Thermochimica Acta, 47 (1981) 105—108
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

Note

PHASE TRANSITION BEHAVIOR OF RARE EARTH IODATES

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(Received 7 January 1981)

Considerable attention has been focussed on crystallographic and non-linear optical properties of rare earth iodates [1—5]. Of particular interest is the occurrence of a large variety of crystalline and amorphous compounds which include various hydrates, hemihydrates and anhydrous structural types. Throughout the series three different groups have been recognized, viz. La, Ce to Sm, and Eu to Lu, including Y. However, within these groups considerable variations in structure exist and altogether 13 isostructural types have been reported [3]. During the course of our studies on dielectric properties of rare earth iodates, we have examined phase transition behavior of $Ln(IO_3)_3$ (Ln = La, Pr and Nd) more closely and have observed that more polymorphs do exist. Here we wish to report enthalpy changes that occur during these phase transformations.

EXPERIMENTAL

$Ln(IO_3)_3 \cdot x\ H_2O$ (Ln = La, Pr, Nd) was obtained by mixing hot aqueous solutions of KIO_3 and the rare earth nitrate in a 3 : 1 molar proportion. The mixture was digested on a water bath for 1 h, filtered, and washed freely with water and finally with acetone. The compound was air dried. Thermal analysis was carried out using a MOM derivatograph and a Mettler TA 2000 C thermal analyzer TG—DSC system under an atmosphere of nitrogen at a heating rate of 2°C min^{-1}. Enthalpy changes during phase transitions were evaluated by integrating the area under the DSC scan and comparing these with areas obtained for melting of In and Sn. X-Ray powder patterns were obtained using a Guinear camera with CuK_α radiation.

RESULTS AND DISCUSSION

In $Ln(IO_3)_3 \cdot x\ H_2O$, x is a non-integral varying from 2 to 5. Their dehydration takes place in the temperature range 50—250°C. In each case the hydrated as well as the anhydrous compound prior to any transition is in

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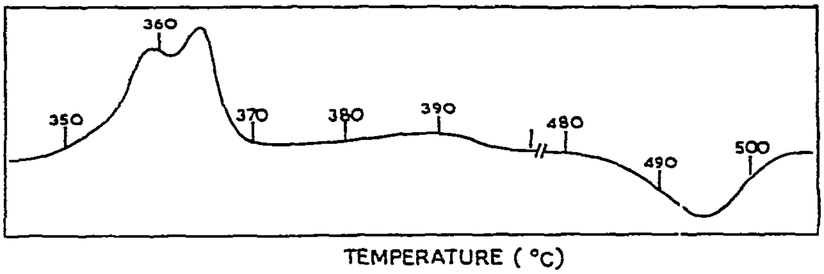

Fig. 1. DSC scan of $La(IO_3)_3$.

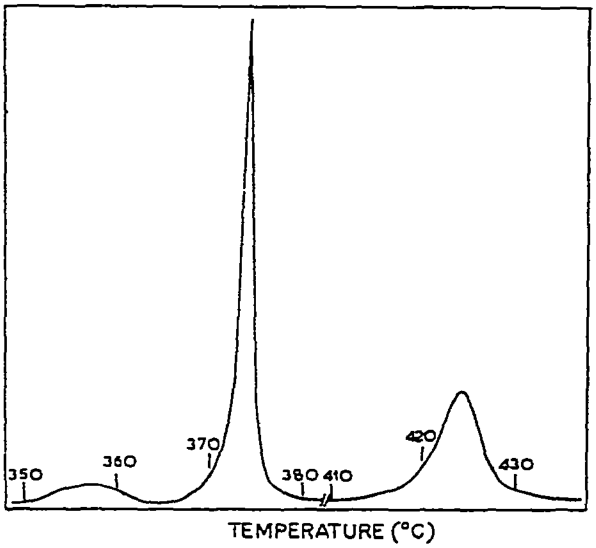

Fig. 2 DSC scan of $Nd(IO_3)_3$.

TABLE 1

Enthalpy changes due to phase transitions of rare earth iodates

Compound	Transition temp. (°C)	ΔH (kcal $mole^{-1}$)
$La(IO_3)_3$	352 355 (endothermic)	4.96
	380 (exothermic)	1.05
	484 (endothermic)	2.45
$Pr(IO_3)_3$	356 (exothermic)	0.50
	371 (exothermic)	4.65
	412 (exothermic)	3.35
$Nd(IO_3)_3$	350 (exothermic)	0.35
	372 (exothermic)	3.10
	418 (exothermic)	2.41

amorphous form. Figures 1 and 2 show the DSC scans of $La(IO_3)_3$ and $Nd(IO_3)_3$ which clearly indicate marked variation in their phase transition characteristics. On the other hand, $Pr(IO_3)_3$ has identical features to $Nd(IO_3)_3$ with some variations in transition temperatures. A characteristic common to all rare earth iodates is the irreversible nature of phase transitions. It may be noted in Fig. 1 that $La(IO_3)_3$ shows three endotherms and one exotherm. However, the first two transitions at 352 and 355°C are so close that these two phases cannot be isolated. Nassau et al. [2,3] have reported

TABLE 2

Observed d-spacings and intensities of the different phases of $Nd(IO_3)_3$

Phase I		Phase II		Phase III	
d	Intensities	d	Intensities	d	Intensities
4.81	m	4.41	w	5.20	vw
4.33	w	4.15	m	4.02	vw
3.68	m	3.89	m	3.91	w
3.25	s	3.69	s	3.67	m
3.00	vs	3.65	w	3.64	m
1.96	w	3.53	m	3.51	s
		3.37	m	3.42	m
		3.28	s	3.35	m
		3.15	s	3 30	vs
		3.00	vs	3.21	vw
		2.98	m	3.12	vw
		2.74	s	3.08	s
		2.61	m	3.00	vw
		2.32	m	2.93	w
		2.03	w	2 76	w
		1.95	m	2.70	vw
		1.73	m	2.65	w
		1.63	vw	2.51	vw
		1.57	w	2.50	vw
		1.47	vw	2.45	vw
		1.36	vw	2.44	vw
				2.40	vw
				2.35	w
				2.25	vw
				2.22	w
				2.12	w
				2.08	vw
				2.05	m
				2.03	vw
				1.95	m
				1.87	w
				1.85	vw
				1.80	m
				1.79	w
				1 78	m
				1.74	m
				1.70	w
				1.67	vw

two transitions for amorphous La$(IO_3)_3$, an exotherm at 360°C and an endotherm at 490°C, which have been referred to O_{IV} and O_{VI} phases. X-Ray powder data of their O_{IV} and O_{VI} phases are in good agreement with our values obtained just past the exotherm at 380°C and the endotherm at 484°C. Table 1 summarizes the enthalpy changes occurring during phase transitions.

Pr$(IO_3)_3$ and Nd$(IO_3)_3$ exhibit three exothermic transitions (Fig. 2 and Table 1). While for Pr$(IO_3)_3$ Nassau et al. [2,3] have identified three phases, viz. O_V (350°C), O_{IV} (400°C) and O_V (450°C), in the case of Nd$(IO_3)_3$ the O_{IV} phase has not been detected. X-Ray powder data of Nd$(IO_3)_3$ at 350°C (phase I), 372°C (phase II) and 418°C (phase III) are shown in Table 2. Isostructural phases have been obtained for Pr$(IO_3)_3$. In general, the powder data obtained by us are in good agreement with previously reported values [3]. A comparison of ΔH values due to phase transitions of Pr$(IO_3)_3$ and Nd$(IO_3)_3$ (Table 1) reveals that for each transition the ΔH value of Nd$(IO_3)_3$ is smaller than the Pr counterpart.

ACKNOWLEDGEMENT

Thanks are due to the Application Laboratories, Mettler Instruments AG, for scanning DSC of the samples.

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