CHEMISTRY LETTERS, pp. 189-190, 1976. Published by the Chemical Society of Japan

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∿1.05 mol and 900°∿1000°C for 6hr, respectively.

So far europium difluoride, EuF_2, has been prepared by reduction of trifluoride EuF_3, with hydrogen[1] or europium metal[1]. 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.

$$4EuF_3 + Si \longrightarrow 4EuF_2 + SiF_4 \qquad (1)$$

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.

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∿1.05 mol and 900°∿1000°C for 6hr, respectively.

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 CuKα 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)

Conditions 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	--
	12	2.11	2.14	2.05
900	3	2.10	2.09	2.17
	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 Lattice constant	Magnetic susceptibility	X-ray fluorescence	Residual Si. (wt.%)
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 Lattice constant	Magnetic susceptibility	X-ray fluorescence	Residual Si. (wt.%)
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" equiped with a lithium fluoride (LiF), a thallium acid phthalate (TAP) and an ethylenediamine d-tartrate (EDDT) analysing crystal, respectively.

References

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(Received December 1, 1975)