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THERMOANALYTICAL STUDIES OF THE FORMATION OF NEODYMIUM TITANATES

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The existence of the compounds with the Nd_2O_3: TiO_2 ratio 1:1, 1:2, 1:4,5 in the system Nd_2O_3-TiO_2 is well known. The compounds $Nd_2O_3 \cdot TiO_2$, $Nd_2O_3 \cdot 2TiO_2$, and $Nd_2O_3 \cdot 4{,}5\ TiO_2$ have been investigated in detail. Their structure and properties have been described in /1,2,3,4,5/. The compound $Nd_2O_3 \cdot 3TiO_2$ with the defect perovskite structure has been synthesized /3/ by coprecipitation and exists in the temperature range 400 to 1000 C. The $Nd_{2-x}Ti_{2+x}O_{7+\frac{x}{2}}$ (x=0,4) phase with the pyrochlore structure has been obtained by the reaction of the coprecipitated hydroxides. The decomposition of pyrochlore into $Nd_2O_3 \cdot 4{,}5TiO$ and $Nd_2O_3 \cdot 2TiO_2$ has been observed above 1000°C /2/. Other published data on properties of the compound $Nd_2O_3 \cdot 3TiO_2$ are not available.

The aim of our work is to investigate the crystallization of the products of coprecipitation with Nd_2O_3 : TiO_2 ratio from 3 to 4,5. The investigations have been carried out by means of thermoanalytical method at the two heating rates with subsequent X-ray analysis of quenched specimens. X-ray data have been obtained on diffractometers DRON-2 and DRON-3 using CuK_α- and CoK_α -radiation. Unit cell parameters have been determined by the least square method using reflections in the range 2θ 80-160°. Thermoanalytical studies of specimens have been carried out using the apparatus constructed at the Silicates Chemistry Institute of the Academy of Sciences of the USSR. As-prepared specimens were rinsed in water and then were heated for two hours at 300°C. Thermographs of specimens with Nd_2O_3 : TiO_2 ratio 1:3, 1:3,5, 1:4, 1:4,5 (the heating rates are 10 and 30°/min) are given in Fig.1. As seen in the figure exothermal effects were observed at 800 to 1100°C, their number and intensity being dependent on specimen compositions and heating rates. The results of X-ray analysis of specimens quenched at different temperatures are given in Table I.

From these results it may be concluded that for the specimens of the composition $Nd_2O_3 \cdot 3TiO_2$ the heating rates effect not only the impurity amount but the composition of the main phase as well.

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At the heating rate 10^{o}/min the main phase of crystallization is pyrochlore; the increase of heating rate up to 30^{o}/min results in the formation of structure $Nd_2O_3 \cdot 2TiO_2$, pyrochlore being not found. Previously in /2/ the product of crystallization for the composition $Nd_2O_3 \cdot 3TiO_2$ was only pyrochlore. The dependence of phase composition of specimens on the heating rate indicates indirectly to the defective-mode structure of pyrochlore formed.

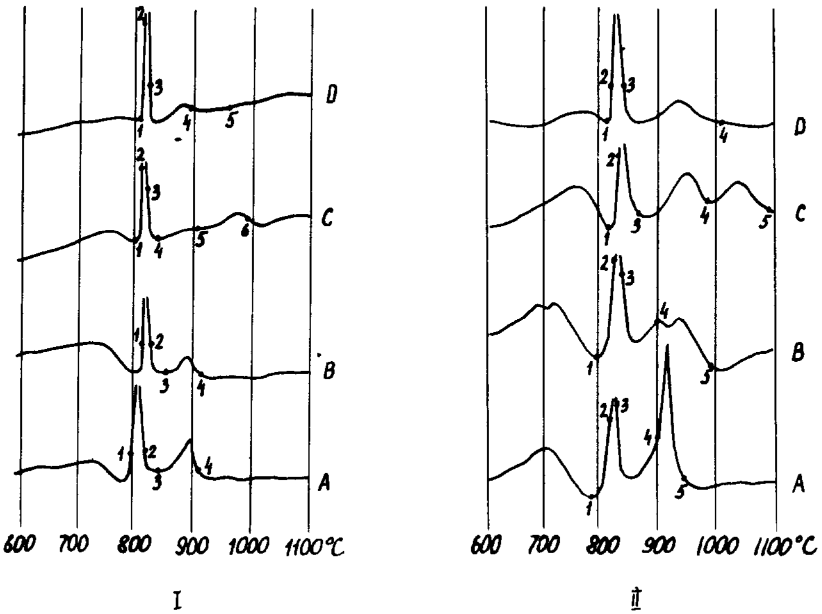

Fig.1. Thermographs of specimens with compositions A - $Nd_2O_3 \cdot 4,5TiO_2$ B - $Nd_2O_3 \cdot 4TiO_2$; C - $Nd_2O_3 \cdot 3,5TiO_2$, D - $Nd_2O_3 \cdot 3TiO_2$ at the heating rates 10^{o}/min (I) and 30^{o}/min (II). The figures indicate the temperature of specimen quenching.

The phase with pyrochlore structure initially crystallizes in $Nd_2O_3 \cdot 3,5\ TiO_2$ specimens, the impurity amount increasing with the increase of the heating rate from 2% at 10^{o}/min to 10% at 30^{o}/min. The temperature increase results in decomposition of pyrochlore into $Nd_2O_3 \cdot 2TiO_2$ and $Nd_2O_3 \cdot 4,5\ TiO_2$. Investigations of specimens in the composition range from $Nd_2O_3 \cdot 3TiO_2$ to $Nd_2O_3 \cdot 3,7\ TiO_2$ show that pyrochlor with the minimum impurity amount (less than 5%) is being formed in the $Nd_2O_3 \cdot (3,3 \div 3,5)\ TiO_2$ specimens. Besides pyrochlore the impurities $Nd_2O_3 \cdot 2TiO_2$ and $Nd_2O_3 \cdot 4,5\ TiO_2$ are observed in the compositions with $TiO_2 : Nd_2O_3 < 3,3$ ratio, and the impurities

$Nd_2O_3:4{,}5TiO_2$ more than 5% are observed in the compositions with $TiO_2:Nd_2O_3>3{,}5$ ratio.

Studies of crystallization of $3Nd_2O_3\cdot 10TiO_2$ and $Nd_2O_3\cdot 3{,}5TiO_2$ specimens have been carried out at the heating rates 5^o/min. In this case the thermograph shows one exothermal effect at 825^oC which corresponds to the pyrochlore crystallization. The temperature increase leads to the following sequence of formation of the impurity phases: TiO_2, $Nd_2O_3\cdot 4{,}5TiO_2$, and finally, the decomposition of pyrochlore into $Nd_2O_3\cdot 2TiO_2$ and $Nd_2O_3\cdot 4{,}5\ TiO_2$.

Taking into account the concentration range of pyrochlore existence, the specimens of the compositions $3Nd_2O_3\cdot 10TiO_2$ and $Nd_2O_3\cdot 3{,}5TiO_2$ and with the impurity amount less than 5% at $t_{quench}=830^oC$ were chosen for the detailed studies. Table 2 gives the data on the chemical analysis and unit cell parameters of pyrochlore at the different temperatures of quenching for above specimens. The specimen $Nd_2O_3\cdot 3{,}5\ TiO_2$ quenched at 830^oC is found to consist of one phase as it could be proved within the sensitivity of the X-ray analysis. This allows to ascribe the pyrochlore the composition $Nd_2O_3\cdot 3{,}5TiO_2$.

Table 2. Chemical analysis and unit cell parameters of pyrochlore at different temperatures of specimen quenching.

Composition of specimens	Quenching temperature, ^oC	Parameter of the cubic phase with pyrochlore structure, A^o
$Nd_2O_3\cdot 3{,}51TiO_2$	830	$10{,}209 \pm 0{,}001$
	850	$10{,}214 \pm 0{,}001$
	870	$10{,}221 \pm 0{,}002$
	890	$10{,}224 \pm 0{,}002$
	990	$10{,}246 \pm 0{,}001$
$Nd_2O_3\cdot 3{,}33TiO_2$	830	$10{,}213 \pm 0{,}001$
	850	$10{,}215 \pm 0{,}001$
	940	$10{,}235 \pm 0{,}001$
	970	$10{,}238 \pm 0{,}002$

As seen in Table 2 the increase of the quenching temperature results in the increase of the cubic phase parameter of pyrochlore. As pointed above the increase of temperature is followed by the formation of TiO_2 and $Nd_2O_3\cdot 4{,}5\ TiO_2$ phases. Thus the formation of titanium-rich phases appears to result in decreasing of vacancy concentrations in the cation sublattice, in consequence, the parameter increases.

CONCLUSIONS

As a result of investigations in question the practically impurity-free compound with the pyrochlore structure of the composition

$Nd_2O_3 \cdot 3,5TiO_2$ has been obtained at 830°C. The range of existence of the pyrochlore structure has been determined: $3Nd_2O_3 \cdot 10TiO_2 \div Nd_2O_3 \cdot 3,5TiO_2$. As the temperature increases, the unit cell parameter of pyrochlore is also increasing from 10,209±0,001 Å to 10,246±0,001 Å. Above 1000°C the compound $Nd_2O_3 \cdot 3,5TiO_2$ decomposes to $Nd_2O_3 \cdot 4,5TiO_2$ and $Nd_2O_3 \cdot 2TiO_2$.

Table 1. X-ray analysis of specimens with $Nd_2O_3(3 \div 4,5)TiO_2$ composition quenched at different temperatures.

	$Nd_2O_3 \cdot 3TiO_2$	$Nd_2O_3 \cdot 3,5TiO_2$
The heating rate 30°/min	1. The amorphous phase 2. $Nd_2O_3 \cdot 2TiO_2$ starts to crystallize 3. $Nd_2O_3 \cdot 2TiO_2$ + the amorphous phase 4. $Nd_2O_3 \cdot 2TiO_2 + Nd_2O_3 \cdot 4,5TiO_2$	1. Pyrochlore starts to crystallize 2. Poorly formed pyrochlore + the amorphous phase 3. Pyrochlore + $Nd_2O_3 \cdot 4,5TiO_2$ (~10%) 4. Pyrochlor + $Nd_2O_3 \cdot 2TiO_2$ 5. $Nd_2O_3 \cdot 4,5TiO_2 + Nd_2O_3 \cdot 2TiO_2$
The heating rate 10°/min	1. Pyrochlore starts to crystallize 2. Poorly formed pyrochlore + traces $Nd_2O_3 \cdot 2TiO_2$ 3. Pyrochlore + $Nd_2O_3 \cdot 2TiO_2$ 4. Pyrochlore + $Nd_2O_3 \cdot 2TiO_2$ + $Nd_2O_3 \cdot 4,5TiO_2$ 5. $Nd_2O_3 \cdot 2TiO_2 + Nd_2O_3 \cdot 4,5TiO_2$	1. Pyrochlore starts to crystallize 2. Poorly formed pyrochlore 3. Pyrochlore + traces of the amorphous phase 4. Pyrochlore + traces $Nd_2O_3 \cdot 4,5TiO_2$ (~2%) 5. Pyrochlore + $Nd_2O_3 \cdot 4,5TiO_2$ 6. $Nd_2O_3 \cdot 4,5TiO_2$ + $Nd_2O_3 \cdot 2TiO_2$
	$Nd_2O_3 \cdot 4TiO_2$	$Nd_2O_3 \cdot 4,5TiO_2$
The heating rate 30°/min	1. The amorphous phase 2. Pyrochlore + poorly formed $Nd_2O_3 \cdot 4,5TiO_2$ 3. The amount of the phases is increasing 4. Pyrochlore + completely formed $Nd_2O_3 \cdot 4,5TiO_2$ 5. $Nd_2O_3 \cdot 4,5TiO_2$ + + $Nd_2O_3 \cdot 2TiO_2$	1. The amorphous phase 2. Poorly formed $Nd_2O_3 \cdot 4,5TiO_2$ 3. The amount of the phase is increasing 4. $Nd_2O_3 \cdot 4,5TiO_2$

The digits in the table indicate the temperatures of specimen quenching. They correspond to digits in the fig.1 at heating rates 10°/min (I) and 30°/min (II).

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