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THERMAL ANALYSIS, THERMAL EXPANSION OF $Pr_{1-x}La_xInO_3$ PRASEODYMIUM-LANTHANUM INDATES

Praseodymium, lanthanum indates solid solutions $Pr_{1-x}La_xInO_3$ were synthesized by ceramic method for the first time. It was found that in $PrInO_3$ – $LaInO_3$ binary system there was a continuous range of praseodymium-lanthanum indates solid solutions $Pr_{1-x}La_xInO_3$ with the structure of orthorhombically distorted perovskite. Thermal elongation of synthesized samples was investigated in 400–1,120 K temperature range. Complex thermal analysis of the samples synthesized was carried out up to 1,273 K. Temperature dependences of relative elongation had no anomalies due to the phase transitions and using these dependences average linear coefficients of thermal elongation were calculated by least-squares technique. On the differential scanning calorimetry (DSC) curves for all the samples investigated no thermal effects were observed.

Introduction. About all modern prospective materials special attention is drawn to rare-earth oxide compounds with perovskite structure that are widely used in electronic and chemical industry [1–3]. In particular, perovskite-type solid solutions of aluminates, gallates, indates of lanthanum and other rare-earth elements ($LnMO_3$, Ln – rare-earth element, M – Al, Sc, Ca, In) have been explored to be perspective materials for active laser elements [4–6]. Indates doped with rare-earth elements are considered to be good photo- and cathodoluminescent phosphors [7, 8] and could be used in fabrication of white LEDs. Among the advantages of these phosphors one can see a possibility of excitation by near UV or VIS irradiation and stability in humid atmosphere [8, 9].

The aim of the present work is to synthesize solid solutions within $PrInO_3$ – $LaInO_3$ pseudo-binary system, investigate their thermal expansion and perform their thermal analysis.

Experimental technique. Praseodymium, lanthanum indates solid solutions $Pr_{1-x}La_xInO_3$ (x = 0.0–1.0) were synthesized by ceramic method for the first time using indium oxide In_2O_3, praseodymium oxide Pr_6O_{11}, lanthanum oxide La_2O_3 as starting materials. Lanthanum oxide La_2O_3 had been previously annealed in air at 1,173 K for 1 h. Stoichiometric amounts of In_2O_3, Pr_6O_{11} and La_2O_3 were mixed and milled using planetary ball mill "Pulverizette 6" with ethanol added. The resulting mixture was dried in air and then pressed (50–75 MPa) with ethanol into pellets (D = 25 mm, h = 5–7 mm). Pellets were annealed at 1,523 K in air for 5 h, then ground and milled into powder. The powder was pressed with ethanol into 30×5×5 mm bars and sintered at 1,523 K in air for 5 h to obtain the samples of praseodymium-lanthanum indates solid solutions $Pr_{1-x}La_xInO_3$

X-ray analysis was carried out with help of Bruker D8 ADVANCE diffractometer using CuK_α radiaton for the $20^\circ \le 2\Theta \le 80^\circ$ range of angles. Crystal cell parameters of the solid solutions synthesized were calculated using RTP program and the data from International Centre for Diffraction Data (ICDD JCPDS) [10].

Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) was held in air up to 1,273 K (TGA/DSC1 METTLER TOLEDO (Switherland)) with alumina Al_2O_3 as standard in platinum crucibles at heating and cooling rate 10°C/min; sample mass 100 μg). Relative weight determination error was 0.0001%, relative temperature determination error was 0.15%.

Thermal expansion of the ceramic samples of praseodymium-lanthanum indates solid solutions $Pr_{1-x}La_xInO_3$ (x = 0.0–1.0) was measured dynamically in air in the 300–1,100 K temperature interval with dilatometer with vertical quartz push rod (heating and cooling rate 3–5 K/min). Heating and cooling was realized in electric furnace

Results and discussion. The results of the X-ray analysis showed that all the samples were single-phased. It was found that in $PrInO_3$ – $LaInO_3$ binary system there was a continuous range of praseodymium-lanthanum indates solid solutions $Pr_{1-x}La_xInO_3$ with the structure of orthorhombically distorted perovskite. In $Pr_{1-x}La_xInO_3$ solid solutions increasing the substitution level x of Pr^{3+} ions by La^{3+} ions with larger ionic radii leads to gradual increase of crystal lattice parameters a, b, c and unit cell volume V (Table 1) together with gradual decrease of orthorhombic distortion degree ε (ε = $(b - a) / a$). Crystal lattice parameters a, b, c for individual indates $LaInO_3$ and $PrInO_3$ are 0.5718; 0.5932; 0.8214 nm; and 0.5653; 0.5905; 0.8150 nm, respectively and agree quite well with reference data [3].

Temperature dependences of relative elongation ($\Delta l / l_0$) of the ceramic samples of praseodymium-lanthanum indates solid solutions $Pr_{1-x}La_xInO_3$

in 400–1,120 K temperature range are linear and contain no visible anomalies. This fact witnesses the absence of any phase transitions in the samples examined in the temperature range mentioned above. Average coefficients of linear thermal expansion α (Table 2) for the ceramic samples of $Pr_{1-x}La_xInO_3$ solid solutions were calculated by least-squares technique.

Table 1

Crystal lattice parameters *a*, *b*, *c*, unit cell volume *V* and orthorhombic distortion degree ε for praseodymium-lanthanum indates solid solutions $Pr_{1-x}La_xInO_3$ depending on substitution level *x*

x	*a*, nm	*b*, nm	*c*, nm	$V \cdot 10^3$, nm^3	$\varepsilon \cdot 10^2$
0	0.5653	0.5905	0.8150	272.06	4.46
0.1	0.5657	0.5910	0.8154	272.61	4.47
0.2	0.5665	0.5911	0.8156	273.11	4.33
0.3	0.5674	0.5914	0.8162	273.89	4.22
0.4	0.5680	0.5919	0.8173	274.78	4.21
0.5	0.5688	0.5921	0.8176	275.40	4.09
0.6	0.5695	0.5926	0.8185	276.23	4.06
0.7	0.5701	0.5928	0.8194	276.96	3.98
0.8	0.5705	0.5928	0.8204	277.49	3.90
0.9	0.5713	0.5930	0.8207	278.04	3.80
1.0	0.5718	0.5932	0.8214	278.62	3.74

The results obtained show that average coefficients of linear thermal expansion α depend insignificantly on the substitution level *x* and vary from $8.40 \cdot 10^{-6}$ K^{-1} for $PrInO_3$ to $9.19 \cdot 10^{-6}$ K^{-1} for $LaInO_3$.

Table 2

Average coefficients of linear thermal expansion (α) for the ceramic samples of praseodymium-lanthanum indates solid solutions $Pr_{1-x}La_xInO_3$

x	$\alpha \cdot 10^6$, K^{-1}
0	8.40
0.2	9.86
0.4	8.96
0.6	9.18
0.8	8.89
1.0	9.19

On the differential scanning calorimetry (DSC) curves for all the $Pr_{1-x}La_xInO_3$ samples investigated no thermal effects were observed. Though on thermal gravimetric (TGA) curves there is a relatively small mass loss.

Total weight loss Δm_{total} for heating $Pr_{1-x}La_xInO_3$ sample up to 1,273 K vary from 0.1803 to 0.5813 wt % without a certain dependence on substitution level *x* (Table 3).

It should be noted that for praseodymium-lanthanum indates solid solutions $Pr_{1-x}La_xInO_3$ a relatively obvious weight loss Δm (standing for the greater part of total weight loss Δm_{total}) is observed in 443–690 K temperature range, while on thermal gravimetric (TGA) curves for samarium-lanthanum indates solid solutions $Sm_{1-x}La_xInO_3$ similar weight loss is observed in 440–683 K temperature range. For both solid solution systems obvious weight loss Δm, temperatures of the beginning T_1 and of the end T_2 of the stage containing obvious weight loss, the temperature of the peak of obvious weight loss T_{max} vary without a certain dependence on substitution level *x* of Pr^{3+}, Sm^{3+} ions by La^{3+} ions.

Table 3

Total weight loss Δ_{total}, obvious weight loss Δm, temperatures of the beginning T_1 and of the end T_2 of the stage containing obvious weight loss, the temperature of the peak of obvious weight loss T_{max}

x	Δm_{total}, wt %	Δm, wt %	T_1, K	T_2, K	T_{max}, K
0	0.2906	0.0710	533	651	573
0.1	0.2425	0.1038	463	690	548
0.2	0.3043	0.0746	528	642	559
0.3	0.2219	0.1066	443	651	561
0.4	0.2808	0.1058	478	633	563
0.5	0.2061	0.0681	515	667	566
0.6	0.3043	0.1155	483	658	566
0.7	0.5184	0.2276	478	635	563
0.8	0.5813	0.2589	478	653	567
0.9	0.2376	0.1108	443	680	589
1.0	0.1803	0.0614	443	598	532

It is suggested that the origin of the weight losses in the temperature ranges of 443–690 K and 440–683 K for $Pr_{1-x}La_xInO_3$ and $Sm_{1-x}La_xInO_3$ indates, respectively is alike, but not revealed in present work.

Conclusions. It is found that in $PrInO_3$ – $LaInO_3$ binary system there is a continuous range of praseodymium-lanthanum indates solid solutions $Pr_{1-x}La_xInO_3$ with the structure of orthorhombic distorted perovskite. In $Pr_{1-x}La_xInO_3$ solid solutions increasing the substitution level *x* of Pr^{3+} ions by La^{3+} ions with larger ionic radii leads to gradual increase of crystal lattice parameters *a*, *b*, *c* and unit cell volume *V* together with gradual decrease of orthorhombic distortion degree ε.

In 450–1,050 K temperature range relative elongation $\Delta l / l_0$ of the ceramic samples of praseodymium-lanthanum indates solid solutions $Pr_{1-x}La_xInO_3$

increases almost linearly with temperature and this indicate the absence of any phase transitions in the samples examined in the temperature range mentioned above.

Calculated using least-squares technique average coefficients of linear thermal expansion α for the ceramic samples of $Pr_{1-x}La_xInO_3$ solid solutions depend insignificantly on the substitution level x.

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