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THERMAL DECOMPOSITION OF SOME DOUBLE SULFATES OF Ce(III) AND Pr(III) WITH TETRAMETHYLAMMONIUM

A b s t r a c t. By the reaction of Ln(III) sulfate with tetramethylammonium, besides double sulfates of cerium(III) and praseodymium(III) with empirical formula $(CH_3)_4NLn(SO_4)_2 \cdot 3H_2O$ (recently presented [7]), double sulfates with empirical formula $(CH_3)_4NLn(SO_4)_2 \cdot xH_2O$, where x = 10 for Ln = Ce and for Ln = Pr, x = 5 were obtained. Besides these, in higher molar ratio, double sulfates with empirical formula: $[(CH_3)_4N]_4 Ln_2(SO_4)_5 \cdot 10H_2O$ (where Ln = Ce or Pr) were also obtained. The constitution of their formulae were established on the basis of TG curves of their thermal decomposition as well as of their elemental analysis. As a final product at 700°C of the thermal decomposition of both cerium compounds, cerium(III)sulfate is obtained, whereas of both praseodymium compounds, praseodymium oxysulfate. X-Ray powder diffraction patterns of the obtained double sulfates point out an isostructurality of the compounds with the higher stoichiometry.

Introduction

Double sulfates of rare earths(III) with different monovalent cations are a subject of many investigations [1, 2]. There are also a lot of data on the thermal decomposition of double sulfates with nonmetallic monovalent cations, such as: monomethylammonium [3, 10], dimethylammonium [4, 11, 12], trimethylammonium [5, 6], and tetramethylammonium [7]. Recently, the crystal structures of double sulfates of rare earths with dimethylammonium [8] and tetramethylammonium [9] were presented. From the presented results, it can be concluded that rare earths(III) form different crystallohydrates with the same as well as with different monovalent cations.

Besides double sulfates with stoichiometry of $Ln_2(SO_4)_3 : M_2SO_4$ equal to 1 : 1, there are also some data on double sulfates with other stoichiometry with larger monovalent cations such as potassium, cesium and rubidium [2]. We have found data on the double sulfates of neodymium and praseodyimium

As can be seen from Fig. 1a, the dehydration of the double sulfate dekahydrate of cerium(1) begins at a low temperature (about 40 °C) and maximum rate is reached at about 100 °C and takes place in a single step. The thermal decomposition of anhydrous double sulfate up to 500 °C takes place in the same way described previously for trihydrate [7], in two steps related with two exothermic peaks. As a final product cerium(III) sulfate is obtained (Table 1). An intensive exothermic peak at about 555 °C related to a small mass loss can be attributed to the oxidation of liberated carbon.

The dehydration of the double sulfate pentahydrate of praseodymium (2) (Fig. 1b) begins also at a low temperature (about 40 °C) and proceeds at a different rate. On DTA curve, five endothermic peaks can be noticed. The second stage of the thermal decomposition is identical with that of double sulfate trihydrate of praseodymium [7]. At about 550 °C, an intensive exothermic

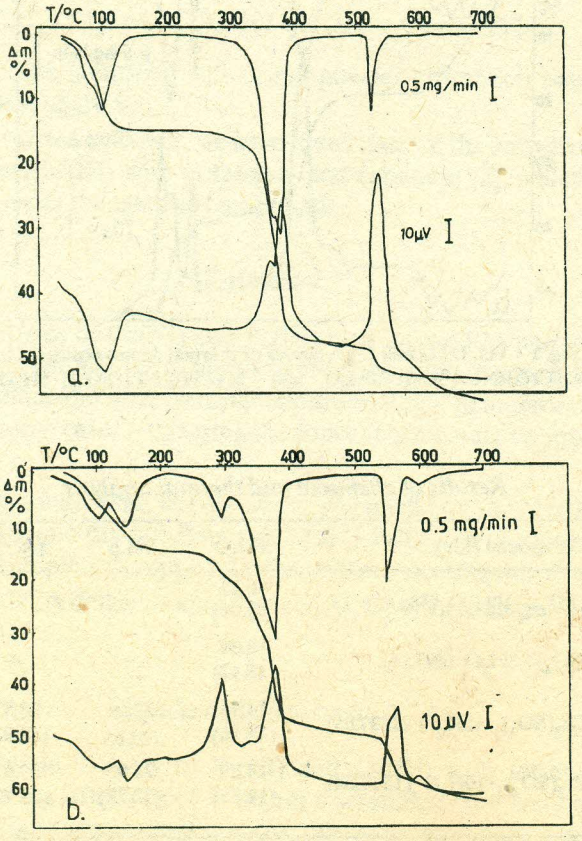

Fig. 2 – TG, DTG and DTA curves of thermal decomposition of $[(CH_3)_4N]_4Ln_2(SO_4)_5 \cdot 10H_2O$: a. Ln = Ce; b. Ln = Pr.

peak can be noticed, which can be also attributed to oxidation of the liberated carbon, as in the case of Ce-compound. At 570 °C praseodymium sulfate is obtained. From the mass of the residue at 700 °C one can conclude that $Pr_2O(SO_4)_3$ as a final product is obtained. An intensive exothermic peak at about 600 °C related to a mass loss, confirmed the possibility of a transformation of praseodymium(III) sulfate to praseodymium(III) oxysulfate.

Double sulfates of cerium(3) and praseodymium(4) with stoichiometry 1 : 2 : 5 (Table 1), are obtained in a molar ratio 1 : 20. From their X-ray powder diffraction patterns, it was concluded that they are isostructural. However, their thermal decomposition (Fig. 2) takes place in a different way and three stages can be noticed. The decomposition of the Ce-compound(3) is similar to that of Ce(1) (compare Figs. 1a and 2a). The dehydration, which is in one step, begins at a temperature higher then 50 °C and ends at about 120 °C, whereas that of Pr-compound begins at the same temperature but ends at about 160 °C and proceeds in two steps. The second stage, where the decomposition of anhydrous salt takes place, in the case of Ce-compound, begins at about 310 °C, ends at about 400 °C and is related to two very close exothermic peaks. The third stage is related to a very intensive exothermic peak at about 540 °C and small mass loss (about 3%). It is possibly due to oxidation of a liberated carbon to carbon oxide identical to that in Ce(1). As a final product at 700 °C cerium sulfate is obtained. The thermal decomposition of the anhydrous double sulfate of Pr begins at about 290 °C and takes place to about 400 °C and is related to two exothermic peaks which are differentiated better than by Ce-compound(3). It indicates the possibility of a formation of intermediate products. At about 567 °C, as with Pr(2), an intensive exothermic peak also appears, but the other one at about 600 °C is not as intensive as the one with Pr(2). As a final product, $Pr_2O(SO_4)_2$ is obtained, suggested from the mass of the residue 38.92%, and the calculated value 39.57%.

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ТЕРМИЧКО РАЗЛОЖУВАЊЕ НА НЕКОИ ДВОЈНИ СУЛФАТИ НА Ce(III) И Pr(III) СО ТЕТРАМЕТИЛАМОНИУМ

(Резиме)

При реакција на лантанид(III)сулфат и тетраметиламониум сулфат, покрај двојни сулфати на Ce(III) и Pr(III) со емпириска формула $(CH_3)_4NLn(SO_4)_2 \cdot 3H_2O$, презентирани не многу одамна [7], се добиени и повисоки кристалохидрати на двојните сулфати на цериум и празеодимиум со емпириски формули $(CH_3)_4NLn(SO_4)_2 \cdot xH_2O$, каде за Ln = Ce x=10, а за Ln = Pr x=5, како и двојни сулфати со емпириска формула: $[(CH_3)_4N]_4Ln_2(SO_4)_5 \cdot 10H_2O$ (Ln=Ce и Pr). Нивните емпириски формули се добиени врз база на термогравиметриските криви на нивното термичко разложување, како и врз база на елементарната анализа. При разложување на двете цериумови соединенија како конечен продукт при 700 °C е добиен цериум(III) сулфат, додека при разложување на празеодимиумовите соединенија се добива празеодимиум(III) оксисулфат. Рендгенските слики на нивните прашкови покажуваат изоструктурност на соединенијата со повисокиот стехиометриски однос.

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