — | 14.7 | 5×4×2 |
| $EuSe+I_2$ | 1687 | 1619 | 68 | 1.0 | 9.3 | 4×4×3 |
| EuS | 2050 | 1950 | 96 | — | 16 | 2×2×2 |

a) *Sublimation of EuTe*: The crystals were a dark red colour and to some degree transparent. Microscopic examination showed that the crystals had small dark inclusions and mechanical stresses.

b) *Sublimation of EuS*: The colour of the crystals was green. The crystals are not transparent because the absorption edge is at 1.645 eV. Microscopic examination showed that the crystals are homogeneous but have stresses.

c) *Iodine transport of EuTe*: The transport temperatures were chosen to fulfil the following conditions: 1) higher than 1550 °C, in order to avoid reaction of iodine with molybdenum, 2) higher than the boiling point of $EuI_2$ (1580 °C), in order to have high vapor pressure of the transporting agent in the gas phase.

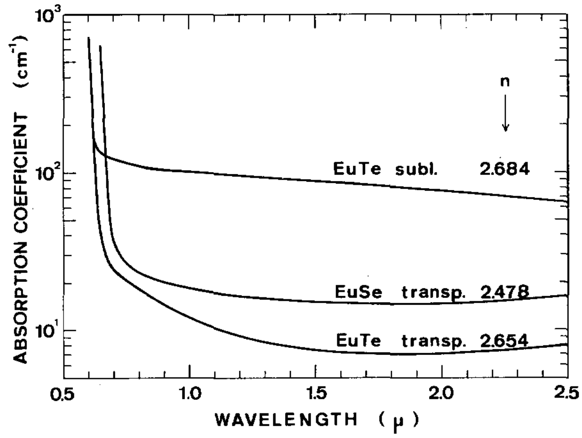

Fig. 2. Optical absorption as a function of the wave length for EuTe (iodine transported and sublimated) and EuSe (iodine transported); $n$ = refractive index.

The EuTe crystals are wine red and transparent. Microscopic investigation with polarised light showed high homogeneity and almost no stresses. This is partly the result of the lower growth temperatures which are only possible with chemical transport.

d) *Iodine transport of EuSe*: Microscopic investigations showed some inclusions of another phase. X-ray diffraction photographs showed this phase to be molybdenum.

## 5. Physical properties of the crystals

For the characterisation of the crystals, optical and magnetic measurements were performed. Fig. 2 shows the optical absorption as a function of the wave length for single crystals of EuTe both transported and sublimated and of transported EuSe. The absorption edges shown by these crystals are the same as the ones given in the literature[7,8,9]). Further they show no appreciable free carrier absorption beyond the absorption edge. The rest absorption and refractive index of transported EuTe are much lower than the one of the sublimated and even lower than any other value mentioned in the literature[10]). The rest absorption of transported EuSe is also much lower than the value previously given in the literature[8]). Therefore, it is clear that the transported crystals are optically pure. A thorough investigation of the refractive indexes as criteria for the purity of these crystals will be given elsewhere[10]).

Three types of magnetic measurements have been performed with iodine transported EuTe crystals. The paramagnetic susceptibility was measured in a field of about 13 kOe between 100 and 300 °K. The effective number of Bohr magnetons per formula unit was found to be 7.65. This is compared to the theoretical value $g(J(J+1))^{\frac{1}{2}} = 7.94$ for the free $Eu^{2+}$ ion with $J = S = \frac{7}{2}$.

Using the method of Busch et al.[11]), the induced ferromagnetic moment of the sample has been determined in a pulsed field. Both experiments show that the number of the effective Bohr magnetons is lower than the theoretical, as it was also previously found[6]). One possible reason is that the crystals used for these measurements had some condensed $EuI_2$ on their surface which hydrolyses in the humidity of the ambient atmosphere to the hygroscopic $EuI_3$. In this case, the formula EuTe used for the calculations was not correct. Another explanation would be the presence of europium, due to the partial decomposition of $EuI_2$ or the incomplete reaction of europium with tellurium.

Under the assumption that part of the europium ions is present as $Eu^{3+}$, it can be calculated from these experiments that the amount of $Eu^{3+}$ is 3–5%.

To determine the ordering temperature, the initial susceptibility $\chi_0$ was measured in an alternating magnetic field of about 10 Oe and 21 c/s. At this small field any increase of the Néel point due to induced ordering is avoided. The susceptibility versus temperature curve (fig. 3) shows a maximum of $d\chi_0/dT$ at $T = 9.58 \pm 0.1$ °K. This result represents a very good experimental confirmation of Fisher's relation[12]), which states that the peak of the specific heat should be located at the same temperature as the maximum slope of the susceptibility.

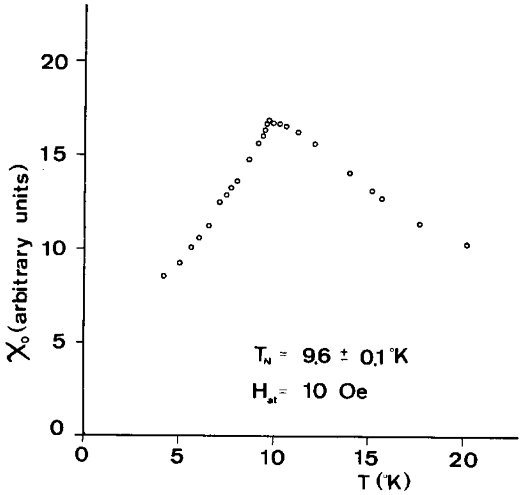

Fig. 3. Initial susceptibility versus temperature curve for iodine transported EuTe.

## 6. Conclusions

Crystal growth of EuTe and EuSe by iodine transport in a closed system can take place at 1700 °C using sealed molybdenum crucibles. A comparison of the physical properties of the transported crystals with values in the literature shows that the transported crystals have better optical properties and similar magnetic ones.

The high temperature transport method described is probably not limited to these compounds but can be used also for other systems at temperatures up to 2000 °C and higher.

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## References

1) M. W. Shafer, J. Appl. Phys. **36** (1965) 1145.
2) P. Schwob and O. Vogt, Phys. Letters **22** (1966) 374; G. Busch, J. Appl. Phys. **38** (1967) 1386.
3) E. Kaldis and R. Widmer, J. Phys. Chem. Solids **26** (1965) 1697.
4) R. F. Rolsten, *Iodide Metals and Metal Iodides* (Wiley, New York, 1961).
5) P. Brinx, S. Hüffner, P. Kienle and D. Quitman, Phys. Letters **13** (1964) 140.
6) G. Busch, P. Junod and O. Vogt, in: *Colloque International du C.N.R.S.* Ed. R. Kern, Sept. 1965 (C.N.R.S., Paris).
7) G. Busch, P. Junod and P. Wachter, Phys. Letters **12** (1964) 11.
8) B. E. Argyle, J. C. Suits and M. J. Freiser, Phys. Rev. Letters **15** (1965) 822.
9) F. Holtzberg, T. R. McGuire and S. Methfessel, J. Appl. Phys. **37** (1966) 976.
10) G. Busch and R. Verrault, to be published.
11) G. Busch, P. Junod, P. Schwob, O. Vogt and F. Hulliger, Phys. Letters **9** (1964) 7.
12) M. E. Fisher, Phil. Mag. **7** (1962) 1731.