THERMOGRAVIMETRICAL STUDY OF GADOLINIUM CHLOROTUNGSTATE IN AIR BETWEEN 25 AND 1500°C

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ABSTRACT

Using DTA, X-ray powder diffraction, chemical and optical methods, the thermostability of $Gd_3WO_6Cl_3$ was investigated. The compound was relatively stable on heating in air up to 710°C. Above this temperature it exhibited two decomposition temperature ranges (710-900°C and 900-1130°C). The final product consisted of a mixture of gadolinium tungstate of different composition. This suggests the decomposition scheme of polyphase products

$$Gd_3WO_6Cl_3 \xrightarrow[-Cl_2]{+\frac{1}{2}O_2} (Gd_3WO_7Cl) \xrightarrow[-\frac{1}{2}Cl_2]{+\frac{1}{4}O_2} Gd_3WO_{7.5}$$

INTRODUCTION

Compounds of composition $LnWO_4Cl$ and $Ln_3WO_6Cl_3$ (Ln=La,Gd) identified by X-ray powder diffraction and some physical chemical methods have been reported to form in solid phase reactions (Brixner *et al* 1982a, 1982b, 1982c).The compounds can be applied in laser technology as efficient phosphors. We reported earlier the optimum conditions for synthesis and phase characterization (Ngassapa *et al* 1993), luminescence, and optical properties (Venskovskii *et al* 1993a, 1993b, 1993c).

MATERIALS AND METHODS

Initial rare earth Gadolinium oxychloride was prepared by dissolving Gadolinium oxide (analytical grade) in concentrated HCl. The Solution was evaporated to dryness and calcinated at 900°C for 2-3 hrs to obtain Gadolinium oxychloride. Tungsten (VI) oxide was prepared by calcinating the hydrated ammonium tungstate at 600°C according to:-

$$(NH_4)_{10}W_{12}O_{41}.nH_2O \xrightarrow{T,^{\circ}C} WO_3 + NH_3 + nH_2O \quad \text{.....(1).}$$

The purity and individuality of Gadolinium oxychloride and tungsten (VI) oxide were monitored by X-ray diffraction methods, crystal-optical and chemical analysis. Initial components at the ratio of 3:1 were well mixed and placed in an air evacuated quartz tube (about 8 cm long) which was sealed and slowly annealed at 900°C for 45 hrs.

Crystal optical analysis, performed on a MIN-8 polarizing microscope, showed the compounds to be pure. $Gd_3WO_6Cl_3$ consisted of well formed colourless lamellar crystals of up to 1 mm in length; the index of refraction was much higher than 1.6, the phase was optically anisotropic, and exhibited high interference colours, with extinction angle $c_{ng} = 5^{\circ}$-12°.

X-ray diffraction patterns were recorded on a DRON-3 diffractometer (with CuK (radiation, graphite monochromator). X-ray diffraction patterns confirmed the existence of the orthorhombical symmetry $Gd_3WO_6Cl_3$ as a single phase product (Table 2). The lattice parameters were calculated as: a = 9.099 Å and c = 5.258 Å. Gd^{3+} was chemicaly determined by chelatometric titration with the use of Trilon B. The ion Cl^- by composition, was determined by the classicalVolhard's method, results of which are shown in Table 1.

Table 1: $Gd^{3+}$and Cl^-composition of $Gd_3WO_6Cl_3$

Compound	Composition Gd^{3+},%		Composition Cl^-,%	
$Gd_3WO_6Cl_3$	Calculated	Experimental	Calculated	Experimental
	58.99	58.77	13.31	13.09

Table 2: Result from X-ray diffraction of GdOCl, WO_3 and $Gd_3WO_6Cl_3$

GdOCl		WO_3		$Gd_3WO_6Cl_3$	
I/I_o	d,Å	I/I_o	d,Å	I/I_o	d,Å
25	6.69	100	3.85	40	7.86
80	3.41	95	3.77	5	4.37
10	3.34	95	3.66	10	3.94
80	2.80	16	3.35	60	3.44
100	2.55	20	3.11	55	3.15
5	2.21	30	2.70	40	2.98
20	1.98	20	2.67	45	2.63
5	1.89	50	2.63	100	2.59
15	1.74	15	2.17	5	2.35
etc	etc	etc	etc	etc	etc

Thermogravimetric analysis was carried out with MOM derivatography (Hungary) within a temperature range of 25-1500°C at a heating rate of 10 K/min within an accuracy of ± 5 K. An Al_2O_3 reagent was employed as reference.

RESULTS AND DISCUSSION

The compound $Gd_3WO_6Cl_3$ was found to be relatively stable on heating up to 710°C. A noted slight loss of weight due to expulsion of absorbed water can be seen from the broad endothermic effect in the DTG curve (Figure 1). Above 710°C the compound began to decompose stepwise to 900°C, then underwent a slow decomposition rate to 1130°C. This temperature range was also marked by a gentle exothermic effect in the DTA curve (Figure 1) which was associated with polymorphic transformation, revealed by quenching the heated product in liquid nitrogen. On further heating, no weight loss was noted.

CONCLUSION

Results of X-ray diffraction and optical crystal analysis of the final product indicated the presence of Gadolinium tungstaten oxide of different composition. This suggests the general decomposition scheme:-

$$Gd_3WO_6Cl_3 \xrightarrow[Cl_2]{+\frac{1}{2}O_2} GdWO_7Cl \xrightarrow[-\frac{3}{2}Cl_2]{+\frac{1}{2}O_2} Gd_3WO_{7.5}$$

During heating, the studied compound underwent stepwise decomposition process fashioned by polymorphic transformation attested by the exothermic effect in the DTA curve

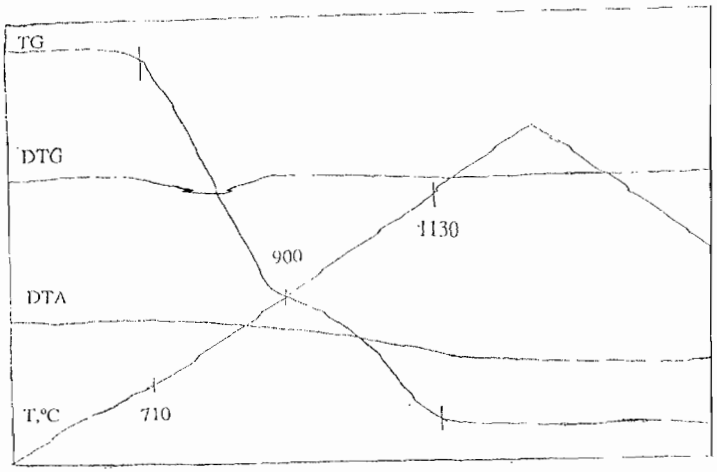

Fig. 1: Thermodecomposition of $Gd_3WO_6Cl_3$ in air

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