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POLYMORPHISM OF HIGH-PURITY RARE EARTH TRIFLUORIDES

O. GREIS and M.S.R. CADER

Department of Chemistry, University of Petroleum and Minerals, Dhahran 31261 (Saudi Arabia)

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ABSTRACT

Polymorphism and melting behavior of high-purity rare earth trifluorides have been studied by differential thermal analysis. Modified sample holders were used to increase the sensitivity of temperature measurements. Melting points and solid–solid transitions are reported as well as the stability fields of the different modifications with space groups $P\bar{3}c1$, $P6_3/mmc$, $Pnma$, and $P\bar{3}m1$. For the first time, the order–disorder transition $P\bar{3}c1 \leftrightarrow P6_3/mmc$ for tysonite-type rare earth trifluorides was detected by differential thermal analysis.

INTRODUCTION

In the last thirty years, anhydrous rare earth trifluorides have attracted considerable interest due to their importance as key substances for lanthanide chemistry and to their applications in many technologies. Recently, the chemistry of rare earth fluorides in general has been reviewed by Greis and Haschke [1]. The major difficulty in the preparation of anhydrous rare earth trifluorides is the elimination of water and oxygen. After high-temperature treatment, any such impurities that have not been removed result in the formation of oxidefluorides of the general formula RO_xF_{3-2x}, accompanied by remarkable changes in the crystal chemistry of the parent compounds. Thus, melting points and solid–solid transition temperatures are significantly influenced, as is the polymorphism [2–9]. Thoma and Brunton [2] were the first to study the polymorphism of rare earth trifluorides systematically. They found that the high-temperature form of each of the substances from SmF_3 to HoF_3 had a tysonite-type structure, while that of ErF_3 to LuF_3 is isostructural with α-YF_3. Several subsequent papers [5–9], however, proved that the substances used by Thoma and Brunton [2] were more or less contaminated with oxidefluorides. In contrast, oxidefluoride-free TbF_3, DyF_3, and HoF_3 were found to be monomorphic, retaining their orthorhombic room-temperature modification up to their melting points. There are only two research groups which studied the polymorphism and melting behavior

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of pure rare earth trifluorides systematically, Spedding et al. [3,4] and Sobolev et al. [8,9]. Therefore, only their data are suitable for systematic comparison, while earlier literature data cited by Sobolev et al. [8] display large discrepancies.

Since about 1970, we have also been involved in research on rare earth fluorides and have developed preparation techniques to yield water- and oxygen-free rare earth trifluorides of high purity [1,10–12]. In this paper, we present the results of differential thermal analyses of such substances and compare the results on melting behavior and polymorphism with those found in previous studies.

EXPERIMENTAL

Anhydrous rare earth trifluorides were prepared from the corresponding sesquioxides and, in the case of CeF_3 and PrF_3, from $Ce(NO_3)_3 \cdot 6\ H_2O$ and Pr_6O_{11}, respectively. All starting materials had a purity better than 99.95%. First, the reactants were dissolved in HCl/HNO_3 and hydrated trifluorides were precipitated with hydrofluoric acid (wet method). The dehydration was then carried out under a stream of HF/N_2 at temperatures gradually raised to about 1000 K (dry method). Further details on the preparation are described by Greis and Petzel [10], Greis [11], and in the Brauer-Handbook [12]. Chemical analyses of the products, with respect to both metal and fluorine content [10,11], proved that the anhydrous rare earth trifluorides were indeed of high purity with typical formulae $RF_{3.000 \pm 0.005}$. This indicates that no detectable contamination with oxidefluorides had occurred.

Differential thermal analyses (DTA) were carried out on a DuPont 990 thermal analyzer using their 1600°C high-temperature cell. The original sample holders were modified. The platinum macro-cups were slit twice vertically in such a way that sealed platinum tubes with a length of about 8 mm could be accommodated horizontally just touching the Pt–Pt/13% Rh thermocouples. Thus, a very sensitive measurement of the sample temperature was guaranteed. About 50 mg of rare earth trifluoride were sealed in these platinum tubes to protect them against vaporization and oxygen contamination at high temperatures. Aluminum oxide, also sealed in a platinum tube, served as the reference material. The instrument was calibrated against sodium sulfate (t.p. 510 K), quartz (t.p. 846 K), gold (m.p. 1336 K), and calcium difluoride (m.p. 1691 K). First-order transition temperatures for melting, freezing, and solid–solid transitions were evaluated graphically from their peaks using the so-called onset technique [13]. The accuracy of these temperature determinations is ±8 K with a reproducibility for the individual measurements of ±2 K. Second-order transition temperatures were taken to be those indicated by the first deviation from the baseline and by the peak

TABLE 1

Phase transitions of high-purity rare earth trifluorides from DTA heating runs (10 K min^{-1})

RF_3	Melting points (K)			1st-order transitions (K)			2nd-order transitions (K)	
	This work [a]	Spedding et al. [3,4]	Sobolev et al. [9]	This work [a]	Spedding et al. [3,4]	Sobolev et al. [9]	Beginning [b]	Maximum [c]
LaF_3	1773	1766	1773				1075	1650
CeF_3	1709	1705	1716				~1000	1380
PrF_3	1674	1672	1677				~1000	1340
NdF_3	1651	1650	1645				~1000	1280
PmF_3	(1617)	—	—					(1280)
SmF_3	1582	1573	1577	753	763	743	~1000	1280
EuF_3	1531	—	—	1125	920	—	~1150	1375
GdF_3	1508	1505	1501	1338	1348	1343	?	?
TbF_3	1455	1450	1439					
DyF_3	1433	1430	1420					
HoF_3	1420	1416	1413					
ErF_3	1420	1419	1407	1392	1390	1377		
YF_3	1435	1428	1425	1355	1350	1343		
TmF_3	1431	1431	1432	1322	1326	1320		
YbF_3	1445	1435	1428	1259	1259	1251		
LuF_3	1453	1457	1455	1216	1230	1236		

[a] $\Delta T = \pm 8$ K.

[b] $\Delta T = \pm 50$ K.

[c] $\Delta T = \pm 25$ K.

maximum ("beginning" and "maximum" in Table 1). The accuracy of these temperature values is naturally less and is estimated as ±50 K for the beginning and ±25 K for the maximum, though their reproducibility is within ±10 K for individual measurements. All heating and cooling runs down to about 700 K were programmed with a rate of ±10 K min^{-1}.

RESULTS AND DISCUSSION

First, we studied the reproducibility of solid–solid transitions and supercooling effects. Some rare earth trifluorides, such as LaF_3, DyF_3, HoF_3, YbF_3, and LuF_3, showed temperature differences as large as 20–150 K between melting and freezing points. Some of the other trifluorides also supercooled somewhat. Similar supercooling effects were observed for solid–solid first-order transitions. Therefore, we report here only data from heating runs (see Table 1 and Fig. 1). The melting points are compared in Table 1 with the results from Spedding et al. [3,4] and Sobolev et al. [9]. The data all agree very well within ±12 K. Our data match those from Spedding et al. [3,4] more closely, though their values average systematically about 4 K lower than ours. Our results also agree with those of the Spedding group as

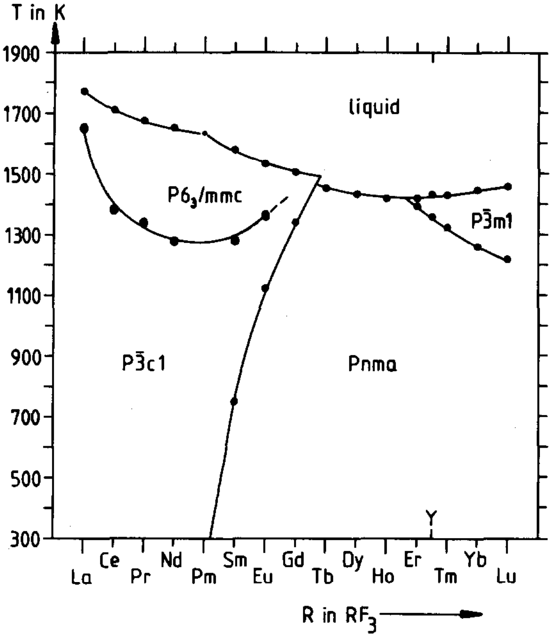

Fig. 1. Stability regions for the different phases of high-purity rare earth trifluorides.

far as first-order transitions are concerned, our 1125 K for EuF_3 against their 920 K [4] being the only exception. No first-order transition has been observed for TbF_3, DyF_3, and HoF_3. Up to this point, our findings well support the results from Spedding et al. [3,4] and Sobolev et al. [8,9].

There is, however, one significant difference between our results and all others. We found for the first time a pronounced second-order or λ-transition within the stability field of the tysonite structure. This effect is strongest in the case of LaF_3. Two heating runs, I and II, recorded with ΔT ranges differing by a factor of ten, are displayed in Fig. 2. At about 1075 K, the first departure from the baseline can be observed, while the maximum at the peak is at 1650 K. Generally, this second-order transition becomes even more pronounced if the heating rates are increased to 20 or 50 K min^{-1}. Similar but weaker and weaker effects were observed as one progresses from CeF_3 to EuF_3. In the case of GdF_3, the two first-order transitions at 1338 and 1508 K are already so close to each other that one cannot judge on the possible presence of this λ-transition between them.

Our results are not unexpected in the light of more recent publications on the structure of LaF_3 [14] and on fast ionic conductivity of tysonite-type rare earth trifluorides at higher temperatures [15–18]. Numerous papers exist on the structure of tysonite and it is difficult to believe that all the contradictory results for unit cell size, space group, and actual atomic structure are just the results of erroneous structure determinations (see also ref. 1, p. 392).

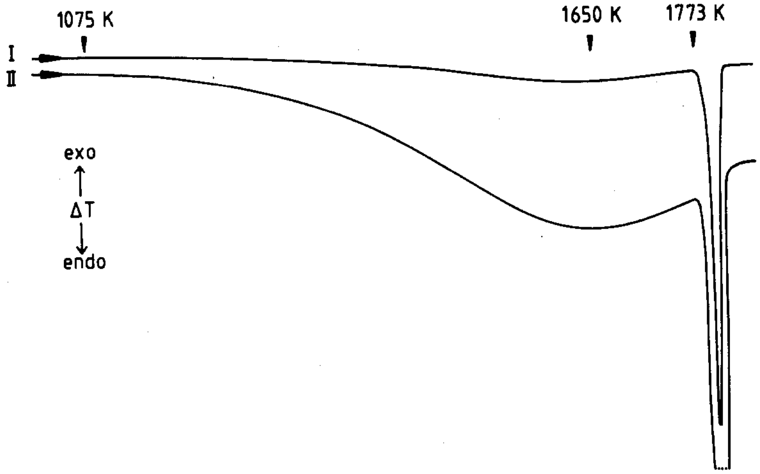

Fig. 2. First- and second-order transitions of LaF_3 recorded with ΔT ranges differing by a factor of ten (I and II).

Undoubtedly, well-annealed LaF_3 to NdF_3 crystallize at room-temperature in a highly ordered structure with the space group $P\bar{3}c1$ and with a superstructure unit cell with $Z = 6$ [19–22]. In many other structural investigations a smaller unit cell with $Z = 2$ and space group $P6_3/mmc$ was found, the so-called Schlyter-structure [23]. Recently, Greis and Bevan [14] showed, in an electron diffraction study of high-purity LaF_3 single crystals, that both structures actually exist in the same sample. Obviously, at lower temperatures the highly ordered superstructure ($P\bar{3}c1$, $Z = 6$) dominates, while the anion-disordered basis structure ($P6_3/mmc$, $Z = 2$) becomes more and more important at higher temperatures. X-ray powder diffraction patterns from well-annealed LaF_3 to NdF_3 also show superstructure reflections, but not substances quenched from 1500 K. Somewhere between the stability regions of these two structure types there occurs a gradual order–disorder transition, also indicated by a substantial increase in fast fluorine anionic conductivity [15–18]. Now, in this paper, further evidence has been found for this second-order transition using differential thermal analysis. This allows us to draw the thermal boundary between both structure types as indicated in Fig. 1 by the maxima of the λ-transitions, though the beginnings of these disorder phenomena already occur at about 1000 K.

The stability field of phases isostructural to α-YF_3 is indicated in Fig. 1 by the space group $P\bar{3}m1$, which is also the space group of the parent or basis structure of the isostructural α-UO_3. The actual atomic structure of α-UO_3 is rather complicated and obviously several superstructures exist. All of these structures are related to the same basis structure with $a = 3.950$ Å, $c = 4.157$ Å, $Z = 1$, $P\bar{3}m1$ [24,25]. Until the structural details of the α-YF_3 type are available, we prefer a description of this high-temperature form in the basis cell with space group $P\bar{3}m1$.

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