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THERMAL STABILITY OF Eu^{3+} ACTIVATED RARE EARTH HYDROGENSELENITES

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ABSTRACT

The thermal behaviour of Eu^{3+} activated rare earth (La, Gd, Y, Lu) hydrogen selenite hydrate was studied. After dehydration $REH(SeO_3)_2$ decomposes to corresponding selenite at 670 – 77 K depending on the rare earth. The selenite decomposes further to oxyselenite at about 970 K. The stability range of the oxyselenite phase is 100 – 150 degrees decrasing with decreasing with decreasing ionic radius. The behaviour of lanthanum compound differs from that of the others.

The Eu^{3+} luminescence was found to be a sensitive probe of the thermal decomposition scheme of rare earth hydrogenselenites.

INTRODUCTION

In luminescence spectroscopical manner the rare earth oxycompounds with a general formula of $(REO)_n^{n+}X^{n-}$ form uniform groups. The luminescence properties of compounds where $X = S^{2-}$, Cl^-, Br^-, I^-, SO_4^{2-} and MoO_4^{2-} have so far been studied /1/.

In the present work the preparation of Eu^{3+} activated (1 mole %) rare earth oxyselenites, $(REO)_2SeO_3$ (RE = La, Gd, Y, Lu), by thermal decomposition of corresponding hydrogen selenites was studied. The luminescence properties of these compounds were characterized, too.

EXPERIMENTAL

The rare earth hydrogen selenites were prepared as described elsewhere /2/. According to chemical analysis and X-ray diffraction (XRD) studies the formula of the compounds corresponded to $REH(SeO_3)_2.2.5H_2O$ except the lanthanum compound which contained only 0.5 – 1 molecule of water. The diffraction pattern of the La compound differed from the others, too.

The thermoanalytical studies were carried out with a Perkin-Elmer TGS-2 thermobalance (T_{max} = 1000 °C) and DTA-1700 equipment connected to System 7/4 controller and TADS data station. Dynamic air atmosphere and a heating rate of 7.5 °C min^{-1} were used. The XRD powder patterns were recorded with a Philips diffractometer. The instrumentation employed in luminescence measurements has been presented elsewhere /3/.

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RESULTS

According to the TG curves of gadolinium, yttrium and lutetium hydrogen selenites their decomposition mechanism can be presented as follows: $REH(SeO_3)_2 \cdot 2.5H_2O \xrightarrow{1.} REH(SeO_3)_2 \xrightarrow{2.} 1/2RE_2(SeO_3)_3 \xrightarrow{3.} 1/2RE_2O_2SeO_3 \xrightarrow{4.} 1/2RE_2O_3$ The DTA-measurements revealed the endothermic nature of all reactions. The calculated weight changes agree with the observed ones. In the first reaction the water molecules are released in two stages (Fig. 1). The stability of the anhydrous hydrogen selenite phase extends to 300 degrees increasing from gadolinium to lutetium (Table 1). The second reaction stage comprises a simultaneous release of SeO_2 and H_2O and H_2O and formation of rare earth selenite. The decomposition temperature of $RE_2(SeO_3)_3$ does not change much along the rare earth series. This is in agreement with an earlier investigation /4/.

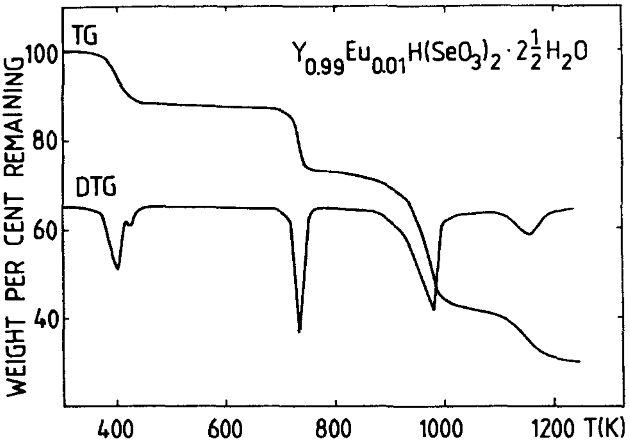

Fig. 1. The TG and DTG curves for $YH(SeO_3)_2 \cdot 2.5H_2O$: Eu^{3+} heated in air.

Table 1. DTG peak temperatures (K) for the decomposition reaction of $REH(SeO_3)_2 \cdot 2.5H_2O$. The reaction numbers corresponds to those presented in the decomposition scheme except the La compound

RE	Reactions			
	1	2	3	4
La	480	750	1065	1275
Gd	410	700	980	1200
Y	410	750	1000	1180
Lu	385	805	955	1105

The formation of an intermediate phase of the formula $RE_2O_2SeO_3$ is clear in the decomposition of rare earth selenite to oxide. In contrast to earlier reports no oxydiselenite phase, $RE_2O(SeO_3)_2$, could be detected in the present work /5,6/. The stability of the oxyselenite phase obtained decreases with decreasing ionic radius of the RE^{3+} (Table 1). The oxyselenite plateau observed in the TG curves is not completely horizontal but a small weight decrease occurs during heating.

The lanthanum hydrogen selenite behaves exceptionally. First the composition and the structure of the starting compound differ from the others. Secondly the weight change to oxyselenite does not correspond well to the calculated value. Thirdly the diffraction diagram of the oxyselenite phase differs from that of Gd, Y and Lu compounds and the diagram shows similarities to that of $La_2O_2SO_4$. Finally the luminescence spectrum of the lanthanum compound was unresolved.

The formation and stability of the crystalline oxyselenite phase can be monitored by measuring the luminescence spectra of the samples fired isothermally at various temperatures. The Eu^{3+} luminescence depends sensitively on the host compound. Moreover, the spectral fine structure becomes unresolved for badly crystallized or multiphase materials (Fig. 2). The optimum firing temperatures found with the aid of luminescence were 970 K for $(GdO)_2SeO_3$ and $(YO)_2SeO_3$ and 920 K for $(LuO)_2SeO_3$.

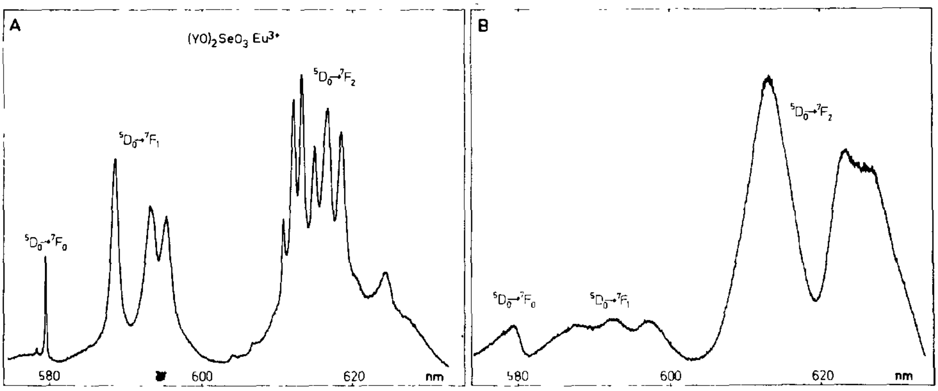

Fig. 2. Part of the Eu^{3+} emission spectra in $(YO)_2SeO_3$ (A) fired at 970 and (B) 1070 K.

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