ELSEVIER

Thermochimica Acta 256 (1995) 47–53

thermochimica acta

Thermoanalytical studies on volatile complexes containing alkali metals ☆

Marja Tiitta [a, 1], Markku Leskelä [b], Erja Nykänen [a], Pekka Soininen [a], Lauri Niinistö [a]

[a] *Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology, FIN-02150 Espoo, Finland*

[b] *Department of Chemistry, University of Helsinki, P.O. Box 6, FIN-00014 Helsinki, Finland*

Abstract

Alkali metal-containing complexes with 2,2,6,6-tetramethyl-3,5-heptanedione (thd) and trifluoroacetylacetone (tfa) as ligands were studied by TG, DTA, DSC and MS methods. Of the complexes studied, Na(thd) and K(thd) sublimed completely, and $NaPr(tfa)_4$ and $KPr(tfa)_4$ sublimed almost completely in vacuum, but in an inert atmosphere the weight remaining was up to $\approx 20\%$. Surprisingly, $KPr(tfa)_4$ had higher volatility than the corresponding sodium complex. The strongest peaks in the mass spectra of the double complexes were due to $NaPr(tfa)_3$ and $KPr(tfa)_3$. The mass spectra of Na(thd) and K(thd) showed several different species. One thd ligand was always bonded to one or several alkali metal ions. The strongest peaks in both spectra were those due to M_3thd_2 and M_2thd.

Keywords: Atomic layer epitaxy; Decomposition; Diketonate; Group I compound; Lanthanon compound

---

1. Introduction

Rare earth-doped zinc and alkaline earth sulphides play an important role in the fabrication and development of multi and full colour electroluminescent (EL) thin film devices [1]. $ZnS:Tb^{3+}$, $SrS:Ce^{3+}$ and $ZnS:Pr^{3+}$ are frequently studied

---

☆ Presented at the 14th Symposium on Thermal Analysis and Calorimetry, Oslo, Norway, 15–17 June 1994.

[1] Present address: Neste Ltd, Technology Centre, Catalysis Research, P.O.B. 310, FIN-06101 Porvoo, Finland.

SSDI 0040-6031(94)02221-6

phosphor materials for green, blue and white EL, respectively. Because of the oxidation state mismatch between the rare earth and the alkaline earth metal ions, charge compensation with alkali cations could enhance the EL properties of these materials.

We have employed the atomic layer epitaxy (ALE) process [2] to fabricate EL structures [3–5]. Volatile and sufficiently stable precursors are needed in the deposition of thin films by ALE. Thermoanalytical methods provide a fast and convenient means of screening the precursors and studying their thermal behaviour under simulated ALE process conditions. We have earlier studied the volatility of alkaline earth and rare earth complexes [6] and applied these complexes for thin film growth by ALE. In the present work we have studied the thermal behaviour of $NaPr(tfa)_4$, $KPr(tfa)_4$, Na(thd) and K(thd). The two former complexes present a case in which the rare earth and alkali ions are simultaneously present and can be deposited onto the substrate in a fixed ratio. In order to be able to change the dopant/codopant ratio, and because not all rare earth ions form double complexes with alkali metal ions, simple Na and K complexes were also studied here and used in the ALE experiments.

2. Experimental

2.1. Synthesis of metal chelates

The ligands (2,2,6,6-tetramethyl-3,5-heptanedione is thd, 1,1,1-trifluoro-2,4-pentanedione is tfa), alkali hydroxides and praseodymium oxide were commercial, analytically pure or pure (ligands) reagents. The alkali thd compounds were synthesized by evaporating aqueous ethanolic solutions of thd and a slight excess of alkali hydroxide to dry powders and subliming them. The alkali praseodymium tfa complexes were synthesized according to Martynova and Nikulina [7]. One mole of alkali hydroxide was reacted with four moles of tfa dissolved in *n*-hexane. This solution was refluxed for several hours with a solution containing praseodymium ions in ethanol. The precipitate formed was washed with distilled water and dried. After drying, the precipitate was purified by sublimation in vacuum.

2.2. Infra-red spectrometry and X-ray diffraction

The purity of the synthesized samples was studied by infra-red (IR) and X-ray diffraction (XRD) techniques. The IR spectra were recorded under vacuum using the KBr technique in a Bruker IF S113v FTIR spectrometer. A Philips MPD 1880 X-ray diffractometer was used for the diffraction measurements.

2.3. Thermogravimetry and differential scanning calorimetry

Thermoanalytical measurements were carried out using Seiko TG/DTA 320 and Perkin-Elmer Series 7 TGA and DSC instruments. The sample size in TG measure-

Table 1
Results of XRD measurements in the range 2000–4000 cm^{-1}

NaPr(tfa)$_4$		KPr(tfa)$_4$	
d-value/pm	rel. int./%	*d*-value/pm	rel. int./%
1033	100	1035	90
936	40	852	100
850	15	614	90
587	15	569	50
515	15	457	90
469	20	434	35
402	30	391	80
383	25	367	30
380	15	348	30
341	15	315	35

ments was ≈ 10 mg and that in DSC measurements 5 mg. The heating rate was 10°C min^{-1} in all measurements, and a flowing argon or nitrogen atmosphere having a pressure of 1000 mbar or 2–7 mbar was employed.

2.4. *Mass spectrometry*

The molecular formulae of the volatilized species were studied in a VG 7070E high-resolution mass spectrometer which has a heated inlet for solid samples. The temperature of the sample chamber was in the range 250–400°C.

3. Results and discussion

The X-diffraction patterns showed that the synthesized metal–tfa precursors were polycrystalline and no impurities such as KNO_3, $NaNO_3$ and $Pr(NO_3)_3$ were present in the samples after sublimation. If the precipitates were not washed with water the XRD patterns showed peaks of $NaNO_3$ or KNO_3 before sublimation. XRD data show that the NaPr(tfa)$_4$ and KPr(tfa)$_4$ complexes are not isomorphous (Table 1). In general, XRD appears to be a good method to characterize the metal complexes in the solid state. Possible degradation of the complex, e.g. because of moisture, can be detected by changes in the XRD pattern.

The IR absorption bands with their assignments are presented in Table 2 for the double cation complexes. The two complexes have quite similar FTIR spectra. The potassium complex showed slightly higher wavenumbers than the sodium complex. The small differences in the wavenumbers of C–C stretching and CH_3 skeletal vibrations are possibly due to the differences in electropositivity and size of the sodium and potassium cations.

Na(thd) and K(thd) showed closely similar thermal behaviour. In a vacuum the sublimation was complete and occurred between 200 and 260°C (DTG peak at

Table 2
Results of FTIR measurements

NaPr(tfa)$_4$		KPr(tfa)$_4$		Assignments [8–10]
Wavenumber/cm^{-1}	rel. int.	Wavenumber/cm^{-1}	rel. int.	
1624	vs	1626	vs	C–F (str.)
1533	s	1537	m	C–O (str.)
1481	s	1492	m	C–C (str.)
1365	m			
1280	vs	1290	vs	CH$_3$ (ske.)
1230	m	1226	m	
1196	s			C–O (str.)
1134	vs	1128	s	CH$_3$ rock and C–C–C as. str.
854	m	850	m	CH$_3$ rock and C–C–C as. str.
		725	m	
559	s	555	s	M–O (str.)

Key: str, stretching; rock, rocking; vib, vibration; ske, skeletal; vs, very strong; s, strong; m, medium.

218°C and 223°C for Na(thd) and K(thd), respectively). However, the TG curve in each case showed an inflection point at ≈ 250°C (Fig. 1) which cannot be plausibly explained. In a nitrogen atmosphere (1000 mbar) the sublimation was not complete but residues typically of 3–5% remained. This shows that decomposition and sublimation are competing processes.

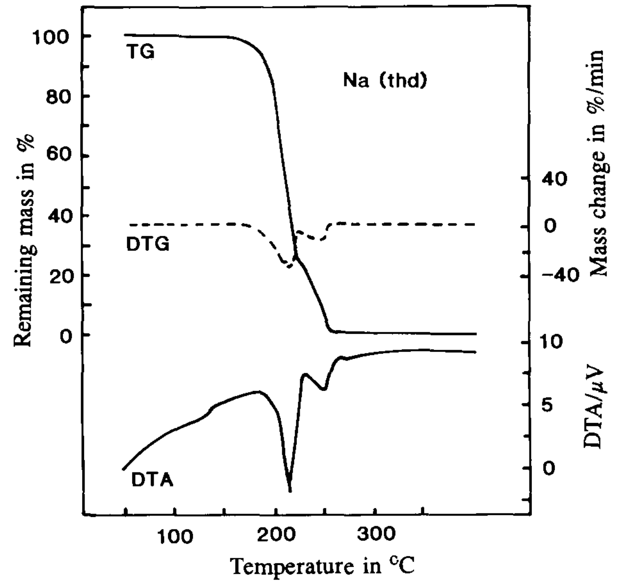

Fig. 1. TG, DTG and DTA curves for Na(thd) recorded at a pressure of 2 mbar.

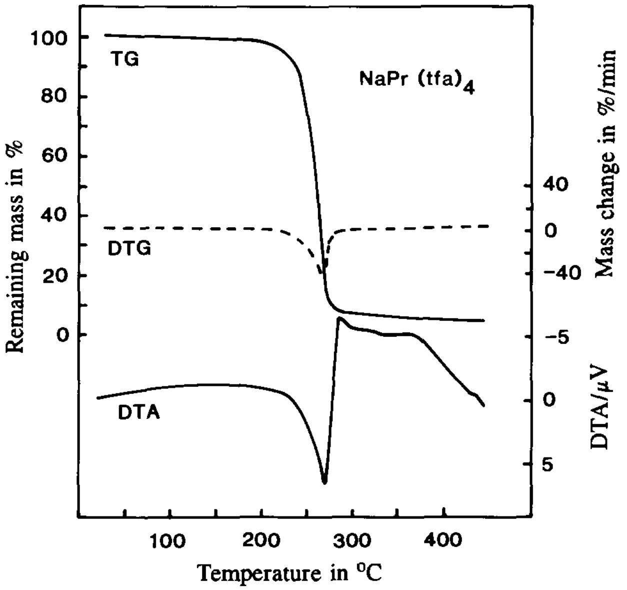

Fig. 2. TG, DTG and DTA curves for NaPr(tfa)$_4$ at a pressure of 7 mbar.

NaPr(tfa)$_4$ and KPr(tfa)$_4$ sublimed almost completely in a vacuum in a single step (Fig. 2). In an inert atmosphere some decomposition took place and the weight remaining was ≈ 20%. The results of TG and DTA measurements are summarized in Table 3. As can be seen, KPr(tfa)$_4$ sublimed at a lower temperature than the NaPr(tfa)$_4$ complex. The opposite behaviour is usually observed: the smaller the molecular weight of the cation the higher its volatility [6,11]. However, both complexes sublimed, as expected, at a higher temperature than the pure Pr(tfa)$_3$ or Pr(thd)$_3$ complexes [6,12]. This is obviously because of the higher molecular weight of the double cation complexes.

The mass spectra of M(thd) complexes showed several different species of alkali metal and thd. An interesting observation was that the thd ligand was always

Table 3
Sublimation temperatures, weight remaining, and DTA peak temperatures recorded in simultaneous TG/DTA measurements carried out at a pressure of 2-7 mbar

Compound	Temperature range of sublimation measured by TG in °C	Residue in wt%	DTA peak temperature in °C
Na(thd)	170-255	≈0	217
K(thd)	165-260	≈0	224
NaPr(tfa)$_4$	240-280	7	270
KPr(tfa)$_4$	220-260	3	255

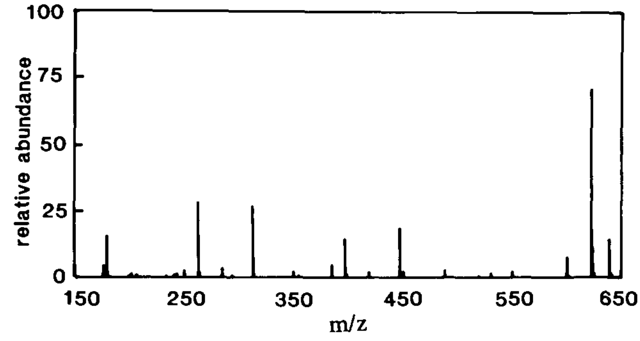

Fig. 3. The high resolution mass spectrum of NaPr(tfa)$_4$.

bonded to one or several alkali metal ions. In both spectra the strongest peaks were those due to M$_2$thd (230, 262) and M$_3$thd$_2$ (436, 485). The small molecular peaks 207 (Na(thd)) and 223 (K(thd)) were also present. The other intense peaks in the mass spectrum of Na(thd) were 643 (Na$_4$(thd)$_3$), 889 (Na$_7$(thd)$_4$), 414 (Na$_2$(thd)$_2$), 620 (Na$_3$(thd)$_3$) and 683 (Na$_6$(thd)$_3$). In the spectrum of K(thd) additional intense peaks were found at 970 (K$_6$(thd)$_4$) and 953, 845 and 623 (unknown). In both spectra there were several peaks below the mass number of 184 originating from fragments of the ligands.

In the mass spectra for MPr(tfa)$_4$ (M is Na or K) the most intense mass numbers were 623 (NaPr(tfa)$_3$) and 639 (KPr(tfa)$_3$) and only very small molecular peaks at 776 (NaPr(tfa)$_4$) and 792 (KPr(tfa)$_4$ were observed. The other intense peaks in the spectra were those at mass numbers 600 (Pr(tfa)$_3$), 449 (Pr(tfa)$_2$), 397 (PrOF$_3$(tfa)), 313 (PrF(tfa)), 263 (PrCF$_5$O), 179 (PrF$_2$), and 153 (tfa), which were common to both spectra (Fig. 3). No mass numbers corresponding to Na(tfa) or K(tfa) could be detected. The spectra contained several peaks below the mass number of 153 originating from fragments of the ligand. Also, peaks corresponding to the mass numbers of sodium (23) and potassium (39) were present. A fragmentation scheme of KPr(tfa)$_4$ is presented in Fig. 4.

The similarity of the mass spectra of NaPr(tfa)$_4$ and KPr(tfa)$_4$ shows that in practice there is only one fragmentation species which contains both the alkali metal and the lanthanoid, viz. MPr(tfa)$_3$. The other species contain only praseodymium, indicating its stronger coordination to tfa in comparison with alkali metals. This will probably affect the alkali/praseodymium ratio in the thin films deposited from the vapour phase.

4. Conclusions

Thermoanalytical measurements show that the alkali metal thd and alkali metal/rare earth tfa complexes are essentially completely volatile in a vacuum. In an inert atmosphere the volatility is somewhat limited. The double complexes show

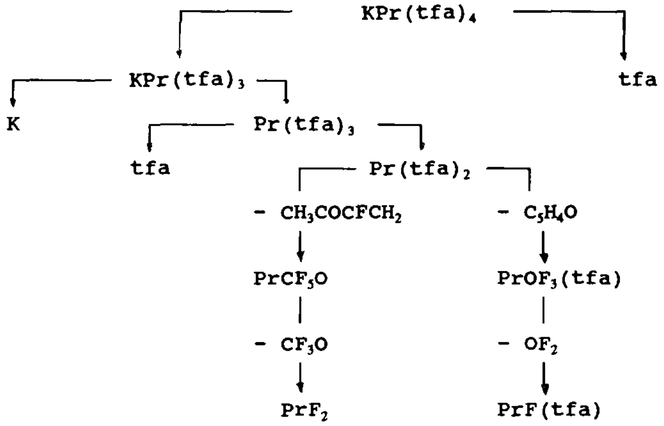

Fig. 4. A fragmentation scheme of KPr(tfa)$_4$.

fragmentation in the gas phase, and in ultra-high-vacuum conditions only the rare earth-containing species dominate. The pressure in a flow-type ALE reactor (10 mbar) is different, however, and preliminary results show that the deposition of alkali doped thin films from these precursors is possible, although the dopant level is difficult to control.

References

[1] M. Leskelä and L. Niinistö, Mater. Chem. Phys., 31 (1992) 7.
[2] M. Leskelä and L. Niinistö, in T. Suntola and M. Simpson (Eds.), Atomic Layer Epitaxy, Blackie, Glasgow 1990, p. 1.
[3] M. Leskelä, L. Niinistö, E. Nykänen and M. Tammenmaa, Chemtronics, 3 (1988) 113.
[4] M. Leskelä, L. Niinistö, E. Nykänen, P. Soininen and M. Tiitta, J. Less-Common Met., 153 (1989) 219.
[5] M. Leppänen, M. Leskelä, L. Niinistö, E. Nykänen, P. Soininen and M. Tiitta, SID 91 Digest, 22 (1991) 282.
[6] M. Leskelä, L. Niinistö, E. Nykänen, P. Soininen and M. Tiitta, Thermochim. Acta, 175 (1991) 91.
[7] T. Martynova and L. Nikulina, Sov. J. Coord. Chem. (Engl. Transl.), 13 (1987) 334.
[8] T. Martynova, L. Nikulina and V. Logvinenko, J. Therm. Anal., 36 (1990) 203.
[9] H.-Y. Lee, F. Cleveland and J. Ziomek, Appl. Spectrosc., 26 (1972) 251.
[10] E. Berg and N. Herrera, Anal. Chim. Acta, 60 (1972) 117.
[11] K. Eisentraut and R. Sievers, J. Inorg. Nucl. Chem., 29 (1967) 1931.
[12] E.W. Berg and J. Chiang Acosta, Anal. Chim. Acta, 40 (1) (1968) 101.