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THERMAL STABILITIES OF SELECTED RARE EARTH OXYIODIDES

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The thermal stabilities of lanthanum, neodymium, samarium and gadolinium oxyiodides were studied in a dynamic air atmosphere. Several intermediate phases with the general formula $\underline{n}REOI \cdot RE_2O_3$ ($\underline{n}$ = 7, 4, 2 and 1) were observed during the decomposition scheme. The thermal stability decreases slightly with increasing atomic weight of the RE cation. Similar decreases with increasing atomic weight of the halide were observed in the lanthanum and in the gadolinium oxyhalide series. This decrease could be correlated to the changes in crystal structure.

The rare earth /RE/ based phosphors have found applications in a wide area, including colour TV, mercury lamps and X-ray intensifying screens. The most efficient phosphors consist of RE oxysalts, mainly RE oxysulphides and RE oxyhalides. The spectroscopic properties of the entire RE oxyhalide series have been studied in detail quite recently [1-4]. For commercial applications the good thermal stability of the host compound is required in addition to the favorable luminescence properties. Accordingly, an investigation into the thermal stabilities of the lanthanum, gadolinium and yttrium oxyhalides, excluding the oxyiodides, has already been carried out [5]. This study showed that the thermal stability of a RE oxyhalide decreases with increasing atomic weight of both the host cation and the host anion. Only one intermediate phase, $REOBr \cdot RE_2O_3$, could be observed before the final decomposition product, RE oxide. On the other hand, the thermal decomposition of RE iodide hydrates proceeds through several stages between the oxyiodide and oxide phases [6]. The aim of the present study is to complement and clarify the earlier work on the thermal stabilities of RE oxyiodides.

EXPERIMENTAL

Preparation of the samples

A large number of methods have been proposed for the preparation of RE oxyhalides [7]. These include the thermal decomposition of RE halides /halide hydrates/, the thermal decomposition of RE compounds containing halogens, and the reactions of RE oxides with gaseous hydrogen halides, with ammonium halides or with anhydrous RE halides. Most of these methods yield a product of mixed phases without any practical value. Pure RE oxyhalides are usually obtained by the reaction of RE oxides with ammonium halides [8], and this method was thus chosen for the preparation of the RE oxyiodide samples. A detailed description of the actual procedure can be found in Ref. 9. The inherent instability of the heavier RE oxyiodides restricted the study to the lanthanum, neodymium, samarium and gadolinium compounds. Lanthanum and gadolinium oxychloride and oxybromide samples were studied for comparison, too. The purity of each sample was routinely checked by X-ray powder diffraction techniques.

Thermoanalytical methods

The simultaneous recording of the T, TG, DTG and DTA curves was achieved by the use of a Stanton-Redcroft STA-780 thermoanalyser. Only a heating rate of $10^{\circ}\mathrm{min}^{-1}$ was applied, since the decomposition schemes were not found to depend significantly on the heating rate. The samples /weighing appr. 15 mg/ were heated in a platinum crucible in a dynamic air atmosphere /flow rate 50 $\mathrm{cm}^3\mathrm{min}^{-1}$/. Alumina was used as the reference material in DTA measurements.

RESULTS AND DISCUSSION

Decomposition of RE oxyiodides

The RE oxyiodides studied begin to decompose below 360°. Despite the small mutual differences in starting temperatures, these tend to decrease with increasing atomic weight of the RE. The same phenomenon has been observed for the majority of RE compounds. The decomposition of RE oxyiodides proceeds through several intermediate phases which correspond to the general formula $\underline{n}REOI \cdot RE_2O_3$; $\underline{n}$ = 7, 4 and 2 for the decomposition of SmOI, whereas LaOI and GdOI give only the $2REOI \cdot RE_2O_3$ phase. The decomposition of NdOI differs slightly from the preceding schemes, as a stable $REOI \cdot RE_2O_3$ intermediate phase is formed. Table 1 lists the decomposition temperatures as well as the stability ranges of the observed intermediate phases for the RE oxyiodides studied.

Table 1

Thermal stabilities of RE oxyiodides

REOI	Start	Intermediate phases				End
		I	II	III	IV	
LaOI	355	-	-	650-730	-	830
NdOI	340	460-515	-	630	720-805	875
SmOI	335	460-510	560-620	640-800	-	885
GdOI	315	-	-	430-560	-	915

Intermediate phases: I $7REOI \cdot RE_2O_3$, II $4REOI \cdot RE_2O_3$,
III $2REOI \cdot RE_2O_3$, IV $REOI \cdot RE_2O_3$.

The stability range of the $2REOI \cdot RE_2O_3$ phase extends in most cases to over one hundred degrees; this clearly exceeds the stability of the other intermediate phases, which remain stable over only a few tens of degrees. The differences in stability of the intermediate phases with respect to the RE cation are quite small, however.

The decompositions of the RE oxyiodides end with the formation of the corresponding oxides at temperatures higher than

830°. In contrast with the starting temperatures, the end-point of the decomposition tends to increase with increasing atomic weight of the RE. This trend is due to the slow decomposition of the heavier RE oxyiodides through several quite stable phases.

The DTA curve for SmOI reproduced in Fig. 1 reveals that the first two steps of decomposition involve exothermic reactions. On the other hand, the following steps seem to be purely endothermic. The reason for complex behaviour of this kind is not apparent. A similar DTA curve was obtained for NdOI, whereas no exothermic effects were observed for either LaOI or GdOI.

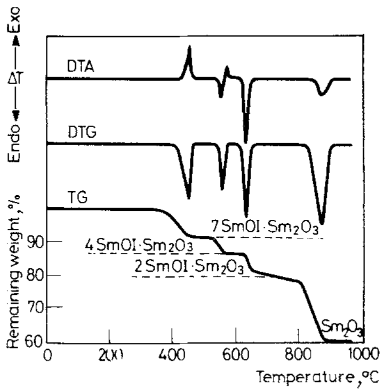

Fig. 1. Thermal decomposition of samarium oxyiodide in air.

Comparison with other RE oxyhalides

The RE oxyiodides begin to decompose at distinctly lower temperatures than the corresponding RE oxybromides /300 to 450°/ or RE oxychlorides /500 to 800°/. The thermal stability of the structurally isomorphic oxyhalides thus decrease strongly with increasing atomic weight of the halide, as the TG curves for GdOCl, GdOBr and GdOI reproduced in Fig. 2 indicate. The decrease in thermal stability along the OCl>OBr>OI series can be correlated to the layer structure of the RE oxyhalides. The distance between the $(REO)_n^{n+}$ complex cation layer and that of the halides increases markedly from the oxychlorides to the oxyiodides [10], thus enabling these bonds to be ruptured by thermal effects more easily for the RE oxyiodides than for the other oxyhalides.

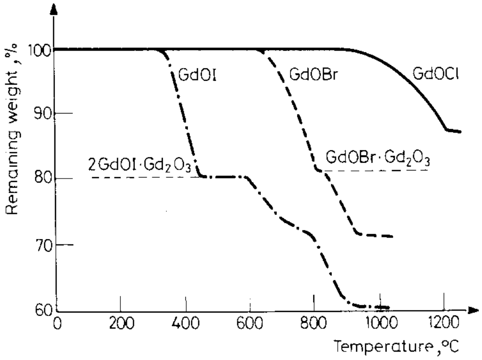

Fig. 2. Comparison between decompositions of gadolinium oxyhalides.

The decompositions of the lighter oxyhalides proceed slightly faster, but with higher starting temperatures. The rapidity of decomposition results from the nearly total absence of the intermediate phases which prolong the decomposition for the RE oxyiodides. Accordingly, only one phase, $REOBr \cdot RE_2O_3$, was observed for the lighter RE oxybromides; the stability of this phase hardly exceeds 30°. RE oxychlorides and oxyfluorides decompose in a single step to the oxides. In spite of the slow decomposition, the final phase in the RE oxyiodide decomposition scheme, RE oxide, is always formed at a lower temperature than in the case of the other RE oxyhalides.

CONCLUSION

The results of the present study show the complexity of the thermal behaviour of the RE oxyiodides with respect to the other oxyhalides. The existence of several, quite stable intermediate phases of general formula $\underline{n}REOI \cdot RE_2O_3$ could be established. The thermal stabilities of the RE oxyiodides, however, were found to be clearly inferior to those of the other RE oxyhalides. This behaviour in the RE oxyhalide series can be correlated to the differences in structure. Together with the hygroscopic nature of the RE oxyiodides, their inferior thermal stability hampers the exploitation of these compounds as commercial phosphors, in spite of their favourable luminescence properties.

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ZUSAMMENFASSUNG – Die thermische Stabilität von Lanthan-, Neodym-, Samarium- und Gadoliniumoxyjodiden wurde in einer dynamischen Luftatmosphäre untersucht. Während der Zersetzung wurde das Auftreten einiger intermediärer Phasen der allgemeinen Formel $\underline{n}REOJ \cdot RE_2O_3$ *(*$\underline{n}$*=7, 4, 2 und 1) beobachtet. Die thermische Stabilität nimmt geringfügig mit steigendem Atomgewicht des RE-Kations ab. Eine ähnliche Abnahme mit steigendem Atomgewichts des Halids wurde sowohl in der Lanthan- als auch in der Gadoliniumoxyhalidreihe beobachtet. Diese Abnahme konnte mit den Veränderungen in der Kristallstruktur in Korrelation gebracht werden.*

Резюме - Изучена термоустойчивость оксийодидов лантана, неодима, самария и гадолиния в динамической атмосфере воздуха. Во время разложения наблюдали образование нескольких промежуточных продуктов с общей формулой $\underline{n}\mathrm{REOI}\cdot\mathrm{RE}_2\mathrm{O}_3$ с $\underline{n}$= 7, 4, 2 и 1. Термоустойчивость соединений слегка уменьшается с увеличением атомного веса редкоземельного катиона. Подобное уменьшение с увеличением атомного веса галоида наблюдалось в ряду оксигалоидных соединений лантана и гадолиния. Это изменение может коррелироваться с изменениями кристаллической структуры.