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DETERMINATION OF THE MIXING ENTHALPY OF SOLID SOLUTIONS IN THE SYSTEM Y_2O_3—Nd_2O_3

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Experimentally established heats of solution of Y_2O_3, Nd_2O_3 *and of three solid solutions in the system* Y_2O_3—Nd_2O_3 *in nitric acid (vol. ratio* $HNO_3 : H_2O = 1 : 1$) *at 298 K were used for determining the enthalpy of mixing for the formation of solid solutions in this system. All the specimens, the heats of solutions of which were measured, had a body-centered cubic lattice. The non-zero values of the enthalpy of mixing have shown, that the solid solutions in the system* Y_2O_3—Nd_2O_3 *are non-ideal.*

INTRODUCTION

The present study had the aim to determine the values of the enthalpy of mixing due to the formation of solid solutions in the system Y_2O_3—Nd_2O_3, which is significant for a better understanding of the chemistry of lanthanides and yttrium. The value of this quantity is a criterion for the determination of the thermodynamic character of these phases.

EXPERIMENTAL

The determination of the enthalpy of mixing of solid solutions in the system Y_2O_3—Nd_2O_3 was based on measurement of the heats of solution of the pure components Y_2O_3 and Nd_2O_3 and of three solid solutions having the composition (the numbers in brackets are numerical values of mole fractions in percent of pure components Y_2O_3 and Nd_2O_3 in the respective solid solution): $Y_2O_3(75)$—$Nd_2O_3(25)$, $Y_2O_3(50)$—$Nd_2O_3(50)$ and $Y_2O_3(30)$—$Nd_2O_3(70)$ in dilute HNO_3 (in vol. ratio 1 : 1) at 298 K.

The specimens were prepared from yttrium oxide (mark ITO-1) containing 99.96 wt. % Y_2O_3, and neodymium oxide (mark NO-SS) cotaining 99.99 wt. % Nd_2O_3, as follows: The calculated mixture of the oxides was dissolved in dilute HNO_3 (in vol. ratio 1 : 2) at 80 °C. Hydrates of the oxides were precipitated by introducing the acid solution into a concentrated aqueous ammonia solution (pH > 10). The precipitate, which was probably a solid solution of the oxide hydrates, was dried at 200 °C for four hours, and then fired for three hours in air at 600 °C, thus yielding the respective solid solution of oxides with the given composition. All the solid solution specimens used in the measurements of the heat of solution had a body-centered cubic lattice characteristic of rare earth oxides (the so-called C-structure [1]).

The heats of solution of the individual specimens were determined in the solution calorimeter, described in [2] together with the respective measuring procedure.

RESULTS

Using X-ray diffraction data, the lattice parameters a of the cubic solid solutions in the system Y_2O_3—Nd_2O_3 were determined; a plot of their dependence on composition is shown in Fig. 1.

The heats of solution ($\Delta H_{sol,\varphi}$) determined for Y_2O_3, Nd_2O_3 and for three solid solutions as mean values of two or three measurement for each specimen are listed in Table I (φ is a designation of arithmetic mean) with a maximum relative error of 2.8 %.

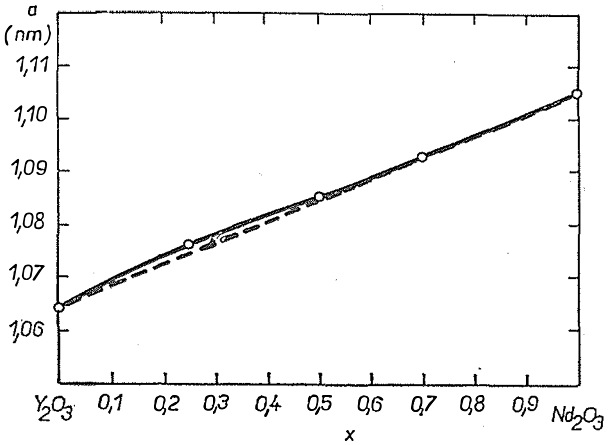

Fig. 1. Dependence of parameter a of the elementary cell on composition of solid solution in the system Y_2O_3—Nd_2O_3.

Table I

Composition of solid solution	$\frac{\Delta H_{sol,\varphi}}{kJ\ mol^{-1}}$	$\frac{\Delta H_{sol,id}}{kJ\ mol^{-1}}$	$\frac{\Delta H_{mix}}{kJ\ mol^{-1}}$
Y_2O_3	−364.6	−364.6	0
$Y_2O_3(75)$—$Nd_2O_3(25)$	−377.4	−354.9	22.5
$Y_2O_3(50)$—$Nd_2O_3(50)$	−377.7	−345.1	32.6
$Y_2O_3(30)$—$Nd_2O_3(70)$	−323.5	−337.3	−13.8
Nd_2O_3	−325.6	−325.6	0

The enthalpy of mixing values for the formation of solid solutions, ΔH_{mix}, were determined from the differences ($\Delta H_{sol,id} - \Delta H_{sol,\varphi}$) for the specimens of the respective compositions. $\Delta H_{sol,id}$ is the value of the heat of solution of an ideal solution of a given composition given by the equation

$$\Delta H_{sol,id} = (1 - x)\, \Delta H_{sol,Y_2O_3,\varphi} + x\, \Delta H_{sol,Nd_2O_3,\varphi} \qquad (1)$$

where x is the mole fraction of Nd_2O_3 in the respective specimen. The values of $\Delta H_{sol,id}$ and ΔH_{mix} are likewise listed in Table I.

Whereas the concentration dependence of the lattice parameter is almost linear throughout the entire range (Fig. 1), the ΔH_{mix} values first increase with increasing

Nd_2O_3 content in solid solution with Y_2O_3 (the composition range 0—50 mole % Nd_2O_3) thereafter showing a decrease (the composition range 50—70 mole % Nd_2O_3) (Table I). The relatively great errors involved in the determination of ΔH_{mix} do not affect the character of the dependence. The concentration dependence of the enthalpy of mixing for the system Y_2O_3—Nd_2O_3 thus indicate, that the solid solutions of its components are non-ideal. The non-ideality of the solid solutions of this system may be the result of formation of ordered solid solutions arising at the considerable difference in the ionic radii: $r(^{VI}Y^{3+}) = 0.090$ nm, $r(^{VI}Nd^{3+}) = 0.0983$ nm [3]; the same behaviour is exhibited, for instance, by the systems La_2O_3—Dy_2O_3, La_2O_3—Er_2O_3, La_2O_3—Yb_2O_3 [4].

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STANOVENIE ZMIEŠAVACEJ ENTALPIE TUHÝCH ROZTOKOV SÚSTAVY Y_2O_3—Nd_2O_3

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Pripravili sa tri tuhé roztoky sústavy Y_2O_3—Nd_2O_3, Y_2O_3 a Nd_2O_3 s kubickou, priestorovo centrovanou mriežkou, ktorej odpovedá približne lineárna závislosť mriežkového parametru od koncentrácie. V kalorimetri pre meranie rozpúšťacích tepiel sa namerali ich rozpúšťacie teplá v kyseline dusičnej (1 : 1) pri teplote 298 K. Z hodnôt zmiešavacej entalpie pri vzniku tuhých roztokov sústavy Y_2O_3—Nd_2O_3 vyplynulo, že tuhé roztoky tejto sústavy vykazujú neideálne chovanie.

Obr. 1. Závislosť parametra a elementárnej bunky od zloženia tuhého roztoku sústavy Y_2O_3—Nd_2O_3.

ОПРЕДЕЛЕНИЕ ЭНТАЛЬПИИ СМЕШИВАНИЯ ТВЁРДЫХ РАСТВОРОВ СИСТЕМЫ $У_2O_3$—Nd_2O_3

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Были получены три твёрдые раствора системы $У_2O_3$—Nd_2O_3, $У_2O_3$ и Nd_2O_3 с кубической объёмноцентрированной решеткой, которой соответетствует приблизительно линейная зависимость параметра решетки от концентрации. С помощью калориметра для определения теплоты растворения, измеряли их теплоты растворения в азотной кислоте (объёмное соотношение $HNO_3 : H_2O = 1 : 1$) при температуре 298 К. Из величин энтальпии смешивания при образовании твёрдых растворов системы $У_2O_3$—Nd_2O_3 следует, что твёрдые растворы данной системы имеют неидеальное поведение.

Рис. 1. Зависимость параметра a элементарной ячейки решетки от состава твёрдого раствора системы $У_2O_3$—Nd_2O_3.