Study of the precursors structure for preparation of nanopowders with the perovskite type phase

Shyrokov O. V., Chudinovych O. V., Lobunets T. F., Ragulya A. V.

Frantsevich Institute for Problems of Materials Science of NASU, Krzhyzhanovsky St., 3, Kyiv 03142, Ukraine

shyrokovav@gmail.com

INTRODUCTION

The development of powder nanotechnologies for the creation of transparent functional ceramics is one of the promising areas of modern materials science. In recent years, great practical interest has been shown in materials based on rare earth elements (REE) phase with perovskite type structure. The interest in optical ceramics as laser, scintillation media is due to the high optical transparency in a wide range of wavelengths, radiation resistance, high thermal conductivity, good thermomechanical properties, chemical and thermal stability. Ceramics have high manufacturability, wide variation in chemical composition and can be obtained in the form of composite elements with different structure [1,2].

EXPERIMENTAL

To obtain nanopowders of complex oxide phases $LnLn'O_3$ (Ln, Ln' = REE) with the perovskite type structure, precursors were synthesized by heterogeneous precipitation from nitrate solutions of rare-earth elements in ammonia solution with urea percentage from 5 to 20 vol. % and at different temperatures. The porous structure study of the obtained precursor samples was conducted by adsorption-structural method. The general characteristics of the porosity are given in the table. The phase composition of precursor powders was determined by X-ray diffraction in CuKα radiation using diffractometer DRON-3M. Phase analysis of X-ray spectra of the studied precursor powders synthesized in ammonia solution with urea content of 10 vol. % at temperatures 40, 60 and 80 °C and different urea content of 5, 10, 20 vol. % at temperature 80 °C showed that in the angular range of 2θ = 25-35° and 40-65° a halo is observed, which indicates the amorphous nature of the samples (Fig. 1, 2). In addition, on the X-ray of the sample No. 3 there are also clear lines characteristic of lanthanum hydroxide.

Table – General porosity characteristics of the synthesized samples

No.	Synthesis conditions		V_Σ, cm^3/g	BET		BJH		
	vol. %	°C		S_{BET}, m^2/g	$\bar{D}_{BET}$, nm	V_{me}, cm^3/g	S_{me}, m^2/g	$\bar{D}_{me}$, nm
1	10	40	0,0187	14,01	5,3	0,0175	13,1583	5,3
2	10	60	0,0153	9,72	6,3	0,0132	9,5900	5,5
3	10	80	0,0500	23,70	8,4	0,0499	33,4176	6,0
4	5	80	0,1530	107,13	5,7	0,1573	140,1462	4,5
5	20	80	0,2458	121,55	8,1	0,2486	173,7280	5,7

Nitrogen sorption isotherms on the samples of synthesized precursors belong to type IV isotherms according to the Brunauer, Deming, Deming and Teller (BDDT) classification, which characterizes them as mesoporous bodies (Fig. 3, 4). The type of hysteresis loops of samples isotherms obtained at 40 and 60 °C, according to IUPAC classification, should most likely be attributed to type H3, which is typical for materials with a layered structure or composed of plane-parallel particles (Fig. 3 a). In addition, samples have similar structures, as evidenced by the differential size distributions of mesopores volumes and surfaces (Fig. 3 b, c), and close values of the general porosity characteristics – specific surface area (14-9.7 m^2/g) and average diameter of mesopores (5.3-5.5 nm).

Raising solution temperature up to 80 °C during the synthesis of precursors leads to a significant increase in the values of their general porosity characteristics.

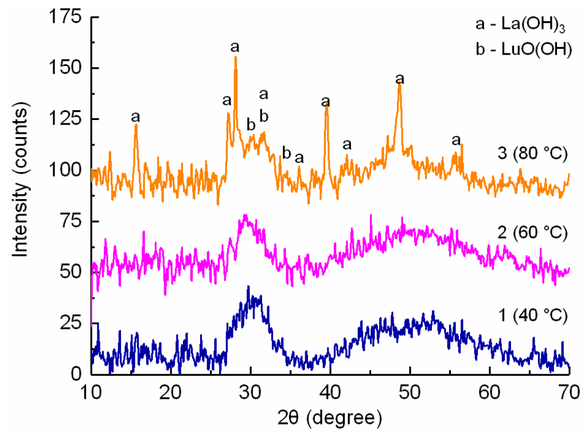
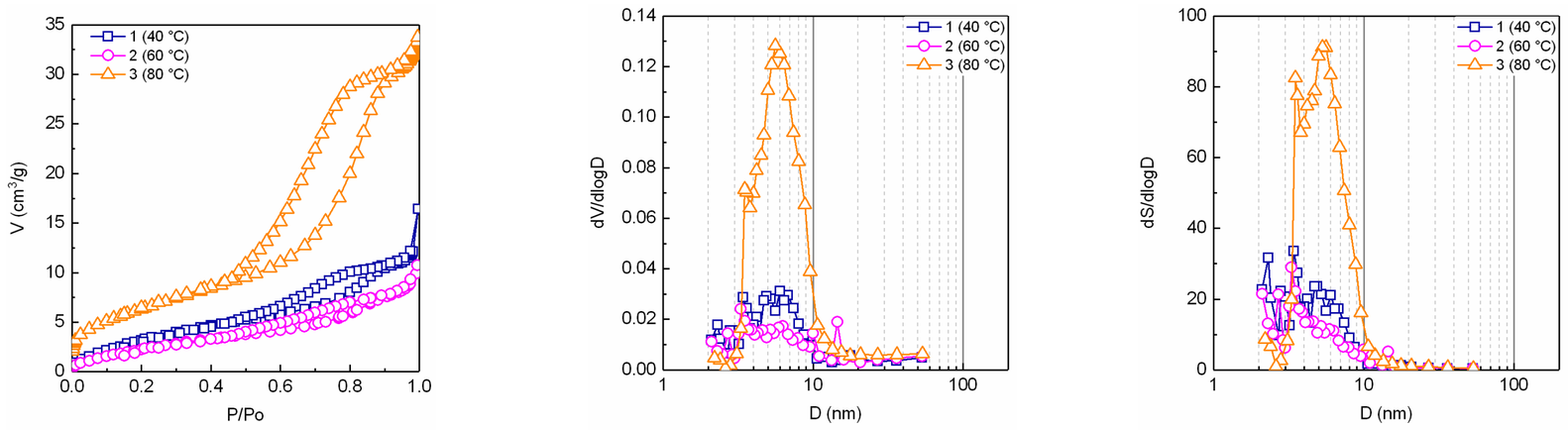


Fig. 1 X-ray diagrams of precursor powders synthesized in ammonia solution with urea content 10 vol. % at temperature 40, 60 and 80 °C



a b c

Fig. 3 Nitrogen sorption isotherms and differential size distributions of mesopores volumes (b) and surfaces (c) on synthesized precursors samples obtained at different solution temperatures and 10 vol. % urea content

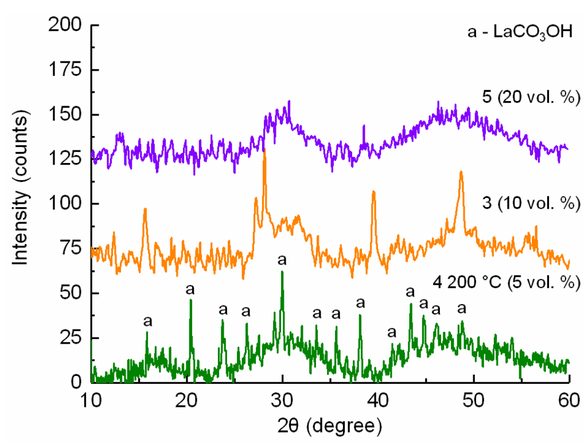
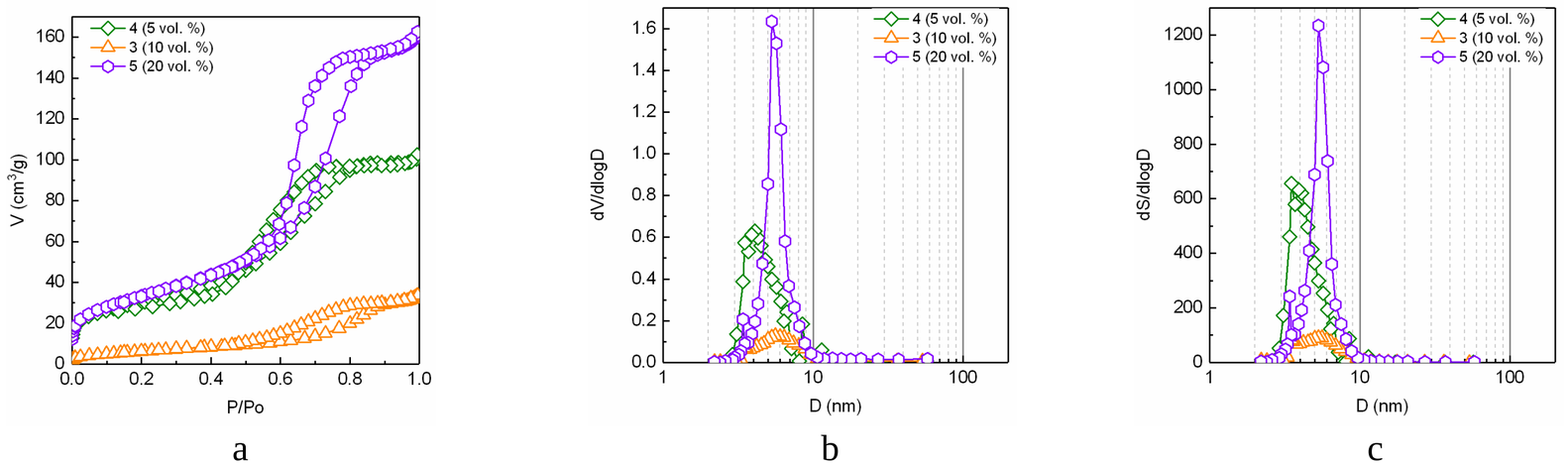


Fig. 2 X-ray diagrams of synthesized precursors samples obtained at solution temperature of 80 °C, depending on the urea percentage



a b c

Fig. 4 Nitrogen sorption isotherms (a) and differential size distributions of mesopores volumes (b) and surfaces (c) on synthesized precursors samples obtained at solution temperature 80 °C, depending on the urea percentage

CONCLUSIONS

Practically non-porous precursors at low synthesis temperatures of 40-60 °C with 10 vol. % urea content in the solutions are formed, which can be attributed to systems with a layered porous structure, and at a solution temperature of 80 °C their porosity increases, and the porous structure, most likely, approaches the corpuscular systems. An increase in solution temperature during precursor synthesis leads to the formation of more porous materials. Depending on the synthesis conditions the precursors have mainly amorphous or amorphous-crystalline structure.

REFERENCES

1. Artini C. Crystal chemistry, stability and properties of interlanthanide perovskites: A review // Journal of the European Ceramic Society.-2017.-**37,** N 2.-P. 427-440.

2. Akiyama J., Sato Y. and Taira T. New Generation of Laser Ceramics with Anisotropic Materials // Advanced Solid-State Photonics, OSA Technical Digest Series (CD) (Optical Society of America, 2009), paper MF1.