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THERMANALYTICAL INVESTIGATIONS ON THE REACTIONS OF LANTHANUM OXIDE WITH AMMONIUM HALIDES

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Abstract

The reactions of lanthanum oxide and ammonium halides were studied by means of dynamic methods of thermal analysis (DTA, TG, EGA). The reactions result in the formation of oxyhalides, trihalides or mixtures of them, depending on the ratio of La_2O_3 and NH_4X (X = Cl, Br). The reaction course and the influence of experimental conditions are discussed. In the case of quasi-isobaric conditions the formation of intermediate compounds corresponding to the formulas $LaX_3 \cdot 3\ NH_3 \cdot H_2O$, $LaX_3 \cdot 2\ NH_3 \cdot H_2O$, $LaX_3 \cdot NH_3 \cdot 0{,}5\ H_2O$ and $LaX_3 \cdot 2\ NH_4X$ were observed.

Introduction

In recent years the oxyhalides of lanthanum have proved to be particularly efficient host lattices for the preparation of rare earth activated X-ray phosphors. Their synthesis may be effected, for example, on the basis of the reaction of La_2O_3 and NH_4X (X = Cl,Br), in which depending on the reaction conditions lanthanum trihalides can also be formed. Although these reactions have been known for a long time /1/, only few results of corresponding thermoanalytical investigations can be found in the literature. Thus MARKOVSKI, PESINA and OMEL'ČENKO /2/ report that LaOCl is formed when 2 mol NH_4Cl are added to 1 mol La_2O_3, whereas for the preparation of $LaCl_3$ a La_2O_3/NH_4Cl molar ratio of 1:6 is necessary. According to the details given by the authors the reactions take place in two stages and $[La(NH_3)_3]Cl_3$ is said to be formed as an intermediate compound. HÖLSÄ and NIINISTO /3/, however, postulate for the corresponding reaction of La_2O_3 and NH_4Br the formation of a furhter intermediate product which has the composition $[La(NH_3)_{1,5}]X_3$. By varying the analytical conditions and by including additional methods of investigation we tried to obtain further information on the reaction course.

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Methods

The simultaneous thermoanalytical measurements were carried out by means of a MOM-Q-derivatograph combined with a thermo-gas-titrimeter. Different sample holders (open and covered standard crucibles, polyplate sample holders, labyrinth crucibles) were used. Moreover, heating rate ($0,6 < q < 10$ K min^{-1}) and atmosphere (air and N_2 resp.) were varied. α -Al_2O_3 served as a reference material for the DTA measurements. The X-ray diffraction study of the final products of the reactions investigated was carried out using a diffractometer.

Results and Discussion

Fig.1 shows the recorded TG, DTG and DTA curves for the reactions of 1 mol La_2O_3 with 2 mol NH_4Br using a covered standard crucible ($q = 2,5$ K^{-1}) and a labyrinth crucible ($q = 0,6$ K min^{-1}).

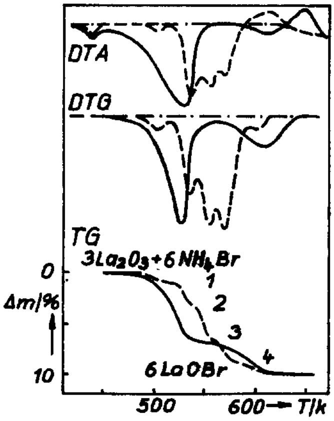

Fig.1: 1 - $2La_2O_3+2[LaBr_3 \cdot 3NH_3 \cdot H_2O]$,
2 - $2La_2O_3+2[LaBr_3 \cdot 2NH_3 \cdot H_2O]$,
3 - $2La_2O_3+2[LaBr_3 \cdot NH_3 \cdot 0,5H_2O]$,
4 - $2La_2O_3+2[LaBr_3 \cdot 0,5H_2O]$

This figure demonstrates that the course of thease reactions depends to a large extent on the NH_4Br partial pressure which can be obtained in the sample environment. If a covered standard sample holder was used two stages of reaction were observed. In contrast to this, the TG curve obtained under quasi-isobaric conditions (labyrinth crucible) shows several breaks and plateau-like slopes, which seem to indicate a more complex "reaction mechanism". In all cases investigated the final product was LaOBr. This could also be proved by means of X-ray diffraction and chemical analytical methods.

It is interesting to note that in addition to the endothermic effects corresponding to the DTG signals and the phase transition of NH_4Br respectively, the DTA curves also exhibit characteristic exothermic peaks. The corresponding change of enthalpy is only observed after the TG plateau which is characteristic for LaOBr has been reached. The suggestion that this exothermic DTA effect might be related to the solid state reaction

$$La_2O_3 + LaBr_3 \longrightarrow 3\ LaOBr \qquad (1)$$

could be confirmed by comparative measurements /4/.

The gaseous compounds released during the reaction (NH_3,H_2O) do not differ very much as regards their mol-ar masses. Thus it is difficult to draw conclusions from the thermogravimetric measurements alone on the composition of the intermediarily formed phases and to formulate the corresponding reaction equations. Therefore Fig.2 represents the results of the thermogastitrimetric NH_3 analysis (TGT) for the reaction of 1 mol La_2O_3 with 2 mol NH_4Br which was performed in the labyrinth crucible ($q=0{,}6\ K\ min^{-1}$). From this figure it becomes clear that ammonia related to a reaction mixture composed of $3La_2O_3+6\ NH_4Br$ is released in three separate stages of 2 mol each. Simultaneously 1 mol $H_2O(g)$ is being produced in the region between 538 and 558 K. A further mol H_2O is released at the beginning of the reaction, whereas the remaining amount of H_2O (1 mol) is only released immediately before LaOBr is formed. Summing up our results we can say that the pattern of the reaction course we obtained considerably differs from that reported on in the literature. The course is characterised by the partial formation of a compound with the composition $LaBr_3 \cdot 3NH_3 \cdot H_2O$, its step-like decomposition and by the reaction of the formed $LaBr_3$ with the unreacted La_2O_3 (Fig.1). In this connection it must be taken into account that reaction (1) already starts before the last H_2O is released.

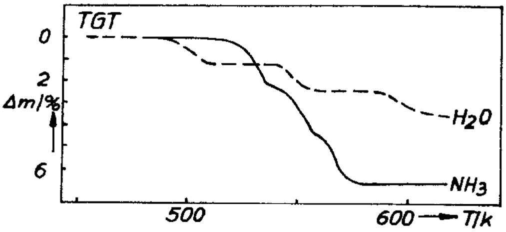

Fig.2: TGT-measurements

In the reactions of La_2O_3 with 6 mol NH_4X the full amount of La_2O_3 first reacts to $LaX_3 \cdot 3NH_3 \cdot H_2O$. In the labyrinth crucible the decomposition of the $LaX_3 \cdot NH_3 \cdot 0{,}5H_2O$ complex starts at 640 K(X = Cl) and 650 K(X = Br) respectively. However, it does not result in a pure LaX_3 compound /5/ (cf.Fig.3), no matter whether air or an inert atmosphere is used. This is obviously due to the hydrolysis of LaX_3 caused by the $H_2O(g)$ evolved during the decomposition of the $LaX_3 \cdot NH_3 \cdot 0{,}5H_2O$ complex.

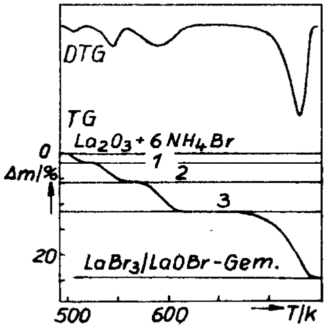

Fig.3: TG-DTG curves for the reaction of La_2O_3 with 6 moles NH_4Br ($q = 0{,}6\ K\ min^{-1}$, static air)
1 - $2[LaBr_3 \cdot 3NH_3 \cdot H_2O]$
2 - $2[LaBr_3 \cdot 2NH_3 \cdot H_2O]$
3 - $2[LaBr_3 \cdot NH_3 \cdot 0{,}5H_2O]$

Anhydrious lanthanum trihalides are only formed when the amount of the NH_4X added is further increased. As can be seen from Fig.4 the LaX_3 formation is mediated by the production of an intermediate $LaX_3 \cdot 2NH_4X$ compound. These results are in good agreement with the findings of MEYER and AX /6/ on the basis of high-temperature X-ray-diffraction studies. The formation of $(NH_4)_3LaCl_6$ ($LaCl_3 \cdot 3NH_4Cl$ resp.) phases could, however, not be observed by us, even when a much higher amount of NH_4X (> 12 mol) was added.

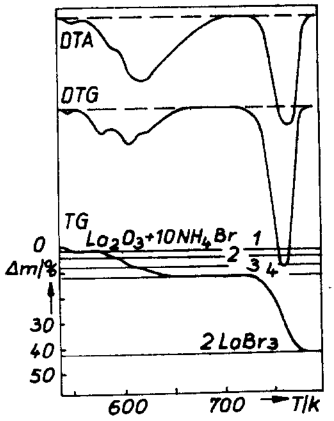

Fig.4: TG-DTG curves for the reaction of La_2O_3 with 10 moles NH_4Br (Labyrinth crucible, $q = 2{,}5\ K\ min^{-1}$, static air) 1 - $2[LaBr_3 \cdot 3NH_3 \cdot H_2O] + 4NH_4Br$, 2 - $2[LaBr_3 \cdot 2NH_3 \cdot H_2O] + 4NH_4Br$, 3 - $2[LaBr_3 \cdot NH_3 \cdot 0{,}5H_2O] + 4NH_4Br$, 4 - $2[LaBr_3 \cdot 2NH_4Br]$

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