

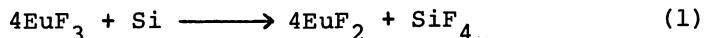
NEW PREPARATION METHOD OF EUROPIUM DIFLUORIDE

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Silicon reduction of EuF_3 to EuF_2 is described. Optimum conditions to prepare EuF_2 are as follows; quantities of Si and heating temperature to reduce 4 mol of EuF_3 are $1.0 \sim 1.05$ mol and $900^\circ \sim 1000^\circ\text{C}$ for 6hr, respectively.

So far europium difluoride, EuF_2 , has been prepared by reduction of trifluoride EuF_3 , with hydrogen¹⁾ or europium metal¹⁾. However, these processes are not so handy because of necessity of high temperature or expensive pure europium metal.

A new reduction process which we should like to propose here comprises using metallic silicon as a reductant instead of hydrogen or europium metal.



There are two main advantages in this process, namely:

- 1) extremely fine and pure metallic silicon powder is easily available, and
- 2) SiF_4 , a product of this reduction, is a gas at room temperature and goes off from the solid product.

Appropriate mixture of silicon powder (99.99%, 200mesh) and europium trifluoride were ground together in a dry box. They were then pressed into pellets and heated in a vacuum furnace (10^{-4} mmHg).

Europium difluoride belongs to a CaF_2 type face centered cubic symmetry and forms an f.c.c. solid solution with EuF_3 over a very limited region.²⁾

The Vegard's law holds for this region and the lattice parameter is a good indicator for composition of this solid solution. Therefore, we measured lattice parameters besides X-ray fluorescence analysis of F/Eu ratio and magnetic susceptibilities for products.

Tables 1,2 and 3 show reduction results.

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Europium trifluoride was prepared by fluorination of Eu_2O_3 with ammonium hydrogen fluoride. Europium trifluoride obtained was then heated at 800°C for 3hr under vacuum in order to remove occluded NH_4F generated from NH_4HF_2 .

X-ray patterns of the products were taken using $\text{CuK}\alpha$ radiation with a graphite monochromater on a Rigaku Denki Diffractometer "Rotaflex".

Table. 1 Reaction results for a mixture of Si and EuF_3 (1:4)

| Temp. °C | Time hr | F/Eu ratio in products by means of | | |
|-------------|------------|------------------------------------|----------------------------|-----------------------|
| | | Lattice constant | Magnetic susceptibility | X-ray fluorescence |
| 700 | 6 | 2.22 | 2.26 | -- |
| | 12 | 2.21 | 2.25 | -- |
| 800 | 3 | 2.10 | 2.14 | -- |
| | 6 | 2.12 | 2.18 | -- |
| 900 | 12 | 2.11 | 2.14 | 2.05 |
| | 3 | 2.10 | 2.09 | 2.17 |
| 1000 | 6 | 2.04 | 1.97 | 2.04 |
| | 12 | 2.01 | 1.99 | 2.11 |
| 1000 | 3 | 2.03 | 1.96 | 2.19 |
| | 6 | 2.04 | 1.90 | 2.11 |

Table. 2 Reduction results for 900°C, 6hr heating

| Amount of Si added to 4 mol of EuF_3 | F/Eu ratio in products by means of | | | Residual Si. (wt.%) |
|---|------------------------------------|----------------------------|-----------------------|------------------------|
| | Lattice constant | Magnetic susceptibility | X-ray fluorescence | |
| 1.0 mol | 2.04 | 2.03 | 2.04 | 0.16 |
| 1.05 | 2.02 | 2.03 | 2.05 | 0.16 |
| 1.1 | 2.02 | 2.00 | 2.07 | 0.25 |
| 1.2 | 2.01 | 2.05 | --- | 0.46 |
| 1.5 | 2.08 | 2.05 | --- | 0.53 |
| 2.0 | 2.08 | --- | --- | --- |

Table. 3 Reduction results for 1000°C, 6hr heating

| Amount of Si added to 4 mol of EuF_3 | F/Eu ratio in products by means of | | | Residual Si. (wt.%) |
|---|------------------------------------|----------------------------|-----------------------|------------------------|
| | Lattice constant | Magnetic susceptibility | X-ray fluorescence | |
| 1.0 mol | 2.04 | 1.90 | 2.11 | 0.53 |
| 1.05 | 2.00 | 1.98 | 2.08 | 0.88 |
| 1.1 | 2.01 | 1.99 | 2.09 | 1.35 |
| 1.2 | 2.01 | 1.95 | 2.07 | 1.70 |

The measurements of magnetic susceptibilities of the samples were performed with a Shimazu Magnetic Balance "MB-11".

The determinations of Eu, F and residual Si were carried out by a Rigaku Denki X-ray fluorescent spectrometer "GF-S" equipped with a lithium fluoride (LiF), a thallium acid phthalate (TAP) and an ethylenediamine d-tartrate (EDDT) analysing crystal, respectively.

References

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