

## PHASE DIAGRAM OF THE SYSTEM $\text{EuF}_2\text{--GdF}_3$ IN THE SOLIDUS–LIQUIDUS REGION

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### ABSTRACT

The phase diagram of the system  $\text{EuF}_2\text{--GdF}_3$  was studied in the solidus–liquidus region by differential thermal analysis and X-ray powder diffraction on quenched samples at room temperature. The phase diagram is eutectic with two extended solid solutions related to the cubic fluorite and hexagonal tysonite structure types, respectively. The eutectic coordinates are  $1532 \pm 6$  K and  $63 \pm 1$  mol%  $\text{GdF}_3$ . The melting curves of the solid solutions show maxima at  $1744 \pm 6$  K for  $\text{Eu}_{0.83}\text{Gd}_{0.17}\text{F}_{2.17}$  and  $1561 \pm 6$  K for  $\text{Gd}_{0.82}\text{Eu}_{0.18}\text{F}_{2.82}$ .

### INTRODUCTION

Binary systems  $\text{MF}_2\text{--LnF}_3$  ( $M = \text{Ca, Sr, Ba}$ ;  $\text{Ln} = \text{La, Lu, Y}$ ) have been studied extensively because of their interesting structural and thermal properties and their potential applications [1]. Among the various factors, which determine the properties of these systems at elevated temperatures, the ability of the fluorite and tysonite structures for heterovalent isomorphous substitution of the cations is rather dominant, and many of the nonstoichiometric fluorite- and tysonite-related phases of the type  $\text{M}_{1-x}\text{Ln}_x\text{F}_{2+x}$  and  $\text{Ln}_{1-y}\text{M}_y\text{F}_{3-y}$ , respectively, display the phenomenon of temperature maxima of the fusion curves [2–5]. Because of the close similarity of the ionic radii of  $\text{Sr}^{2+}$  and  $\text{Eu}^{2+}$ , almost equal crystallographic and very similar thermochemical properties of the predominantly ionic compounds of these elements are commonly observed [6,7]. Obviously, the melting behaviour of systems  $\text{MF}_2\text{--LnF}_3$  ( $M = \text{Eu}$ ) has not been investigated so far. One of the reasons for this situation may be that  $\text{EuF}_2$  is very reactive against most refractory and high-melting metallic container materials. As Petzel and Greis [8] and, recently, Petzel [9] were able to show, only graphite withstands the chemical attack of solid and, if prolonged contact is avoided, also of liquid  $\text{EuF}_2$ . In this work the results of a determination of the phase diagram of  $\text{EuF}_2\text{--GdF}_3$  by differential thermal analysis in the temperature region above  $1200^\circ\text{C}$  are reported. This system was chosen because precise crystallographic data on

the solid solutions  $Gd_{1-y}Eu_yF_{3-y}$  [10] and on the fusibility curves of the probably similar system  $SrF_2-GdF_3$  [2] are already available.

## EXPERIMENTAL

### *Substances, preparation and characterization*

The preparation of  $GdF_3$  and  $EuF_3$  (the latter serving as an intermediate compound for the preparation of  $EuF_{2.0}$ ) was carried out by dissolution of the sesquioxides (99.99% purity, Auer-Remy) in hydrochloric acid, precipitation of the hydrated fluorides with hydrofluoric acid and subsequent dehydration under a gas stream of dry  $HF/N_2$  [6,10].  $EuF_3$  was reduced with hydrogen to yield stoichiometric  $EuF_{2.0}$  [8]. The compounds were characterized by their X-ray powder diffraction patterns (Guinier technique,  $CuK\alpha_1$  radiation, Si with  $a = 543.04$  pm as internal calibration standard), and the lattice parameters were calculated by the computer program LSUCRE [11]. For a quantitative analysis of the starting materials the fluorides were pyrohydrolyzed in steam at  $1100^\circ C$  and the metal content was determined gravimetrically by weighing of the sesquioxide residues. The analytical and X-ray results are summarized in Table 1. These results, and the fact that the Guinier patterns did not show any reflections other than those attributable to the phases in question and that the lattice parameters were in very good agreement with precision data from ref. 6, allowed the conclusion that the starting materials were of well-defined composition and of satisfactory purity.

### *Differential thermal analysis, apparatus and procedures*

The experiments were performed in a Netzsch STA 429 apparatus for simultaneous DTA and TG. The DTA crucibles with tightly fitting lids were

TABLE 1  
Analytical and X-ray diffraction data of  $EuF_{2.0}$  and  $GdF_3$

Analytical data for Ln (mass %)		Lattice parameters (pm)	
Found	Theor.	Found	Lit. [6]
<i>GdF<sub>3</sub></i>			
$73.4 \pm 0.1$	73.392	$a = 657.09$	$a = 656.84$
		$b = 698.47$	$b = 698.30$
		$c = 439.22$	$c = 439.11$
<i>EuF<sub>2.0</sub></i>			
$80.0 \pm 0.1$	79.996	$a = 584.30$	$a = 584.23$

machined from high-density graphite and were outgassed at 1100°C in high vacuum prior to their use. Heating and cooling were performed at a rate of 5 K min<sup>-1</sup> in a stream of purified argon with a flow rate of 3.5 l h<sup>-1</sup>. Corundum powder, also contained in a graphite crucible, was used as inert material. Carefully mixed samples of 200–300 mg were used for each experiment, and new crucibles were used in most cases in order to avoid cross contaminations. By separate weighing of the samples and the empty crucibles after the experiments, it was found that the weight losses of the samples were ≤ 1% in all cases and could, hence, be considered as negligible. The weight loss effect of the crucibles was more pronounced and was attributed to reactions with residual traces of oxygen and to humidity; thus, the crucibles served as effective “chemical shields” preventing significant oxidation and/or hydrolysis of the samples by the trace amounts of practically unavoidable impurities of the furnace atmosphere. The differential temperature was measured with Pt–Pt/Rh thermocouples, which were protected against contact with the graphite crucibles by miniature platinum caps. Temperature calibration was carried out by measurement of the melting points of CaF<sub>2</sub> (1691 ± 5 K [12]) and GdF<sub>3</sub> (1505 K [13]). Since undercooling effects were generally observed, only DTA signals obtained on heating could be considered for the data evaluation. Solidus, eutectic and congruent melting temperatures were evaluated by determining the extrapolated peak onsets [14]. Liquidus temperatures were found according to the procedure outlined by Gäumann [15] and Gäumann and Oswald [16]. The accuracy of the temperature results is ± 6 K. Guinier powder patterns of all residues were taken at room temperature, and the lattice parameters of the phases present were determined in most cases.

## RESULTS AND DISCUSSION

The phase diagram for the temperature range 1500–1800 K is presented in Fig. 1, and the experimental results are listed in Table 2. The system is of a eutectic type with  $T_{\text{eut}} = 1532 \pm 6$  K, characterized by two extended solid solution ranges related to the cubic fluorite and hexagonal tysonite structures. The melting curves of both solid solutions show distinct maxima at  $1744 \pm 6$  and  $1561 \pm 6$  K, respectively. The related thermal and compositional data are summarized in Table 3, which also contains the respective data of the systems CaF<sub>2</sub>–GdF<sub>3</sub> [17] and SrF<sub>2</sub>–GdF<sub>3</sub> [2]. It is noteworthy that the systems with M = Ca, Sr, Eu show a very similar thermal behaviour, especially at the GdF<sub>3</sub>-rich side. Since the cooling rate of the DTA experiments was too high for any phase ordering to occur in the subsolidus region within the composition range 20–45 mol% GdF<sub>3</sub> [18], the X-ray diffraction results of our work can be considered only as approximately representative for the high temperature phase relations. As shown in Fig. 2, the lattice

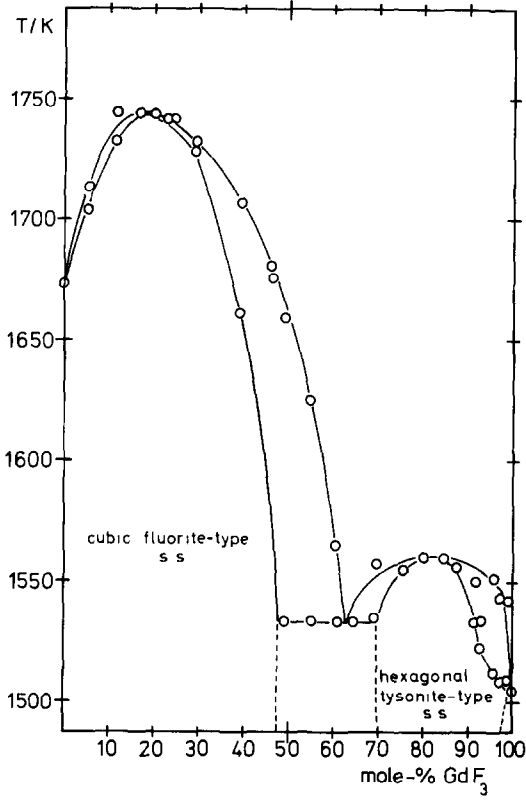


Fig. 1. Phase diagram of the system EuF<sub>2</sub>-GdF<sub>3</sub>.

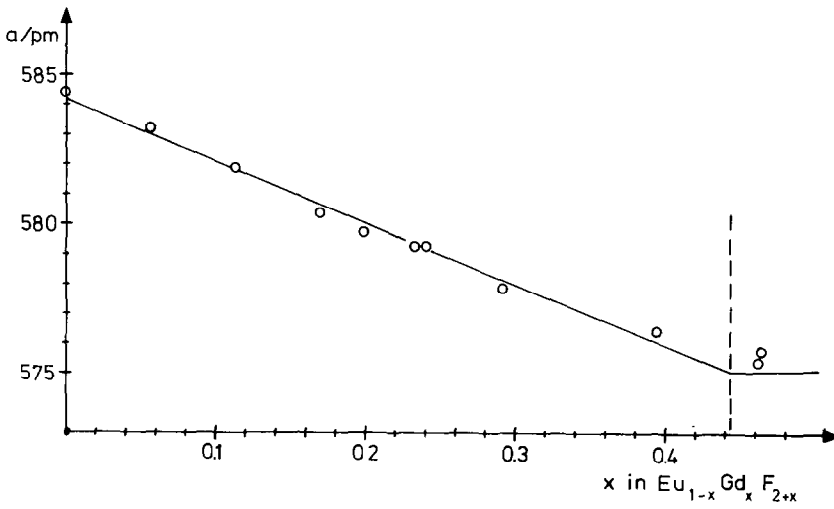


Fig. 2. Variation of lattice parameters of cubic solid solutions Eu<sub>1-x</sub>Gd<sub>x</sub>F<sub>2+x</sub> as a function of GdF<sub>3</sub> content.

TABLE 2

Melting and structural data for different compositions in the system  $\text{EuF}_2\text{-GdF}_3$ 

No.	Composition (mol% $\text{GdF}_3$ )	Temperature (K) <sup>a</sup>		Phases <sup>b</sup>	Lattice parameters (pm)		
		solidus	liquidus		<u>a</u>	<u>b</u>	<u>c</u>
1	0	–	1674	<u>A</u>	584.4	–	–
2	5.6	1704	1713	<u>A</u>	583.2	–	–
3	11.3	1732	1744	<u>A</u>	581.9	–	–
4	16.9	1743	–	<u>A</u>	580.4	–	–
5	19.8	1744	–	<u>A</u>	579.8	–	–
6	23.3	1742	–	<u>A</u>	579.3	–	–
7	24.1	1742	–	<u>A</u>	579.3	–	–
8	29.1	1728	(1731)	<u>A</u>	578.4	–	–
9	39.4	(1661)	1707	<u>A</u>	576.9	–	–
10	46.2	–	1681	<u>A</u>	575.4	–	–
11	46.4	–	1676	<u>A</u>	575.8	–	–
12	49.1	1533 <sup>c</sup>	1660	<u>A,B</u>	–	–	–
13	54.9	1533 <sup>c</sup>	1625	<u>A,B</u>	574.7	–	–
14	60.7	1532 <sup>c</sup>	(1565)	<u>A,B</u>	–	–	–
15	64.6	1532 <sup>c</sup>	–	<u>A,B</u>	697.0	–	714.9
16	69.5	1535 <sup>c</sup>	(1557)	<u>A,B</u>	–	–	–
17	75.3	1555	–	<u>B</u>	696.1	–	714.3
18	80.0	1560	–	<u>B</u>	695.3	–	713.7
19	84.8	1560	–	<u>B</u>	693.6	–	711.4
20	87.2	1556	–	<u>B</u>	692.6	–	710.4
21	91.7	1533	(1550)	<u>B,(C)</u>	–	–	–
22	92.5	1523	1534	<u>B,(C)</u>	–	–	–
23	95.7	1513	1551	<u>C</u>	661.9	701.9	435.4
24	97.6	1509	1544	<u>C</u>	–	–	–
25	98.6	1509	–	<u>C</u>	658.4	699.1	438.6
26	99.2	1507	1542	<u>C</u>	–	–	–
27	100.0	–	1505	<u>C</u>	657.5	698.6	439.0

<sup>a</sup> Data in parentheses are uncertain.<sup>b</sup> Observed in Guinier patterns: A = cubic (fluorite-type, ss) B = hexagonal ( $\alpha$ - $\text{GdF}_3$ -type, ss); C = orthorhombic ( $\beta$ - $\text{GdF}_3$ -type, ss); lattice parameters refer to underlined symbol.<sup>c</sup> Eutectic.

parameter of the cubic phase decreases linearly with increasing content of  $\text{GdF}_3$  and thus obeys Vegard's rule. Beside the broad homogeneity range of the hexagonal tysonite-type phase a narrow but definite orthorhombic solid solution range could be detected. The lattice parameter data of both types of solid solution were found to be in good agreement with results from a previous phase study of this system [10]. The orthorhombic–hexagonal phase transition of pure  $\text{GdF}_3$  was found by DTA at  $1341 \pm 5$  K (1348 K, ref. 13;  $1338 \pm 10$  K, ref. 19). It could not, however, be detected by this technique for any of the solid solutions investigated in this study.

The congruent melting behaviour of fluorite- and tysonite-type solid

TABLE 3

Melting and eutectic data of systems  $\text{MF}_2\text{-GdF}_3$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Eu}$ )

M	Data of melting curve maxima				Eutectic data		
	$T$ (K)	Composition <sup>a</sup>	$T$ (K)	Composition <sup>b</sup>	$T$ (K)	mol% $\text{GdF}_3$	Ref.
Eu	$1744 \pm 6$	$0.17 \pm 0.01$	$1561 \pm 6$	$0.18 \pm 0.01$	$1532 \pm 6$	$63 \pm 1$	this work
Sr	$1773 \pm 10$ <sup>c</sup>	$0.17 \pm 0.01$ <sup>c</sup>	1561	0.17	1533	63	2
Ca	$1701 \pm 10$	0.05	$1555 \pm 5$	0.15	$1506 \pm 5$	60	17

<sup>a</sup>  $x$  in  $\text{Eu}_{1-x}\text{Gd}_x\text{F}_{2+x}$  (fluorite-type solid solution).<sup>b</sup>  $y$  in  $\text{Gd}_{1-y}\text{Eu}_y\text{F}_{3-y}$  (tysonite-type solid solution).<sup>c</sup> Limits of accuracy estimated, because data had to be taken from graphical representations in ref. 2.

solutions occurring in many of these systems is a most interesting feature, which deserves a thorough discussion from the thermodynamic point of view.

The state of order and the kind of binding forces in a solid compound generally determine its entropy of fusion. Hence, within a group of compounds of practically equal bonding type, e.g., alloys composed of typically metallic elements, differences in the entropies of fusion should predomi-

TABLE 4

Entropies of fusion of the alkaline earth and rare earth fluorides

Compound	$T_m$ (K)	$\overline{\Delta S_m^0}$ $\text{J (mole of ion)}^{-1} \text{K}^{-1}$	Structure type at melting point
$\text{CaF}_2$	1689	5.86	fluorite
$\text{SrF}_2$	1750	5.65	
$\text{BaF}_2$	1641	4.74	
$\text{EuF}_2$	1670	5.83	
$\text{LaF}_3$	1777	7.06	tysonite
$\text{CeF}_3$	1705	8.59	
$\text{PrF}_3$	1672	8.57	
$\text{NdF}_3$	1646	8.32	
$\text{SmF}_3$	1577	8.29	
$\text{EuF}_3$	1549	(7.76)	
$\text{GdF}_3$	1502	8.70	
$\text{TbF}_3$	1445	10.14	$\beta\text{-YF}_3$
$\text{DyF}_3$	1426	10.27	
$\text{HoF}_3$	1415	9.98	
$\text{ErF}_3$	1414	4.88	$\alpha\text{-YF}_3$
$\text{TmF}_3$	1431	5.05	
$\text{YbF}_3$	1431	5.19	
$\text{LuF}_3$	1455	5.17	

nantly reflect differences of the state of order [20]. It is reasonable to assume that the fluorides of the alkaline earth and the rare earth elements form a group of compounds of very similar ionic character with only minor contributions of covalent bonding. From the examples given in Table 4 it is obvious that significant differences in the average entropy of fusion per mole of ion exist for this group. These differences mainly reflect the state of order of the anion sublattices, which is lowest for the fluorite-type difluorides with  $M = \text{Ca, Sr, Ba, Eu}$ , and for the  $\alpha\text{-YF}_3$ -type trifluorides, intermediate for the tysonite-type trifluorides and highest for the trifluorides with the  $\beta\text{-YF}_3$  structure.

With respect to the cubic pseudo-binary solid solution systems of the type  $M_{1-x}\text{Ln}_x\text{F}_{2+x}$ , no enthalpies or entropies of fusion have been experimentally determined so far. The question arises of whether the melting point

TABLE 5

Calculated average entropies of fusion for cubic solid solutions of the type  $M_{1-x}\text{Ln}_x\text{F}_{2+x}$  at the compositions of melting curve maxima

M	Ln	$x$ in $M_{1-x}\text{Ln}_x\text{F}_{2+x}$	$T_m$ (K)	$\overline{\Delta S_m^0}$ (calc.) $\text{J (mole of ion)}^{-1} \text{K}^{-1}$	Ref.
Eu	Gd	0.20	1744	5.96	this work
	—	0.0	1670	5.83	9
Ca	Sm	0.05	1701	5.91	3
	Gd	0.05	1701	5.91	
	Tb	0.04	1693	5.96	
	Ho	0.10	1697	6.08	
	—	0.0	1689	5.86	21
Sr	La	0.31	1852	5.78	2
	Ce	0.30	1820	6.22	
	Pr	0.27	1805	6.14	
	Nd	0.26	1799	6.05	
	Sm	0.21	1791	5.89	
	Gd	0.17	1773	5.88	
	Tb	0.13	1767	5.95	
	Dy	0.11	1765	5.90	
	Ho	0.09	1742	5.90	
—	0.0	1750	5.65	21	
Ba	La	0.31	1761	5.26	5
	Ce	0.27	1721	5.60	
	Pr	0.25	1706	5.52	
	Nd	0.21	1688	5.35	
	Sm	0.14	1651	5.16	
	Gd	0.09	1637	5.04	
	Tb	0.03	1635	4.89	
	—	0.0	1641	4.74	21

maxima typical of many of these systems at seemingly irrational compositions [2–5,17] have to be interpreted as points of increased thermal stability due to a special ordering of lattice defects. In this case the average entropies of fusion per mole of ion should be at least higher than the respective values for the cubic solvent,  $\text{MF}_2$ , and could even be higher than average hypothetical “mixed” values which can be calculated for these compositions from the enthalpy of fusion data of the pure solvents,  $\text{MF}_2$  [21], and the solutes,  $\text{LnF}_3$  [1], and the equilibrium temperatures of the melting point maxima. These calculated hypothetical entropies of fusion for the congruently melting compositions are summarized in Table 5. It is worth emphasizing that the hypothetical data do not vary much for a group of solid solutions with equal M and varying Ln, despite significant variations of  $x$  and  $T_m$ . This observation allows the conclusion that some common degree of order can probably be related to all compositions of these solutions, which are characterized by melting point maxima. A calorimetric determination of the actual enthalpies and entropies of fusion should therefore be an important step on the way to a better understanding of the state of order in these solid solutions.

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