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Effect of Mechanical Activation on the Synthesis of Lead Ferroniobate

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Abstract

The synthesis of lead ferroniobate from lead, iron and niobium oxides taken in the stoichiometric ratio was investigated for the purpose of choosing the optimal compositions, conditions of mechanical activation and subsequent thermal treatment. The process was carried out in the presence of the excess of lead oxide to prevent the deviation from the stoichiometry of the ceramics obtained after sintering. The changes of the phase composition of mixtures during mechanical activation and subsequent thermal treatment were followed. It was demonstrated that the most attractive structure and properties are those characterizing lead niobate obtained with some excess of lead oxide over the stoichiometric composition. It was established that with the help of mechanical activation it is possible to vary within a broad range the temperature of the magnetic phase transition for the powders and ceramics of lead ferroniobate.

Key words: lead ferroniobate, thermal synthesis from iron, niobium and lead oxides using mechanical activation

INTRODUCTION

Lead ferroniobate $\text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ (PFN) has the crystal structure of perovskite of the oxygen octahedral type built of NbO_6 octahedrons. It belongs to the family of ferroelectromagnetics or multiferroics, because it possesses both ferroelectric and magnetic properties [1–3]. The materials of this kind may be used, for example, to manufacture multilayered ceramic capacitors, piezoelectric and pyroelectric sensors, multilayer microwave resonators and filters, sensors, actuators, inductors, as well as memory elements recorded with electric field and read with magnetic field [2–6]. Lead ferroniobate is obtained in the form of single crystals [7], thin films [8], in the amorphous state [9]; however, polycrystalline ceramic materials obtained by sintering initial oxides are of the major practical significance [4–7, 10, 11].

According to the classical technology, the synthesis of samples is carried out by means of solid-phase reactions from oxides PbO , Fe_2O_3 and Nb_2O_5 by annealing in two stages, with intermediate grinding, at a temperature within the range 800–900 °C and exposure for 4 h [10, 11]. Agglomeration of ceramic blanks is usually carried out at 1080–1120 °C for 2–4 h [10, 11].

The duration of synthesis process and its high labour consumption forced the search and development of new methods of synthesis of PFN-based materials, in particular, mechanochemical one [12–14], based on the use of high-energy grinding. In the present work we study the mechanism of the mechanochemical synthesis of lead ferroniobate using the high-energy strain centrifugal planetary mill AGO-2 [15], subsequent pressing and annealing of the synthesized powders.

It is known that a part of lead gets evaporated during the agglomeration of lead-containing ceramics, because of the high pressure of lead and lead oxide vapour. In order to compensate these losses, lead was introduced in excess at the stage of mechanical activation and the effect of its content on the formation of lead ferroniobate $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ structure during the synthesis was investigated.

EXPERIMENTAL

The following reagents were used to synthesize the indicated material: niobium oxide Nb_2O_3 (card Nos. 16-53, 37-1468, the card indexing corresponds to the American Society for Testing Materials, ASTM) of monoclinic modification, with sp. gr. *P2*, os. ch. reagent grade; hematite Fe_2O_3 (85-599), of rhombohedral modification, space group *R3C*, ch. d. a. reagent grade; massicot PbO (72-93) of orthorhombic modification, space group *Pbcm*, ch. d. a. reagent grade, with an admixture of Pb_3O_4 (41-1493) of tetragonal modification, space group *P42/mbc*.

Initial powder mixtures were activated using the planetary centrifugal activator mill AGO-2 with ball acceleration 40g for 3–25 min. Steel balls 8 mm in diameter were used as milling bodies; the mass of the balls was 200 g, sample mass was 10 g. After every 5 min of activation, the cylinders were opened; the powder was taken out, mixed, and then returned back to the cylinders to continue mechanical activation. The samples were pressed from mechanically activated powders as tablets 10 mm in diameter and thickness about 2 mm. The samples were pressed with a hydraulic press with the load of 10 t/cm².

X-ray phase analysis of initial reagents, activation products in the mixture before and after thermal treatment was carried out by means of powder diffraction with a DRON-3 diffractometer (CuK_α radiation, focusing scheme according to Bragg–Brentano). The mass of samples was determined with the help of UW 220H balance (Shimadzu, Japan), the accuracy of weighing 0.001 g, geometric size – with the help of micrometer, accuracy 0.001 mm. After pressing, the samples were placed in a crucible with aluminium oxide filler and annealed within temperature range 400–1100 °C.

The rate of sample heating to 600 °C was 20 °C/min, from 600 °C to higher temperatures – 10 °C/min. At any given temperature, the samples were annealed for 2 h. Sample cooling was carried out together with the furnace, after it was switched off.

RESULTS AND DISCUSSION

Synthesis from a mixture of lead, iron and niobium oxides

In this series of experiments (series A), a mixture of lead, iron and niobium oxides, in stoichiometric ratios for lead ferroniobate $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ was used. There are also reflections of unreacted iron oxide in the diffraction patterns of the sample after the activation for 15 min, along with the reflections corresponding to the formation of lead ferroniobate structure. Then, the resulting powder was pressed into tablets and subjected to annealing. One can see (Fig. 1, curve 1) that even after annealing at 500 °C the phase that starts to dominate is $\text{Pb}_2\text{Fe}_4\text{Nb}_4\text{O}_{21}$ (50-445, *Fd3m*, X-ray density $D_X = 7.567 \text{ g/cm}^3$) with pyrochlore structure. This phase is isostructural to lead pyroniobate with the structure of deficient pyrochlore $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ (23-322, *Fd3m*, $D_X = 6.766 \text{ g/cm}^3$). With an increase in annealing temperature, the amount of this phase starts to decrease noticeably, however, after annealing

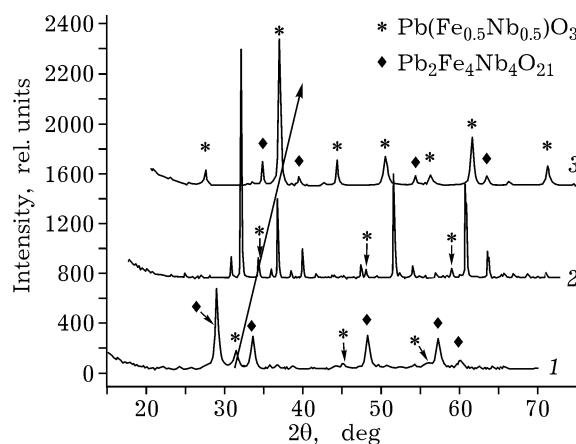


Fig. 1. Diffraction patterns of the samples after annealing at a temperature of 500 (1) and 1000 °C (2, 3) and subsequent polishing (3).

at 1000 °C this phase dominates (see Fig. 1, curve 2); also small reflections of cubic lead ferroniobate $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (32-522), $Pm\bar{3}m$, $D_x = 8.456 \text{ g/cm}^3$ are detected. The $\text{Pb}_2\text{Fe}_4\text{Nb}_4\text{O}_{21}$ phase is formed mainly on the surface of sintered sample. However, even after polishing (see Fig. 1, curve 3) this is not pure $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ but with noticeable admixture of $\text{Pb}_2\text{Fe}_4\text{Nb}_4\text{O}_{21}$, that is, an evident lack of lead oxide is observed in these samples.

Synthesis of lead ferroniobate from a mixture of preliminarily synthesized iron niobate and lead oxide

A mixture of iron and niobium oxides of the composition of FeNbO_4 (series B) was activated for 15 min, then pressed into a tablet and annealed at a temperature of 1000 °C. According to XPA data, iron niobate FeNbO_4 of the monoclinic modification with sp. gr. P^*/a is formed. Then sintered iron niobate was triturated and mixed with lead oxide $\beta\text{-PbO}$ as calculated for reaction $\text{FeNbO}_4 + 2\text{PbO} = 2(\text{PbFe}_{0.5}\text{Nb}_{0.5}\text{O}_3)$. Then this mixture was activated in the mill for 15 min.

It follows from the data shown in Fig. 2 that nearly monophasic lead ferroniobate of cubic modification starts to form as a result of mechanical activation (curve 1). Then samples pressed from the material obtained were annealed within a broad temperature range. It follows from XPA data that up to the temperature of 700 °C a two-phase system is formed,

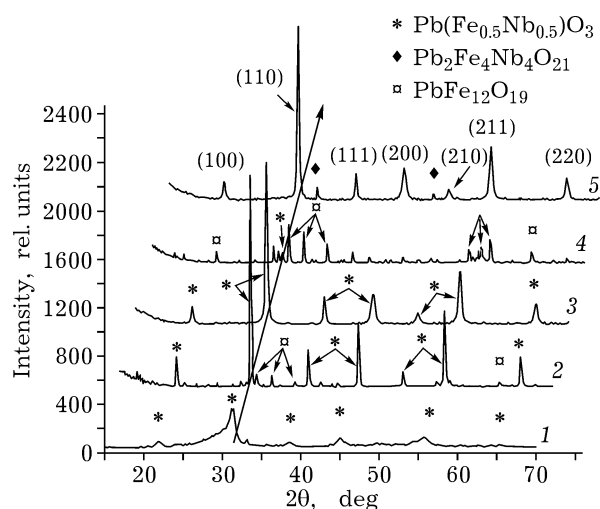


Fig. 2. Diffraction patterns of samples: 1 – after mechanical activation of a mixture of iron niobate and lead oxide for 15 min; 2, 3 – annealed at 1000 °C and then polished, respectively; 4, 5 – annealed at 1100 °C and then polished, respectively.

and the dominating phase is the phase with perovskite structure; a small amount of pyrochlore phase is present. Admixture-free lead ferroniobate is already formed at 750 °C. However, magnetoplumbite phase $\text{PbFe}_{12}\text{O}_{19}$ (84-046) of hexagonal modification $P63/mmc$ appears on the surface of the samples annealed at 1000 °C (see Fig. 2, curve 2). The formation of this phase starts at a temperature nearly 900 °C, and the amount of this phase increases with an increase in sintering temperature; the sample gets depleted of lead. However, this phase is also formed only on the surface of sintered sample. After polishing off the sur-

TABLE 1

Lattice parameters, size and microdeformations of coherent blocks, sample densities (series B) after activation for 15 min

Annealing temperature, °C	Lattice parameter (a), Å	Size, nm	Microdeformations, %	Density, g/cm ³
–	4.011	13	0.35	–
400	4.022	14	0.1	6.06
500	4.017	15	0.2	6.20
700	4.001	38	0.09	6.14
800	4.004	43	0.07	6.64
900	4.005	41	0.1	7.48
1000	4.004	46	0.09	8.04
1000*	4.009	26	0.13	8.04
1100*	4.010	28	0.08	7.59

* Diffraction patterns were recorded from polished surface.

face layer 0.05–0.1 mm thick, the traces of this phase were not detected (see Fig. 2, curve 3). A similar picture is also observed in the diffraction patterns of the sample annealed at 1100 °C (see Fig. 2, curves 4, 5). Table 1 shows the data on lattice parameters, size and microdeformation of coherent blocks, sample density for this series of experiments. In the case of annealing temperatures 1000 and 1100 °C diffraction patterns were recorded from polished surface of samples.

Samples of series B annealed at 1000 °C are characterized by the maximal density of 8.04 g/cm³, which corresponds to 95 % of the X-ray density. Samples of A series are less dense; their maximal density after agglomeration at 1000 °C reaches 7.57 g/cm³. The density change at temperatures from 400 to 800 °C may be explained by the fact that the synthesis of two phases proceeds simultaneously within this temperature range (Fig. 3). One of these phases has perovskite structure with X-ray density $D_x = 8.456$ g/cm³ (32-522), another phase has perovskite structure with the density of 6.766 g/cm³ (23-322).

Effect of the excess of lead oxide and the method of its introduction into the mixture on the formation of the structure of lead ferroniobate $Pb(Fe_{0.5}Nb_{0.5})O_3$

Since the agglomeration stage cannot be avoided in the synthesis of lead ferroniobate,

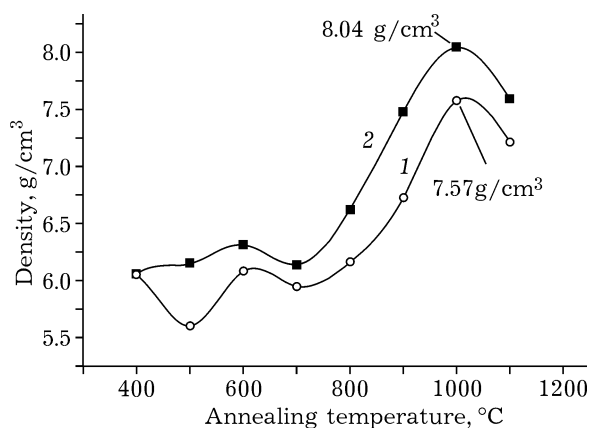


Fig. 3. Sample density depending on sintering temperature: 1 – sintering after mechanical activation of three oxides (series A); 2 – sintering after mechanical activation of previously synthesized iron niobate with the addition of lead oxide (series B).

it is necessary to study the effect of the excess of lead oxide introduced at the stage of the mechanical activation, for the purpose of establishing its optimal amount. We carried out experiments with lead in excess over the stoichiometry of 10, 7 and 3 mass %.

The mechanical activation of a mixture of three oxides containing 10 mass % of excess of lead was carried out for 3, 6, 12, 15 and 25 min (series B). One can see (Fig. 4) that the amorphization and initial stage of the formation of perovskite structure of lead ferroniobate proceed slower than in case when the initial components are taken in the stoichiometric ratio. The excess of lead, which is soft in comparison with iron and niobium oxides, may cause a decrease in the efficiency of the chemical interaction between components and the formation of $Pb(Fe_{0.5}Nb_{0.5})O_3$.

Figure 5 shows the diffraction patterns of the initial mixture after the activation for 15 min (curve 1). One can see that the formation of the perovskite structure of lead ferroniobate starts from the moment when initial compounds are mixed and partially amorphized. The diffraction pattern of the sample after annealing at 600 °C is shown in Fig. 5, curve 2. One can see that compounds $Pb_2Fe_4Nb_4O_{21}$ are formed along with the formation of lead ferroniobate; the amount of the former phase dominates. After annealing at 800 °C, pure lead

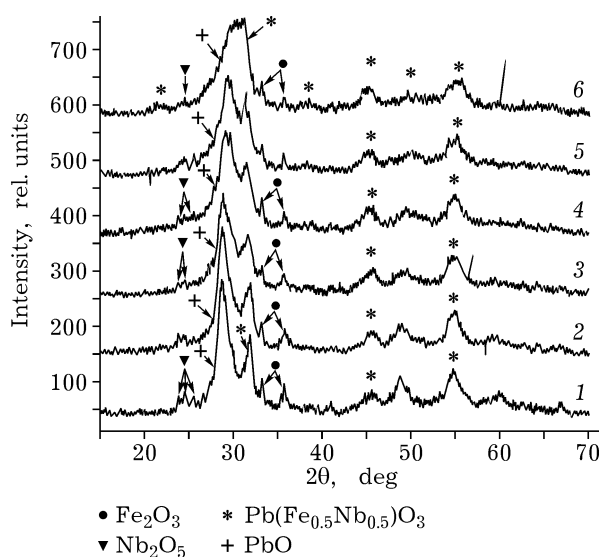


Fig. 4. Diffraction patterns of samples after mechanical activation for 3 min (1), 6 (2), 9 (3), 12 (4), 15 (5) and 25 min (6).

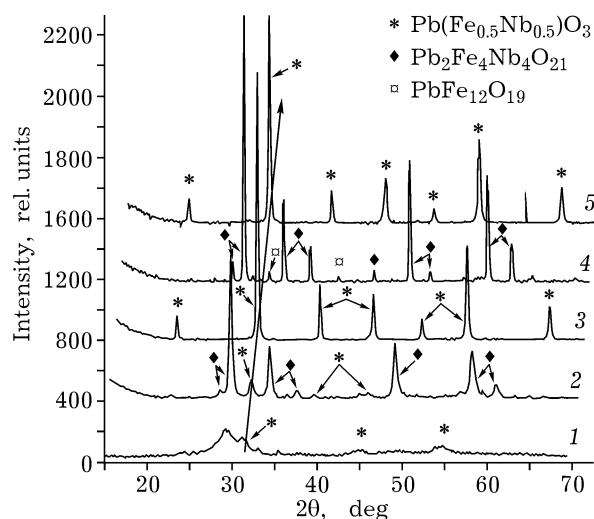


Fig. 5. Diffraction patterns of samples: 1 – after mechanical activation for 15 min; 2–4 – after annealing at 800 (2), 1000 (3) and 1100 °C (4); 5 – polished after annealing at 1100 °C.

ferroniobate $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ is formed, similarly as after annealing at 1000 °C (see Fig. 5, curve 3). Previously, with the stoichiometric ratio of lead oxide in the mixture, the $\text{PbFe}_{12}\text{O}_{19}$ phase was formed on sample surface at annealing temperature of 1000 °C. In the case of annealing at 1100 °C, again $\text{Pb}_2\text{Fe}_4\text{Nb}_4\text{O}_{21}$ phase is formed on the sample surface, with a small amount of $\text{PbFe}_{12}\text{O}_{19}$ (see Fig. 5, curve 4), while the major reflections of lead ferroniobate only insignificantly exceed the background level. However, similarly to the previous cases, this is the surface phase. After polishing off a 0.07 mm layer (see Fig. 5, curve 5) again lead ferroniobate phase without foreign admixtures is detected.

After the mixture activation for 25 min, similar results were obtained. However, samples from the mixture activated for 15 min and agglomerated at 1000 °C are denser than samples obtained from the mixture activated for 25 min: the density is equal to 7.7 and 7.55 g/cm³, respectively. So, the mechanical activation of the mixture for 15 min may be considered optimal.

Investigations of the synthesis and sintering of the samples of three oxides with lead oxide in excess over stoichiometry in the amount of 7 % showed that all the processes occur similarly to the case of synthesis with a 10 mass % lead oxide excess over stoichiometry.

In the next series of experiments (series D), we studied the effect of the method of lead

oxide introduction into the reaction mixture. A 7 mass % excess of lead oxide was added into the stoichiometric mixture activated preliminarily for 15 min and annealed at 1000 °C, then the mixture was thoroughly mixed. After pressing and annealing, it was established that even at a temperature of 700 °C lead ferroniobate phase with a small admixture of $\text{Pb}_2\text{Fe}_4\text{Nb}_4\text{O}_{21}$ phase is formed. The diffraction patterns of the sample annealed at 1000 °C and after polishing the intensity of the reflections of admixture phase is comparable with the level of background. The maximal density of the samples obtained in these experiments is 7.54 g/cm³.

In another series of experiments (E), lead oxide was added into the cylinders after mechanical activation of a mixture of oxides, and activation was continued. Lead oxide was taken in excess over the stoichiometric ratio by 3 mass %. The diffraction patterns of this mixture after activation for 10 min (Fig. 6, curve 1) exhibits only starting to show reflections corresponding to the formation of lead ferroniobate phase, and the reflections of unreacted iron oxide and lead oxide, though strongly amorphized are observed.

After the mechanical activation for 15 min, all the reflections of $\text{Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ appear, along with the reflections of iron and lead oxides. The formation of solid solution based on

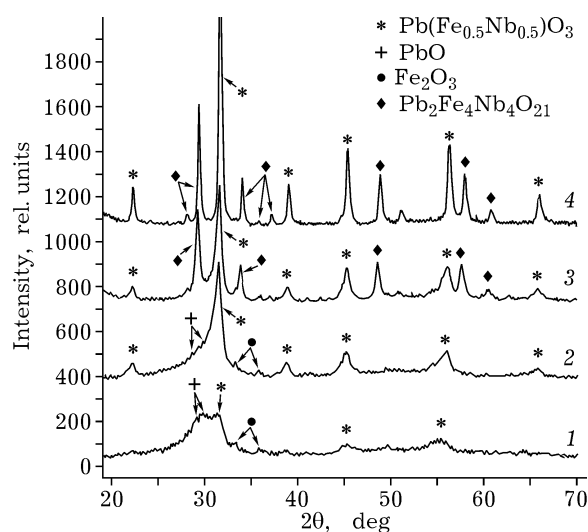


Fig. 6. Diffraction patterns of samples: 1, 2 – after mechanical activation for 10 and 15 min, respectively; 3, 4 – after annealing at 500 and 600 °C, respectively.

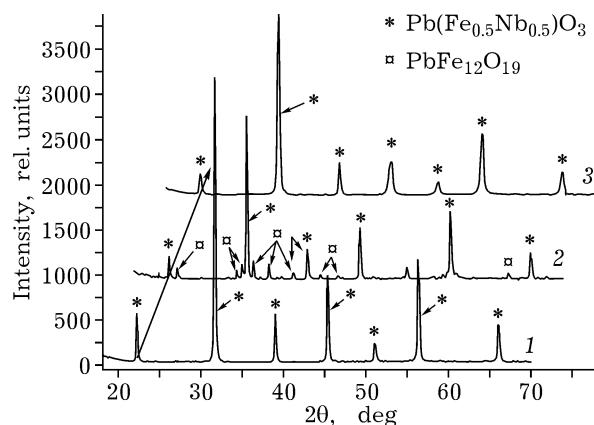


Fig. 7. Diffraction patterns of the samples after annealing at 800 (1), 1000 °C (2) and subsequent polishing (3).

niobium oxide proceeds (see Fig. 6, curves 1, 2). Sample annealing at 500 °C results in the formation of the cubic phase $\text{Pb}_2\text{Fe}_4\text{Nb}_4\text{O}_2$ in addition to lead ferroniobate. The amount of the cubic phase after annealing at 600 °C (see Fig. 6, curves 3, 4) is rather substantial, but it decreases rapidly with temperature rise, and pure lead ferroniobate is formed without any admixture of other phases after annealing at 800 °C (Fig. 7, curve 1). After sintering at a temperature of 1000 °C, the $\text{PbFe}_{12}\text{O}_{19}$ phase is formed on the surface of these samples (see Fig. 7, curve 2); it may be removed by surface polishing (see Fig. 7, curve 3).

So, in this experiment we obtained lead ferroniobate with the maximal density of 8.05 g/m^3 (95.6 % of X-ray density), and rather labour-intensive preliminary sintering of the intermediate iron niobate phase was excluded. There-

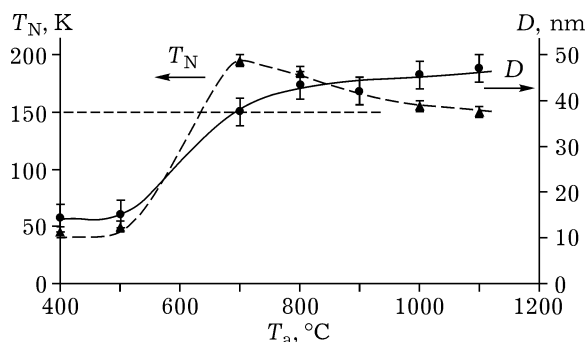


Fig. 8. Dependences of the average size of coherent blocks (D) and the temperature of magnetic phase transition (T_N) on annealing temperature (T_a) for the stoichiometric mixture of $\text{PbO} + \text{FeNbO}_4$ activated for 15 min. Dashed line marks T_N for PFN single crystal.

fore, to obtain high-quality lead ferroniobate ceramics, it is sufficient to add 3 mass % of lead oxide at the stage of the mechanical activation of the mixtures.

The data on lattice parameters, size and microdeformation of the blocks of coherent scattering, density of samples obtained in this series of experiments are presented in Table 2.

Mechanical activation and subsequent annealing affect the magnetic properties of PFN. The dependences of the average size of coherent blocks (D) and the temperature of magnetic phase transition (T_N) on annealing temperature (T_a) for the stoichiometric mixture of PbO and FeNbO_4 activated for 15 min are shown in Fig. 8. The values of (T_N) were determined with the help of express measurements of Mössbauer spectra at different temperatures.

TABLE 2

Lattice parameters, size and microdeformations of coherent blocks, sample densities (series E) after activation for 15 min

Annealing temperature, °C	Lattice parameter (a), Å	Size, nm	Microdeformations, %	Density, g/cm^3
—	4.020	11	0.64	—
500	4.013	4	0.25	6.49
600	4.005	25	0.11	6.62
800	4.008	35	0.12	6.73
1000	4.004	76	0.21	8.01
1000	4.006	27	0.13	8.01
1000*	4.003	44	0.09	8.05
1000*	4.006	26	0.13	8.05

* Diffraction patterns were recorded from polished surface.

CONCLUSION

In the present work, for the purpose of choosing optimal compositions and conditions for the mechanical activation and subsequent thermal treatment, the synthesis of lead ferroniobate from lead, iron and niobium oxides was studied for the reagents taken in stoichiometric ratios and in the presence of excess lead oxide added to prevent deviation from the stoichiometry in the ceramics obtained after sintering. The changes of the phase composition during the mechanical activation and subsequent thermal treatment were followed. The results of calculations of lattice parameters, size and microdeformation of the blocks of coherent scattering were presented for several series of experiments, in which the densest ceramics was obtained. It was shown that lead ferroniobate obtained with lead oxide taken in excess over the stoichiometry by 3 mass % had the most perfect structure. It was established that mechanical activation may be used to vary the temperature of the magnetic phase transition in powders and ceramics of lead ferroniobate within a broad range.

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