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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Synthesis of Phases of Composition $PbNb_2O_6$ and $BaNb_2O_6$ with the Use of Active Precursors

A. A. Nesterov, E. V. Karyukov, and K. S. Masurenkov

Southern Federal University, Rostov-on-Don, Russia

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Abstract—Low-temperature method for synthesis of phases of composition $PbNb_2O_6$ and $BaNb_2O_6$ and solid solutions based on these phases was developed using the results obtained in a study of the interaction of α-$Nb_2O_5{\cdot}xH_2O$ with $PbO{\cdot}xH_2O$ and $Ba(OH)_2$.

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The solid-phase synthesis of $Ba_xPb_{1-x}Nb_2O_6$ with a perovskite structure has a number of disadvantages, one of which is the high temperature and long duration of this process, which leads to deviations from the stoichiometric composition because of the loss of volatile oxides from samples. In addition, phases with a pyrochlore structure are formed in most cases in the system in the initial stages of synthesis. This sharply diminishes the formation rate of the final product and, in some cases, yields multiple-phase samples with poor electrical parameters. In the second stage, secondary recrystallization of the samples occurs at a high rate in the course of sintering of ceramics because of the defectiveness of the phases formed, which leads to a decrease in the density of the final articles.

To eliminate these disadvantages, we made an attempt to lower the activation energy of the synthesis processes of these phases by using active precursors. To solve this problem, we studied the interaction of α-$Nb_2O_5{\cdot}xH_2O$ with $PbO{\cdot}xH_2O$ and $Ba(OH)_2$.

EXPERIMENTAL

We used 0.5 M (in terms of Nb_2O_5) solutions of citrate complexes as precursors in synthesis of the primary phase α-$Nb_2O_5{\cdot}xH_2O$. These solutions were prepared by dissolving niobium(V) halides in a saturated solution of citric acid. Analysis of the products obtained shows that it contains a varying amount of citrate ions, which favors formation of lead and barium citrates upon addition of $PbO{\cdot}xH_2O$ and $Ba(OH)_2$ to the system. This changes the formation mechanism of the final phases and sharply raises the formation temperature of $PbNb_2O_6$ and $BaNb_2O_6$.

To diminish the effect of citrate ions on the phase formation kinetics of these niobates, primary α-$Nb_2O_5{\cdot}xH_2O$ was dissolved in 40% nitric acid. The final form of α-$Nb_2O_5{\cdot}xH_2O$ was precipitated from the resulting solution (0.4–0.46 M in terms of Nb_2O_5) with a 10% solution of ammonia at 2–7°C (final pH 9). The compound $PbO{\cdot}xH_2O$ was prepared by reacting a 1 M solution of lead(II) nitrate with a 10% solution of ammonia at 2–7°C (final pH 7). The number of moles of the phases formed was set on the basis of the concentrations and volumes of the starting solutions of niobium and lead compounds. To synthesize $PbNb_2O_6$, we mixed the resulting gel-like precipitates in a prescribed ratio (composition 1). To form phases of composition $B_xPb_{1-x}Nb_2O_6$, a calculated amount of a barium hydroxide suspension was added to the gel-like precipitates taken in required relative amounts (composition 2). When preparing $BaNb_2O_6$, we treated the niobium hydroxide gel with a calculated amount of a barium hydroxide suspension (composition 3). The mixtures were ground for 1 h and part of the interaction products obtained was studied by DTA and TG on a Perkin–Elmer Diamond TG/DTA derivatograph. The remaining part was transferred to a

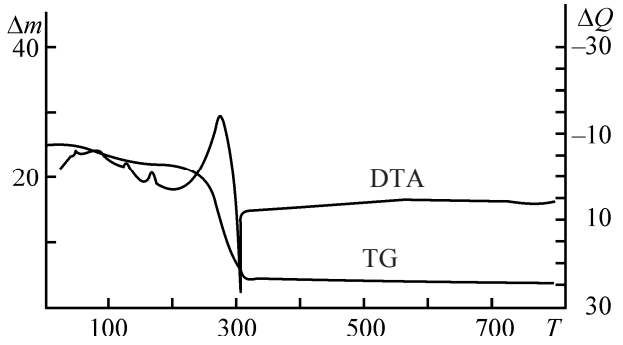

Fig. 1. DTA and TG curves for a sample of composition α-$Nb_2O_5 \cdot xH_2O$ + $PbO \cdot xH_2O$. (Δm) Change in mass, (ΔQ) heat effect, and (T) temperature; the same for Fig. 2.

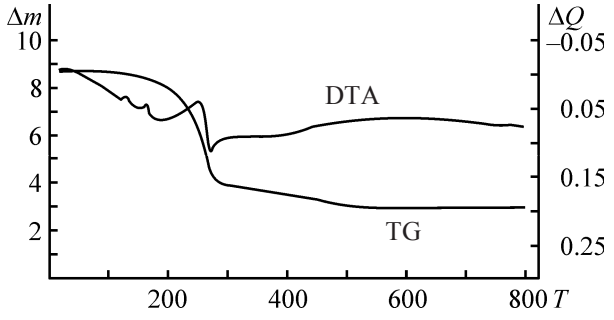

Fig. 2. DTA and TG curves for a sample of composition α-$Nb_2O_5 \cdot xH_2O$ + $Ba(OH)_2$.

porcelain cup and dried at 100°C for 2 h. The semi-transparent solid mass formed upon drying was ground, compacted into disks 12 mm in diameter (compaction pressure 50 MPa), and calcined at temperatures of 327–927°C with a step of 50°C (isothermal keeping for 1 to 6 h). An X-ray phase analysis of the samples was made with a DRON-2.0 diffractometer (CuK_α radiation, Ni-β filter).

According to the data obtained, X-ray-amorphous phases are formed in all the systems on grinding the mixture of the starting components. These phases decompose at 27–327°C for samples of composition 1 and at 27–527°C for samples of composition 3 (Figs. 1, 2).

As follows from these data, sorbed and chemically bound water is removed from samples of system 1 at temperatures of up to 317°C. The exothermal effect observed at 277–327°C is accounted for by decomposition of the by-product of the reaction, NH_4NO_3, and by oxidation of residual citrate ions. According to XPA, this exothermic effect initiates crystallization of the mixture of pyrochlore phases ($Pb_2Nb_2O_7$, $Pb_3Nb_4O_{13}$, etc.). To the interaction of these phases with the amorphous form of Nb_2O_5 (yielding the rhombohedral phase $PbNb_2O_6$) corresponds the exothermal effect at 577°C. It should be noted that, according to XPA, this process begins already at $T \approx$ 477°C and, as the calcination temperature is raised further, its rate rapidly increases. However, pyrochlore phases completely disappear from the system only at 877°C (isothermal keeping duration 2 h). Simultaneously with this process, the rhombohedral phase starts to be transformed to the rhombic phase at 827–877°C (Table 1). Calcination of the samples at 1077°C yields a single-phase product (rhombic phase) in 1 h, which is, on the average, 100–150°C lower as compared with the case of the conventional solid-phase technique.

According to the DTA and TG data (Fig. 2), the change in the mass of samples of composition 3 occurs in a wide temperature range (27–527°C) and is due, as also in the first case, to removal of chemically bound and sorption water and NH_4NO_3 (exothermal effect at 287°C) from the system. At the same time, no thermal effects associated with crystallization of barium niobates are observed, which points to the nucleation mechanism of phase formation in the given system (originally formed nuclei of the crystalline phases

Table 1. Composition of phases formed in system 1 at various sample calcination temperatures[a]

T_{calc}, °C	Method of solid-phase reactions	Suggested method
277	Peaks of the starting components	Amorphous phase
377	The same	Onset of formation of pyrochlore phases
477	Peaks of the starting components + P	P + R_1
577	P	R_1 + P
727	P + R_1	R_1 + P
827	R_1 + P	R_1 + R_2
877	R_1	R_1 + R_2
1027	R_1	R_2

[a] P, phases with pyrochlore structure of composition $Pb_2Nb_2O_7$, $Pb_3Nb_4O_{13}$, etc.; R_1, rhombohedral phase $PbNb_2O_6$; R_2, rhombic phase $PbNb_2O_6$ (the phase predominant in the system is the first indicated).

Table 2. Density of ceramics[a] of composition $B_xPb_{1-x}Nb_2O_6$, synthesized by different methods

Composition	Theoretical density, g cm^{-3}	Density of samples synthesized by the solid-phase method[b], g cm^{-3}	Percent relative to the theoretical density	Density of samples synthesized by the gel method[c], g cm^{-3}	Percent relative to the theoretical density
$BaNb_2O_6$	5.44	4.02	73.90	5.40	99.26
$Ba_{0.9}Pb_{0.1}Nb_2O_6$	5.59	4.03	72.06	5.53	98.92
$Ba_{0.8}Pb_{0.1}Nb_2O_6$	5.85	4.35	72.68	5.74	98.12
$Ba_{0.7}Pb_{0.1}Nb_2O_6$	5.94	3.99	67.20	5.90	99.32
$Ba_{0.6}Pb_{0.1}Nb_2O_6$	6.01	3.91	65.18	5.97	99.33
$Ba_{0.5}Pb_{0.1}Nb_2O_6$	6.20	5.42	87.38	6.10	98.38
$Ba_{0.4}Pb_{0.1}Nb_2O_6$	6.27	5.42	86.53	6.20	98.89
$Ba_{0.3}Pb_{0.1}Nb_2O_6$	6.40	5.59	87.30	6.29	98.28
$Ba_{029}Pb_{0.1}Nb_2O_6$	6.42	5.68	88.43	6.35	98.90
$Ba_{0.1}Pb_{0.1}Nb_2O_6$	6.66	5.81	87.29	6.61	99.25
$PbNb_2O_6$	6.77	5.58	82.47	6.70	98.96

[a] Density measured by the hydrostatic method in octane.
[b] Sintering at T = 1277°C, τ = 2 h.
[c] Sintering at T = 1202°C, τ = 1 h.

gradually grow at the expense of the surrounding amorphous phase). This is confirmed by XPA data, according to which, primary nuclei of the intermediate pseudocubic phase $BaNb_2O_6$ with a perovskite structure are formed already at 427°C.

Further increase in the calcination temperature favors gradual transformation of this phase first to a tetragonal phase, and then to a rhombic phase at 827°C. It should be noted that the XPA method did not reveal formation of phases with a pyrochlore structure in the system under consideration at any calcination temperature of the starting amorphous phase.

Thus, the use of active precursors in synthesis of $BaNb_2O_6$ made it possible to diminish the sample synthesis time by a factor of 1.5–2 and to lower the formation temperature of the ferroelectric phase by, on the average, 350°C as compared with the solid-phase method.

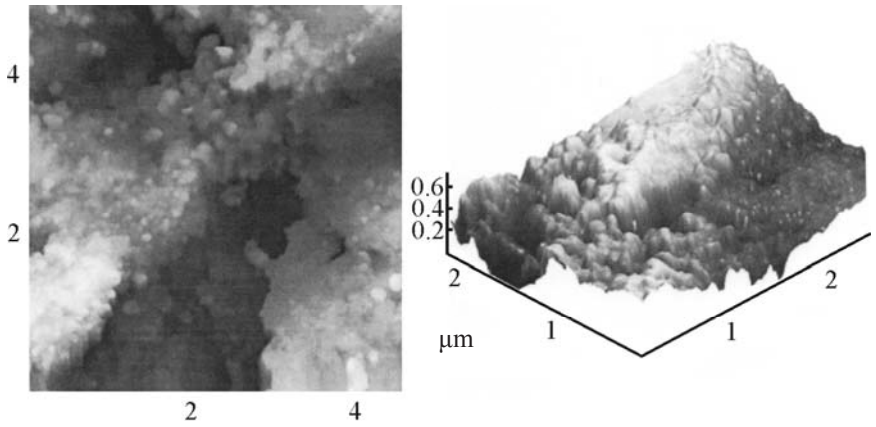

Fig. 3. SEM micrograph of a product formed in decomposition of α-$Nb_2O_5 \cdot xH_2O$. Thermal treatment at T = 87°C, τ = 1 h, average particle size 250 nm (scanning electron microscope Solover Pro-M).

Taking into account the above data, we synthesized phases of composition $B_xPb_{1-x}Nb_2O_6$ at temperatures of 727–927°C (depending on x). In the second stage, the stock was ground and compacted and the resulting samples were sintered at T = 1127–1227°C (τ = 2 h). Table 2 compares the densities of the ceramics obtained with the densities of ceramics of the same composition, produced by the conventional technique.

It follows from the results obtained that the sintering temperature of samples prepared from the stock synthesized by the method we suggest is, on average, 50–100°C lower than that of samples produced from the stock synthesized by the method of solid-phase reactions. The density of the former is higher and reaches 99.3% of the theoretical value, whereas the maximum density of samples synthesized by the method of solid-phase reactions is 10% lower.

The decrease in the synthesis temperature of the intermediate and final phases, increase in the rate of ceramic sintering processes, and decrease in their temperature are presumably predetermined by use of active precursors, which enables a substantial lowering of the activation energy of processes in which the phases under consideration are formed [1, 2]. By analogy with the synthesis of phases with a perovskite structure, it can be assumed that, in the given case, intermediate metastable amorphous phases are formed via interaction of functional hydroxo groups OH^- of the ole form of niobium hydroxide with lead hydroxide or barium hydroxide [3, 4] and via sorption of cations and anions from solutions [5, 6]. Subsequently, the amorphous phase is transformed into a crystalline phase by several possible mechanisms, whose obligatory stage is nucleation under high supersaturation conditions. The last circumstance accounts for the formation in the first stage of a large number of nuclei with small and approximately the same sizes, predetermined by the particle size of the starting hydroxide (Fig. 3). This, in turn, makes lower the probability of secondary recrystallization of samples prepared from a stock of this kind at high calcination temperatures. At the same time, particles formed at comparatively low temperatures contain an increased concentration of nonequilibrium defects, which makes higher the Gibbs energy of the system, i.e., enables identification of these phases as active phases [1].

CONCLUSIONS

(1) A study of phase formation processes in the systems α-$Nb_2O_5{\cdot}xH_2O$–$PbO{\cdot}xH_2O$, α-$Nb_2O_5{\cdot}xH_2O$–$Ba(OH)_2$, and α-$Nb_2O_5{\cdot}xH_2O$–$PbO{\cdot}xH_2O$–$Ba(OH)_2$ at 7–1027°C demonstrated that use of active precursors can lower the temperature of the rhombohedral $PbNb_2O_6$ → rhombic $PbNb_2O_6$ phase transition by 100–150°C because of the nanometer size of grains of the resulting stock.

(2) The ferroelectric phase $BaNb_2O_6$ and phases of composition $Ba_xPb_{1-x}Nb_2O_6$ are synthesized at temperatures by 200–350°C lower compared with the method of solid-phase reactions.

(3) Piezoceramics can be synthesized from these phases at lower temperatures with a higher density.

(4) The fact that the activation energies of parallel processes (in particular, processes in which phases with pyrochlore structure are formed in system 1) become closer to the activation energy of formation of the target product results in that the rate and completeness of side reactions are strongly suppressed.

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