PHASE TRANSFORMATIONS IN COMPLEX OXIDES OF
RARE EARTH ELEMENTS

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ABSTRACT

Thermal transformations in rare earth aluminates, germanates and phosphates have been studied. The existence of phase transitions was established for rare earth aluminates of the perovskite type. A wide range of transformations and structural types were observed for germanates and phosphates of the whole series of lanthanoids. Hydrated forms of phosphates are of special interest.

INTRODUCTION

A complex study of the whole classes of rare earth compounds - aluminates, germanates and phosphates - permitted us to establish certain regularities of the formation and thermal transformations for each homologous group and the whole family of rare earth compounds.

METHODS OF INVESTIGATION AND RESULTS

Various methods were used for the study: DTA, TGA, X-ray diffraction, microscopy, chemical analysis and IR-spectroscopy.

For the homologous group of rare earth aluminates, the existence of four types of compounds was established: $Ln_4Al_2O_9$, the perovskite-like $LnAlO_3$, the garnet-like $Ln_3Al_5O_{12}$ and the β -type alumina with the hypothetic formula $LnAl_{11}O_{18}$ /1,2/. The compounds $LnAlO_3$ and phases of the β -alumina structure are characteristic of the beginning of the rare earth series (La-Gd) and stable within a wide temperature range (up to the melting); aluminates of Tb-Y are stable in a narrow temperature range ($\sim$1600-2000°C); the elements H-Lu form only metastable aluminates /3,4/.

Compounds of the β -alumina type have a hexagonal structure and represent phases of non-stoichiometric composition. The limits of homogeneity are Ln_2O_3 : Al_2O_3 = 1:10 ÷ 1:12. The compounds possess high cationic conductivity. The conductivity of Al^{3+} in β -Al_2O_3 was established in /5/. For the end of the rare earth

series, stable compounds are $Ln_4Al_2O_9$ and $Ln_3Al_5O_{12}$ /1,6,7/.

Rare earth germanates form four types of compounds: Ln_4GeO_8, oxyortho- ($Ln_2/GeO_4/O$) and diortho- ($Ln_2Ge_2O_7$) germanates and apatite-like compounds $Ln_{4.67}/GeO_4/_3O$; the latter being found only for the beginning of the rare earth series (La-Gd) /1,8/.

Two subgroups with the boundary element Tb are characteristic of compounds $Ln_2/GeO_4/O$; they have monoclinic crystal structure with different space groups.

The apatite-like germanates are hexagonal and represent cation-deficient oxyapatite $Ln_{9.33}O_{0.67}/GeO_4/_6O_2$. Diorthogermanates fall into four subgroups: compounds of the first (La-Pr) and second (Nd-Gd) groups are triclinic; those of the third (Tb-Lu) and fourth (Sc) subgroups are tetragonal and monoclinic, respectively.

For lanthanum germanates, the sequence and rate of formation of intermediate phases were established under isothermal conditions at temperatures 750-950°C. The Erofeev equation for chemical kinetics was used /9/ :

$$\alpha = 1 - e^{-kt^{-n}} ,$$

where α is the portion of the reacted substance; t is the time in minutes; n is a constant connected with the reaction mechanism. The reaction mechanism is determined by the fact that for all compositions a compound La_4GeO_8 forms at 750°C. With increasing time and temperature of firing, together with the compound La_4GeO_8 germanates with a higher content of GeO_2 form, the apatite-like phase $La_{4.67}/GeO_4/_3O$ being the predominant phase. An exception is La_4GeO_8 for which $La_2/GeO_4/O$ is an intermediate phase. An increase of temperature leads to the formation of germanates with appropriate compositions.

The third homologous group comprises rare earth phosphates. They are represented by a large series of compounds with various Ln_2O_3/P_2O_5 ratios. At high temperatures the following compounds are stable: oxyphosphates (LnO_3)/PO_4/ (3:1); ortho- ($LnPO_4$), meta- ($Ln(PO_3)_3$) and ultra- (LnP_5O_{14}) phosphates /10-13/. The compounds (LnO_3)/PO_4/ are monoclinic and decompose in the solid state. Meta- and ultraphosphates melt incongruently and crystallize in the rhombic and monoclinic structures, respectively. Orthophosphates melt congruently and possess the greatest variety of ther-

mal transformations and structural forms: hexagonal, monoclinic,
tetragonal. Using the coprecipitation methods, hydrated forms of
orthophosphates from La to Dy containing 1-2 water molecules per
formula unit were obtained; they have a hexagonal crystal struc-
ture. As was shown for $LaPO_4 \cdot xH_2O$ and $GdPO_4 \cdot xH_2O$, the removal of
water from the samples goes in two stages, the second step being
reversible (~ 0.4 H_2O). The step-like course of dehydration is
apparently due to the presence in the samples of water molecules
of different degree of mobility; the existence of adsorbed and
zeolitic water is possible here. The high-temperature IR-spectra
show a gradual decrease of water content and the full absence of
water at 700°C. The compositions of the initial samples were es-
tablished to be $LaPO_4 \cdot 1.5H_2O$ and $GdPO_4 \cdot 1.0H_2O$; after the vacuum
pumping at room temperature those compositions were as follows:
$LaPO_4 \cdot 1.1$ H_2O and $GdPO_4 \cdot 0.8$ H_2O. (Fig. 1, a,b).

Thus, a great variety of thermal transformations, structural
forms and their stability were shown for each homologous group of
the aluminates, germanates and phosphates. This is related to the
different degree of participation of $4f$ -orbits in the bonds of
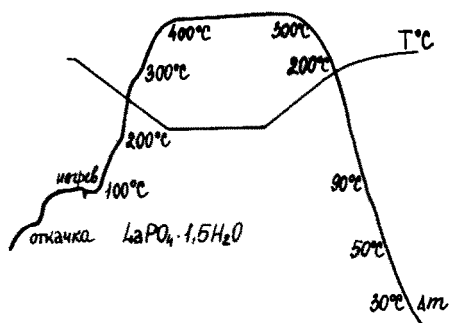La-Lu oxides and to the definite role played by a second oxide
(La_2O_3, GeO_2 or P_2O_5).
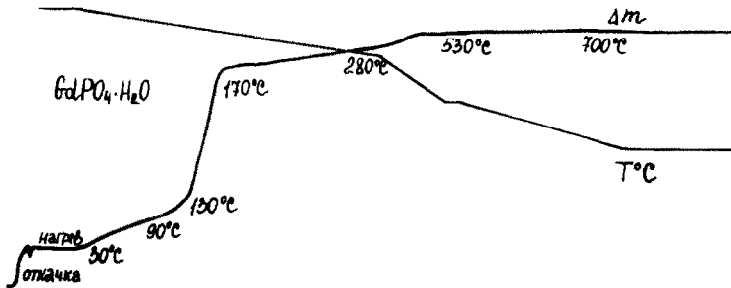

Fig. 1 (a). TGA curves for $LaPO_4 \cdot 1.5$ H_2O .

Fig. 1 (b). TGA curves for $GdPO_4 \cdot 1.0\ H_2O$.

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