Polymorphism in tripotassium lanthanate hexafluorides (Ln = Sm, Eu, Gd, Tb and Er)

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Abstract

The interconversion of different polymorphs of tripotassium lanthanate hexafluoride has been investigated by differential thermal analysis (DTA), dilatometry and powder X-ray diffraction (XRD).

Keywords: DTA; Dilatometry; K_3LnF_6; Polymorphism

1. Introduction

Potassium fluoride is known to react with most rare earth trifluorides at about 700°C and the product formed has the composition K_3LnF_6 [1–7]. By different heat treatments, different polymorphs are produced. Some of these are known to exist in three crystallographic modifications, the α, β and Γ phases. Only tripotassium erbium hexafluoride is reported [7] to have a δ modification. Recently the δ phase of a few more of these compounds has been synthesised [8] by solid state reaction between Ln_2O_3 (Ln = Dy–Lu) and KHF_2. Information to date on polymorphism in these compounds is summarised in Table 1.

In most of these cases, polymorphism was studied using high temperature XRD, but thermal studies have not been carried out. Hence DTA with thermal cycling and dilatometric studies of these compounds have been performed.

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Table 1
Polymorphism reported in K_3LnF_6 compounds

| Sample | Ln | Polymorphs | | | | Ref. |
		α	β	Γ	δ	
1	Sm	Monoclinic (28°C)	–	–	–	[2]
2	Eu	–	–	–	–	–
3	Gd	– (28–495°C)	– (above 495)	–	–	[3]
4	Tb	Orthorhombic (28–315°C)	Tetragonal (315–425°C)	Cubic (above 425°C)	Orthorhombic (28°C)	[4,8]
5	Ho	Orthorhombic (28°C)	Tetragonal (285–400°C)	Cubic (above 400°C)	Orthorhombic (28°C)	[6,8]
6	Er	Monoclinic (28°C)	Tetragonal (at 395°C)	Cubic	Orthorhombic (28°C)	[5,7,8]

2. Experimental

In the present method, K_3LnF_6 with Ln = Sm, Eu, Gd, Tb and Er have been prepared by fusion of mixtures of KHF_2 with the appropriate Ln_2O_3 in a 1:6 molar ratio in a platinum boat at 226°C for 5–8 h. In order to produce a homogeneous, material, the product was twice reground and annealed. All the products were moisture-sensitive and were stored in a desiccator. The rare earth sesquioxides used were preheated to 700°C for 10–15 h. Potassium hydrogen fluoride was AR grade reagent. In most cases powder XRD patterns of the products matched those in the literature. (ref) Since the powder XRD pattern of K_3EuF_6 is not reported, it is given, along with its assignment to an orthorhombic unit cell in Table 2.

Table 2
XRD powder pattern of K_3EuF_6

d/Å	I/I_0	h	k	l
5.642	59	1	1	0
5.406	36	2	0	0
3.663	28	2	1	1
3.312	32	0	2	0
3.163	69	3	1	0
3.090	100	1	1	2
3.048	59	2	0	1
2.909	28	1	2	1
2.239	42	2	0	3
2.183	32	4	0	2
2.120	28	4	2	0
1.969	25	2	3	1
1.852	28	0	0	4

Orthorhombic: $a_0 = 10.835$ Å $b_0 = 6.617$ Å $c_0 = 7.375$ Å

3. Results and discussion

DTA scans of the fluoro complexes prepared in the present study are given in Figs. 1–5. All these complexes exhibit an irreversible endotherm at $100\,°C$ due to water removal. In the discussion that follows, this endotherm has not been taken into account.

The DTA scan of K_3SmF_6 (Fig. 1) shows three endotherms at 538, 664 and $720\,°C$. Thermal cycling was carried out between these temperatures and the endotherms were found to be reversible. The room temperature phase was taken to be the α phase as its powder XRD agrees with that reported for α-potassium samarium hexafluoride [4]. It changes to the β phase at $538\,°C$, and this transforms at $664\,°C$ into the Γ phase which melts at $720\,°C$, i.e.

$$\alpha \xrightarrow{\;538\,°C\;} \beta \xrightarrow{\;664\,°C\;} \Gamma \xrightarrow{\;720\,°C\;} \text{Melt}$$
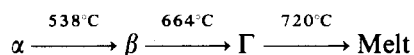
The DTA scans of K_3EuF_6 are shown in Fig. 2. From powder XRD it was inferred that the room temperature phase was the α, and it changed into the Γ phase at $476\,°C$ on first heating. On first cooling, a composite exotherm with a sharp peak at $256\,°C$ was observed, and on subsequent heating, the α to β transition peak at $270\,°C$ was stronger than that due to β to Γ transition. This indicated that the Γ phase was supercooled to $256\,°C$ at which temperature the β to α transition occurred. Finally, the compound melts at $685\,°C$. Hence the following scheme of transitions is proposed for this
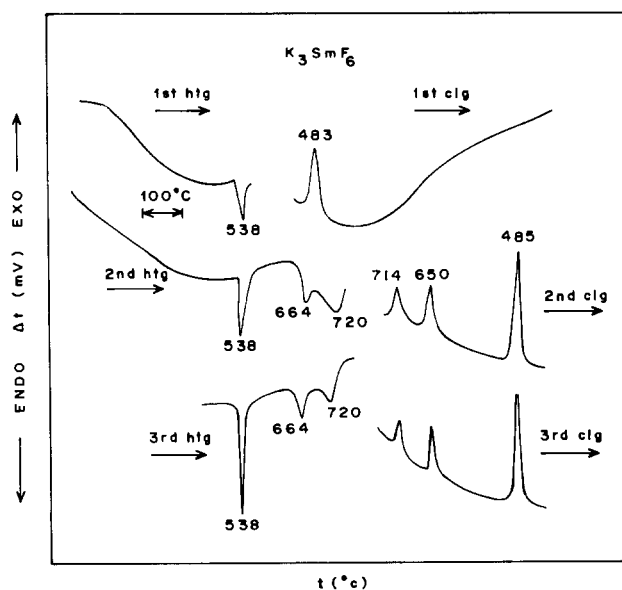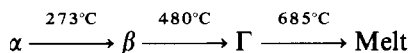

Fig. 1. Thermal cycling through different phase transitions in DTA of K_3SmF_6.

compound.

$$\alpha \xrightarrow{\quad 273^{\circ}C \quad} \beta \xrightarrow{\quad 480^{\circ}C \quad} \Gamma \xrightarrow{\quad 685^{\circ}C \quad} \text{Melt}$$

The DTA scan of K_3GdF_6 (Fig. 3) shows a broad endotherm with an overlapping sharp endotherm at 496°C. On cooling both the endotherms were well separated. The compound melts at 708°C. The α (room temperature) phase converts to β at 496°C and melts without going through Γ. These results are in agreement with high temperature XRD data [3].

$$\alpha \xrightarrow{\quad 496^{\circ}C \quad} \beta \xrightarrow{\quad 708^{\circ}C \quad} \text{Melt}$$
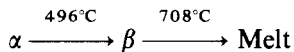
The indexed XRD powder patterns for the α and β phases only of K_3GdF_6 are available in the literature [3]. The XRD powder pattern of the α phase could be fitted to an orthorhombic unit cell with $a_0 = 10.814$ Å, $b_0 = 6.614$ Å and $c_0 = 7.386$ Å and the β phase gave a good fit to a tetragonal unit cell with $a_0 = 6.5324$ and $c_0 = 9.2922$ Å.

All three compounds, after melting, reverted to the α phase on cooling to room temperature.

K_3TbF_6 prepared from KHF_2 showed an XRD pattern close to that of the α phase reported by Dorniva et al. [4]. Despite this, the unit cell dimensions obtained were more in line with those of a δ phase of other compounds in this series. Wani and Rao [8] preferred to designate this compound as the δ phase. DTA was used to resolve this impasse. The DTA scans of this compound are shown in Fig. 4. The sample was stored
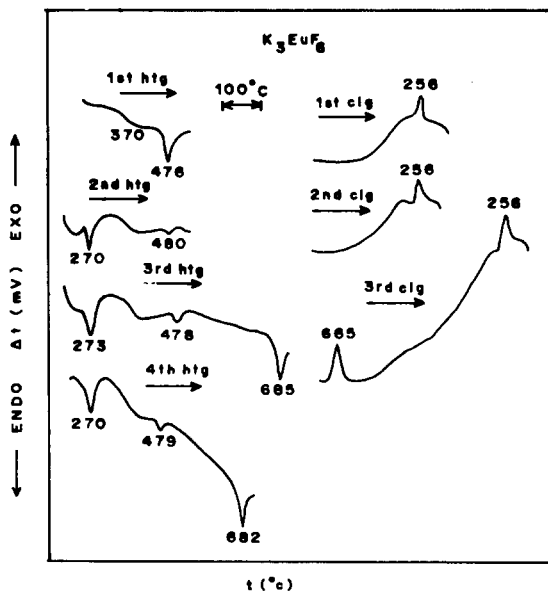

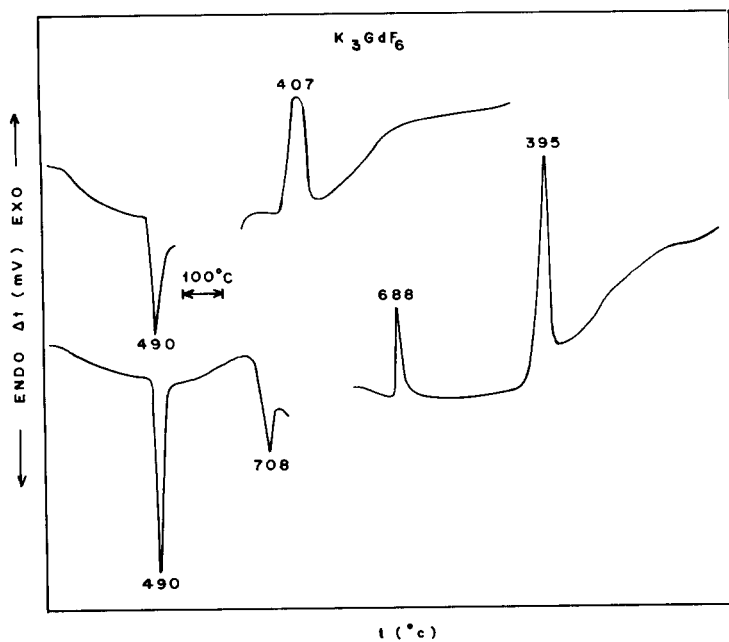Fig. 2. Thermal cycling through different phase transitions in DTA of K_3EuF_6.

Fig. 3. Thermal cycling through different phase transitions in DTA of K_3GdF_6.

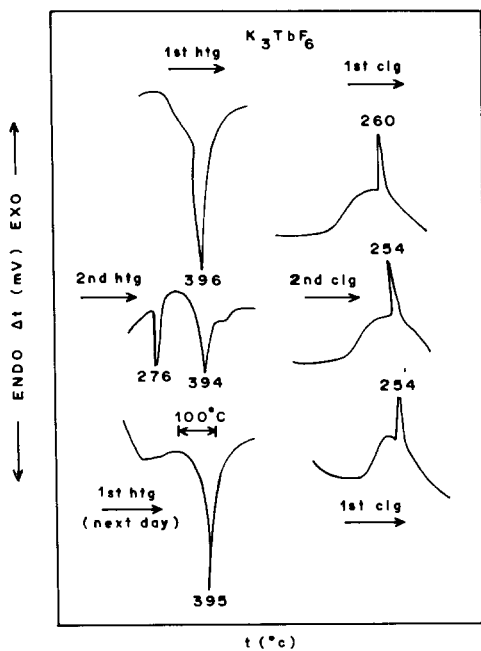
Fig. 4. Thermal cycling through different phase transitions in DTA of K_3TbF_6.

in a desiccator after preparation. During the first heating, a composite peak consisting of a sharp endotherm at 396°C was present on a broad endotherm between 300 and 580°C. On first cooling, the same type of composite curve but with hysteresis was observed. On second heating, two sharp peaks at 276 and 394°C were observed but on subsequent cooling, the composite curve was again obtained. The sample was stored overnight in a desiccator and the DTA run again. On first heating the sample again gave a sharp peak at 394°C but not the first peak at 276°C. Whilst on cooling, the composite peak was observed. On second heating two endotherms at 276 and 394°C were again obtained. Thermal cycling around the sharp 276°C peak is shown in Fig. 4. The compound melts at 734°C. From these observations, the following scheme of phase transitions in this compound are inferred.

$$\alpha \xrightarrow{\text{276°C}} \beta \xrightarrow{\text{396°C}} \Gamma \xrightarrow{\text{734°C}} \text{Melt}$$
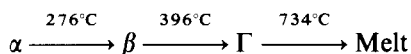
As was mentioned earlier, the XRD could not help in deciding whether the room temperature phase is α or δ. This scheme of phase transitions in K_3TbF_6 based on DTA results is in agreement with that reported from high temperature XRD powder work (Table 1). Hence it is concluded that the room temperature phase of K_3TbF_6 is α and not δ.

The room temperature α phase can be superheated (beyond the transformation temperature, 276°C, of α to β) to 396°C and it changes to the Γ phase. The underlying broad endotherm in the composite peak indicates slow conversion of the superheated α into the β phase.

It should be added that K_3HoF_6 is reported [6] to show three DTA endothermic transitions at 285, 400 and 960°C attributed to α to β, β to Γ and Γ to melt transformations.

The product of our preparation of K_3ErF_6 is the δ phase and there is no ambiguity about this. Its XRD pattern agrees well with that reported for the δ phase by Reshetnikova et al. [7]. The DTA scans of this compound are shown in Fig. 5. During first heating, a sharp endotherm was seen at 332 °C; on cooling this gave a transient at 212°C. On holding the sample at about 400°C for a short time, cooling to room

Table 3
DTA data of K_3LnF_6

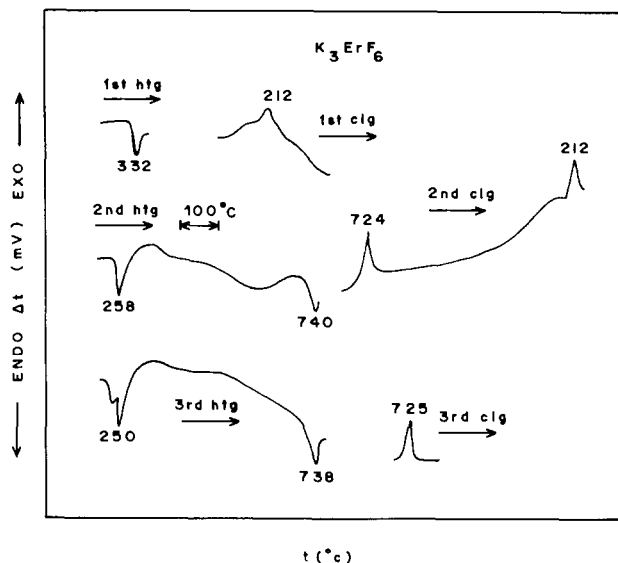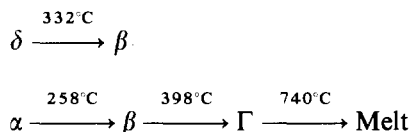| Compound	Peak temperature during	
	Heating/°C	Cooling/°C
K_3SmF_6	105, 538, 664, 720	485, 650, 714
K_3EuF_6	100, 270, 480, 685	265, 665
K_3GdF_6	105, 290–480, 490, 709	170–280, 407, 688
K_3TbF_6	95, 413, 726	270, 714
K_3ErF_6	100, 332, (1st heating)	200 (1st cooling)
	250, 398, 740 (2nd)	210, 724 (2nd)

Fig. 5. Thermal cycling through different phase transitions in DTA of K_3ErF_6.

temperature, and on subsequent heating three endotherms at 258 °C (sharp), at around 398 °C (weak and broad) and at 740 °C (sharp) are observed. The scheme of phase transitions is this compound is inferred as follows:

$$\delta \xrightarrow{\;332^\circ C\;} \beta$$

$$\alpha \xrightarrow{\;258^\circ C\;} \beta \xrightarrow{\;398^\circ C\;} \Gamma \xrightarrow{\;740^\circ C\;} \text{Melt}$$

The 332 °C peak obtained during first heating is attributed to the δ to β transition. Once transformed into the β phase, the δ phase cannot be obtained by thermal cycling. In our method of preparation of K_3ErF_6, the δ phase is formed and not the α phase.

3.1. Dilatometry on K_3REF_6

3.1.1. K_3GdF_6

A plot of % linear thermal expansion as a function of temperature of K_3GdF_6 is shown in Fig. 6. The percent linear thermal expansion is low up to 200 °C, at which point it increases linearly up to 460 °C. However, in the narrow temperature range of 480–500 °C a sudden increase in expansion is observed; this is attributed to the increase in volume associated with the phase transition. The compound further expands normally up to 600 °C. The average linear thermal expansion coefficient (α_1) of the compound in the temperature ranges 27–480 °C and 27–500 °C are found to be
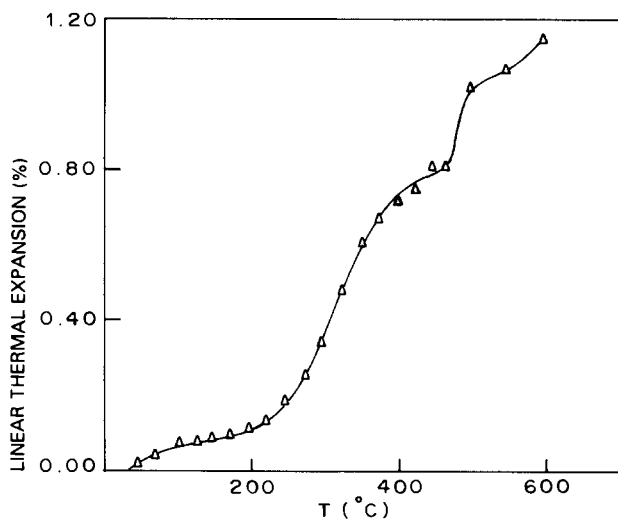
Fig. 6. A dilatometric curve of K_3GdF_6.
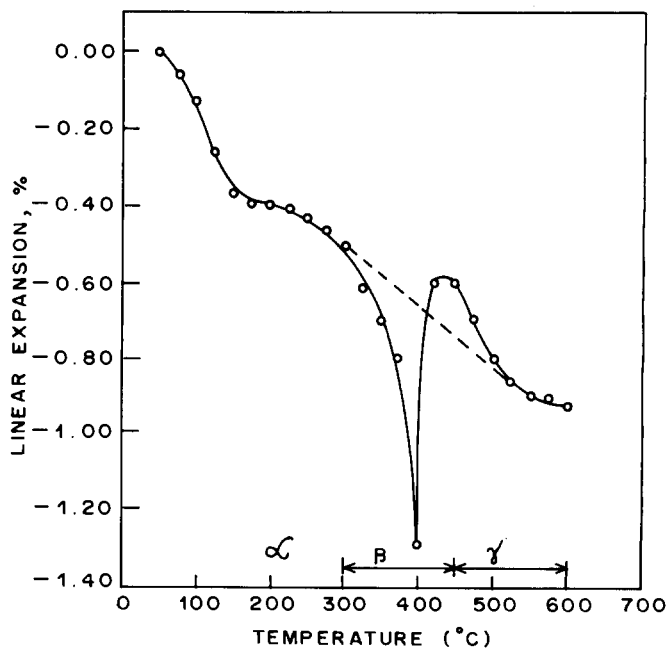
Fig. 7. A dilatometric curve of K_3TbF_6.

17.8×10^{-6} K^{-1} and 21.4×10^{-6} K^{-1}, respectively. The endotherm at 708 °C in the DTA is due to congruent melting of K_3GdF_6.

3.1.2. K_3TbF_6

Fig. 7 shows % linear thermal expansion against temperature for K_3TbF_6. The most striking result is that from room temperature to 600 °C the expansion is negative with the highest rate of decrease, $\approx -1.3\%$, at around 400 °C. From 150–600 °C the linear expansion would have decreased smoothly if there were no sharp transition at 400 °C. This implies that α changes over to Γ very slowly but the 400 °C peak represents the sharp α to β transition. The first transition $\alpha–\beta$ has a large volume reduction while $\beta–\Gamma$ shows slight expansion. The underlying β forms slowly from 150–300 °C as is reflected in the thermal expansion coefficient and further falling very sharply from 350–400 °C at which point β is formed; this has + ve expansion from 400–450 °C. The Γ phase which is formed at 450 °C again has − ve expansion up to 600 °C.

The unit cell volumes of α, β and Γ phases have been calculated from reported cell parameters [34]. The per unit cell volume of α is 265 Å [3] at RT, for β it is 197 Å [3] at 380 °C and for Γ 201 Å^3 at 450 °C. From these values it can be seen that α to β and then β to γ transitions are accompanied by a decrease and an increase in volume, respectively. However, the overall volume changes from α to Γ transition show a decrease in volume. These results are in agreement with dilatometry results.

Acknowledgement

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