

D. BOCHENEK\*, G. DERCZ\*\*, D. OLESZAK\*\*\*

## APPLICATION OF MECHANICAL ACTIVATION IN SYNTHESIZING MULTIFERROIC $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ POWDERS

### WYKORZYSTANIE MECHANICZNEJ AKTYWACJI DO SYNTETYZOWANIA MULTIFERROIKOWYCH PROSZKÓW $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$

In the study, the method of high-energy powder milling – mechanical activation (MA) was used for synthesizing  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (PFN) powders. For the purpose of comparing the influence of high-energy milling on PFN synthesis, two groups of powder samples were used. The first mixture consisting of simple oxide powders; the second one consisting of compound oxide powders. The obtained powders were subjected to structural analysis with the use of XRD and Mössbauer spectroscopy. Tests revealed that during the process of high-energy milling of initial constituents a partial synthesis of PFN material phases occurs. By comparing the two methods of PFN synthesizing it may be stated that mechanical activation in the case of a simple oxide mixture (PFN1) is equally effective as for a compound oxide mixture (PFN2).

*Keywords:* mechanical activation, multiferroics, PFN ceramics, Mössbauer spectra

W pracy, w procesie technologicznym, wykorzystano metodę wysokoenergetycznego mielenia proszków – mechanicznej aktywacji (MA) do syntezy proszków  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (PFN). Do porównania wpływu wysokoenergetycznego mielenia na syntezę PFN wykorzystano dwie grupy próbek proszkowych. Pierwszą mieszaninę stanowiły proszki prostych tlenków (jednoetapowa metoda otrzymywania – PFN1), drugą stanowiły proszki złożonych tlenków (dwuetapowa metoda otrzymywania – PFN2). Otrzymane proszki poddano analizie strukturalnej przy użyciu XRD i spektroskopii Mössbauera. Badania potwierdziły, że podczas procesu wysokoenergetycznego mielenia składników wyjściowych zachodzi częściowa synteza faz materiału PFN. Porównując dwie metody syntetyzowania PFN można stwierdzić, że mechaniczna aktywacja jest jednakowo skuteczna w przypadku mieszaniny prostych tlenków (PFN1) jak i dla mieszaniny złożonych tlenków (PFN2).

## 1. Introduction

The properties of ceramics of a perovskite-type structure depend, to a large extent, on its production technology (the manner of mixing, powdering, synthesis, compacting and sintering of powders), i.e. on chemical homogeneity, crystalline structure and microstructure of ceramics. Because of the broad isomorphism of perovskite-like materials (the possibility of substituting suitable cations at the A and (or) B-positions in the  $A'A''(B'B'')\text{O}_3$  compound), ceramic materials may be obtained for various types of applications [1-3].

Multiferroic  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  (PFN) ceramics has a perovskite-type structure and in certain temperature ranges it shows ferroelectric (at  $T < T_{CE} \approx 114^\circ\text{C}$ ) and antiferromagnetic (at  $T < T_N \approx -130^\circ\text{C}$ ) properties. Thanks to these properties, PFN is an interesting

material from the point of view of modern electrical engineering, and especially as a material for producing multifunctional intelligent elements, i.e. such that react in a particularly strong way to various types of external influences [4-6].

There exist numerous techniques of PFN powder synthesizing such as molten salt synthesis, reaction sintering, columbite, sol – gel, the coprecipitation method and others [7-10]. Main problems during the precipitation technology are the occurrence of a non-perovskite pyrochlore phase, deviation from stoichiometry (PbO escape) and high electric conduction, as well as dielectric losses of PFN ceramics. Thus, currently the search is on for newer and newer technologies while the existing methods of obtaining multiferroic materials are being improved in order to eliminate or minimize unfavorable

\* UNIVERSITY OF SILESIA, DEPARTMENT OF MATERIALS SCIENCE, 41-200 SOSNOWIEC, ŚNIEŻNA 2, POLAND.

\*\* UNIVERSITY OF SILESIA, INSTITUTE OF MATERIALS SCIENCE, 40-007 KATOWICE, BANKOWA 12, POLAND

\*\*\* WARSAW UNIVERSITY OF TECHNOLOGY, FACULTY OF MATERIALS SCIENCE AND ENGINEERING, 02-507 WARSAW, WOŁOSKA 141, POLAND

phenomena created at the stage of their production engineering.

The solid-state reactions initiated by intensive milling in high-energy ball mills could constitute a good choice for the preparation of the ceramic powder (mechanical activation). Intensive milling increases the area of contact between the reactant powder particles due to a reduction in particle size and allows fresh surfaces to come into contact [11]. Mechanical alloying, pioneered by Benjamin [12], was a useful technique for the synthesis of alloys and compound that were very difficult or impossible to obtain by means of other processing routes. It was a high energy milling process whereby the constituent particles are repeatedly impacted, deformed and fractured, creating new and reactive surfaces, leading to mechanochemical reactions and new material phases [13].

There are perovskites that can be formed by a single-step mechanical activation while they cannot be synthesized by a solid-state reaction of mixed oxides. Furthermore, certain perovskites that may steadily be formed by means of a solid-state reaction cannot be formed by mechanical activation. Transitional phases such as pyrochlore phases, which are always involved in the conventional solid-state reaction, can be bypassed in mechanical activation [14]. Very recently, a novel mechanical activation technique has been successfully devised to synthesize a variety of lead-based functional ceramics, such as PMN [15], PZN [16],  $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$  [17] and PZT [18].

In the study, an attempt has been made to use mechanical activation for synthesizing constituent powders in the technology of obtaining  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (PFN) ceramic powders. The impact of high-energy milling of constituents obtained with a one-stage method (based on simple oxides) was compared with the same process performed by means of a two-stage method (based on complex oxides).

## 2. Experiment

A ferroelectromagnetic material with a  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (PFN) composition was selected for the high-energy milling process (mechanical activation). The PFN ceramic powders was obtained through the use of two methods: a one-stage (marked as PFN1) and two-stage (marked as PFN2) one. In the one-stage method, the powder for obtaining PFN constituted a mixture of simple  $\text{PbO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  oxides. In the two-stage method, the powder for obtaining PFN constituted a mixture composed of  $\text{PbO}$  and  $\text{FeNbO}_4$  oxides. The  $\text{FeNbO}_4$  (ferroniobatte) powder was obtained from a mixture of  $\text{Fe}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$ . Synthesizing was conducted by a technique of mixed oxides calcination according

to the following reactions:  $\text{Fe}_2\text{O}_3 + \text{Nb}_2\text{O}_5 \rightarrow 2\text{FeNbO}_4$  at the temperature of  $1000^\circ\text{C}$  for 4h [19]. After calcination, the  $\text{FeNbO}_4$  was subjected to powdering, mixing, and then  $\text{PbO}$  was introduced.

The initial powders for obtaining PFN1 and PFN2 were subjected to initial homogenization in a ball mill for 8h, and next high-energy milling was performed in a “shaker”-type SPEX 8000 D vibrating mill in air at room temperature. During the mill’s operation, the container with powder and steel balls is shaken in three perpendicular directions (frequency of container vibrations – approx. 200Hz, maximum linear speed obtained by balls – around 6m/s, kinetic energy  $<120 [10^{-3}\text{J}/\text{impact}]$ , power  $<0.24 [\text{W}/\text{g}/\text{ball}]$ ). The time of high energy milling equaled 20h.

X-ray diffraction patterns were collected using X-Pert Philips diffractometer equipped with curved graphite monochromator on diffracted beam and with the following slits (in the sequence from Cu tube to counter); divergence ( $1/2^\circ$ ), antiscatter ( $1/2^\circ$ ), Soller ( $2^\circ$ ) and receiving (0.15 mm). The X-ray data collection was performed for  $10\text{-}140^\circ 2\theta$  range with  $0.04^\circ$  step.

Transmission Mössbauer spectra were collected for the 14.41-keV resonant transition in  $^{57}\text{Fe}$  applying commercial  $^{57}\text{Co}(\text{Rh})$  source kept together with the absorbers at room temperature. The thickness of the absorbers was about  $30 \text{ mg}/\text{cm}^2$  of the powder. Experimental spectra were fitted within transmission integral approximation. The isomer shift values are given relative to room temperature  $\alpha\text{-Fe}$ . The values of hyperfine parameters ( $B_{hf}$  hyperfine magnetic field,  $IS$  isomeric shift,  $QS$  quadrupole splitting and the percentage share of constituent phases  $A$ ) were obtained in the process of calculations performed through decomposition into magnetic constituents of the Zeeman sextet and quadrupole doublet constituents corresponding to non-magnetic phases. These parameters describe the specific constituents of the transmission spectrum, taking into account only those phases which include Fe atoms in their composition.

## 3. Results and discussion

PFN powders after mechanical activation characterize irregular shape building and size, which shows on them the enlarged degree of defected, however powders received in two – stage technology PFN possess the larger regularity of shapes (Fig. 1). Larger defected after a mechanical synthesis powder facilitates diffusive processes during synthesis processes. The shape and the appearance of powders the PFN shows, that the process of mechanical activation, the PFN will be more effective during receiving the single-stage method.

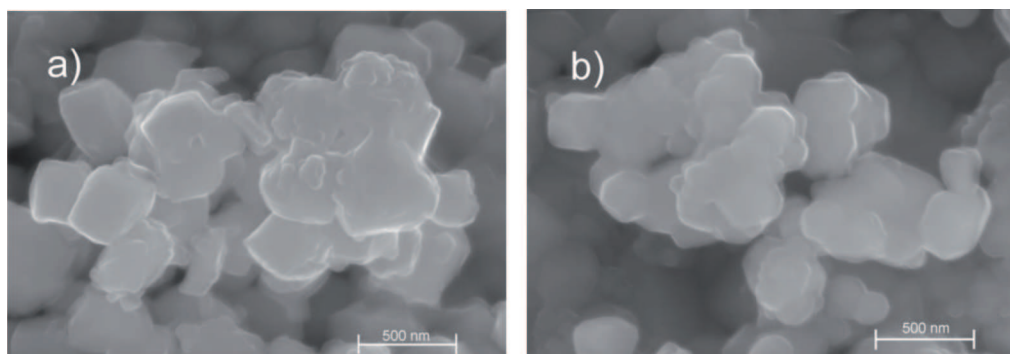


Fig. 1. The SEM of the PFN powders after mechanical activation: (a) in single-stage technology, (b) in two – stage technology.

The X-ray qualitative phase analysis of powders after homogenization for PFN1 prior to high-energy milling confirmed the presence of only initial constituents (Fig. 2). In the case of PFN1 powder, the qualitative phase analysis showed that during high-energy milling of the PFN material for 20h, mechanical synthesis occurs. The tested sample revealed the presence of a  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  (01-089-8042) phases belonging to a tetragonal (P4mm) and regular (Fd3m) crystal structure (Fig. 3). In addition to the phases above, one may also observe the occurrence of diffraction reflection derived from initial constituents ( $\text{Nb}_2\text{O}_5$  and  $\text{Fe}_2\text{O}_3$ ), which confirms the initial (yet not complete) synthesis of the constituent powders. Due to a considerable widening of reflexes on the diffraction pattern, no diffraction reflexes deriving from PbO have been unequivocally identified (Fig. 3).

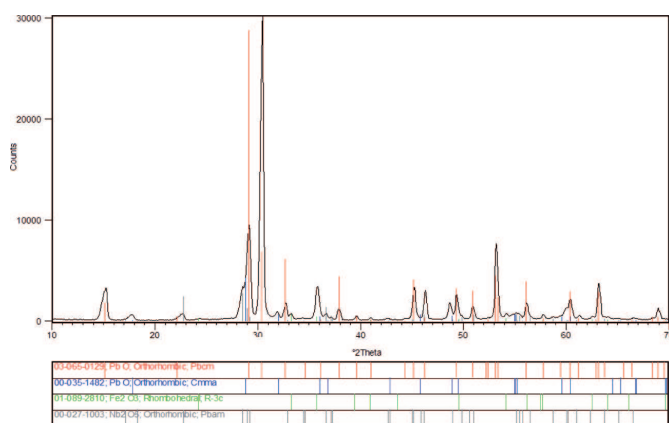


Fig. 2. Diffraction pattern of PFN1 powder after homogenization of initial constituents

The X-ray qualitative phase analysis performed for homogenized PFN2 initial powders has confirmed the occurrence of phases derived from initial constituents (Fig. 4). The presence of other phases which could be the result of the homogenization process, has not been stated.

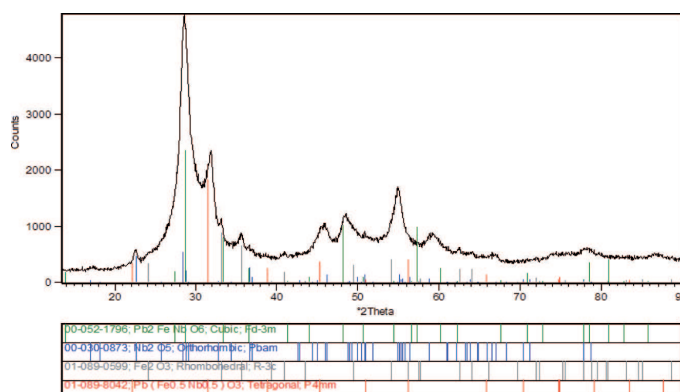


Fig. 3. Diffraction pattern of PFN1 powder after high-energy milling

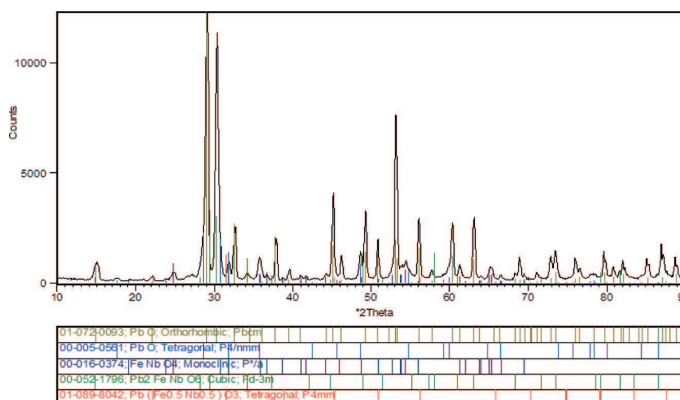


Fig. 4. Diffraction pattern of PFN2 powder after homogenization of initial constituents

Like in the case of a simple oxides' mixture (PFN1), the presence of a tetragonal  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  (01-089-8042) and regular  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  (00-052-1796) phase has been confirmed (Fig. 5). Moreover, diffraction reflexes are observed from one of the  $\text{FeNbO}_4$  (00-016-0374) initial constituents. This means that synthesis of constituent powders does not occur in a complete way. Like as of the PFN1 sample, no diffraction reflexes derived from PbO were identified unequivocally for PFN. This results from a considerable widening of reflexes on the diffraction pattern which is a consequence of interference of

diffraction reflexes from several phases and the change of their profile (Fig. 5).

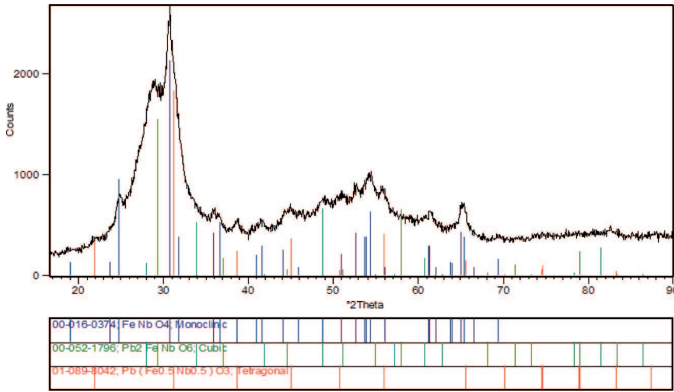


Fig. 5. Diffraction pattern of PFN2 powder after high-energy milling

In Mössbauer studies the percentage share of specific compounds (parameter  $A$ ) was calculated based on the difference between the percentage share of Fe iron before mechanical activation and after the process of high-energy milling. The number, positions, and intensities of the dips (also called peaks) provide information

about the chemical environment of the absorbing nuclei and can be used to characterize the sample. If the nucleus of an atom has a spin larger than one, it will possess a quadrupole moment arising from the non-uniform distribution of charge [20]. The symbol  $A$  stands for contribution of the respective sub-profile (phase) to the total absorption profile, and symbol  $IS$  denotes total shift versus room temperature  $\alpha$ -Fe. The symbol  $QS$  stands for splitting of the quadrupole doublet, while the symbol  $B_{hf}$  denotes magnetic hyperfine field. The symbol  $\Gamma$  stands for the absorber line-width.

Fig. 6a shows the Mössbauer spectrum of a mixture of powdered  $PbO-Nb_2O_5-Fe_2O_3$  oxides for (PFN1), as well as powders obtained after the process of high-energy milling (Fig. 6b).

For PFN1, after an initial homogenization of a mixture of simple oxides ( $PbO$ ,  $Fe_2O_3$ ,  $Nb_2O_5$ ) carried out in a ball mill the spectrum of the initial material consists of a magnetic subspectrum  $Fe_2O_3$  with a hyperfine field 51.5 T and a non-magnetic iron oxide  $FeO$ . The percentage share of specific phases equals 90% for  $Fe_2O_3$  and 10% for  $FeO$  (Table 1).

TABLE 1

The value of hyperfine parameters ( $B_{hf}$ ,  $IS$ ,  $QS$ ),  $A$  and  $\Gamma$  for PFN1 and PFN2 after homogenization of initial constituents and after high-energy milling

	$A$ [%]	$IS$ [mm/s]	$QS$ [mm/s]	$B_{hf}$ [T]	$\Gamma$ [mm/s]
PFN1 – before high-energy milling					
$Fe_2O_3$	90	0.37	-0.22	51.5	0.19
$FeO$	10	0.30	0.80	–	0.70
PFN1 – after high-energy milling					
$Fe_2O_3$	72	0.37	-0.19	51.5	0.24
$PbFe_{1/2}Nb_{1/2}O_3 + FeO$	28	0.30	0.70	–	0.70
PFN2 – before high-energy milling					
$FeNbO_4$	70	0.40	0.38	–	0.19
$FeO$	30	0.41	0.59	–	0.50
PFN2 – after high-energy milling					
$FeNbO_4$	51	0.40	0.41	–	0.21
$PbFe_{1/2}Nb_{1/2}O_3 + FeO$	49	0.35	0.78	–	0.40

where:  $A$  – percentage share of constituent phases;

$IS$  – isomeric shift;

$QS$  – quadrupole splitting;

$B_{hf}$  – hyperfine magnetic field;

$\Gamma$  – absorber line width

Errors for all values are of the order of unity for the last digit shown.

After a mechanical activation of the constituent powder mixture the share of quadrupole doublet increases which favors the creation of  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$ . The Mössbauer analysis showed that approx. 72% of Fe remains in the  $\text{Fe}_2\text{O}_3$  compound while a small portion – approx. 10% of Fe occurs in the non-magnetic iron oxide (FeO). The remaining portion of iron, i.e. approx. 18%, occurs in the newly created  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  compound (Table 1). This is illustrated by the difference between the share of subspectrum  $\text{Fe}_2\text{O}_3$  before and after mechanical synthesis (parameter A) which shows that approximately 18% of iron is transferred from the initial  $\text{Fe}_2\text{O}_3$  to  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$ .

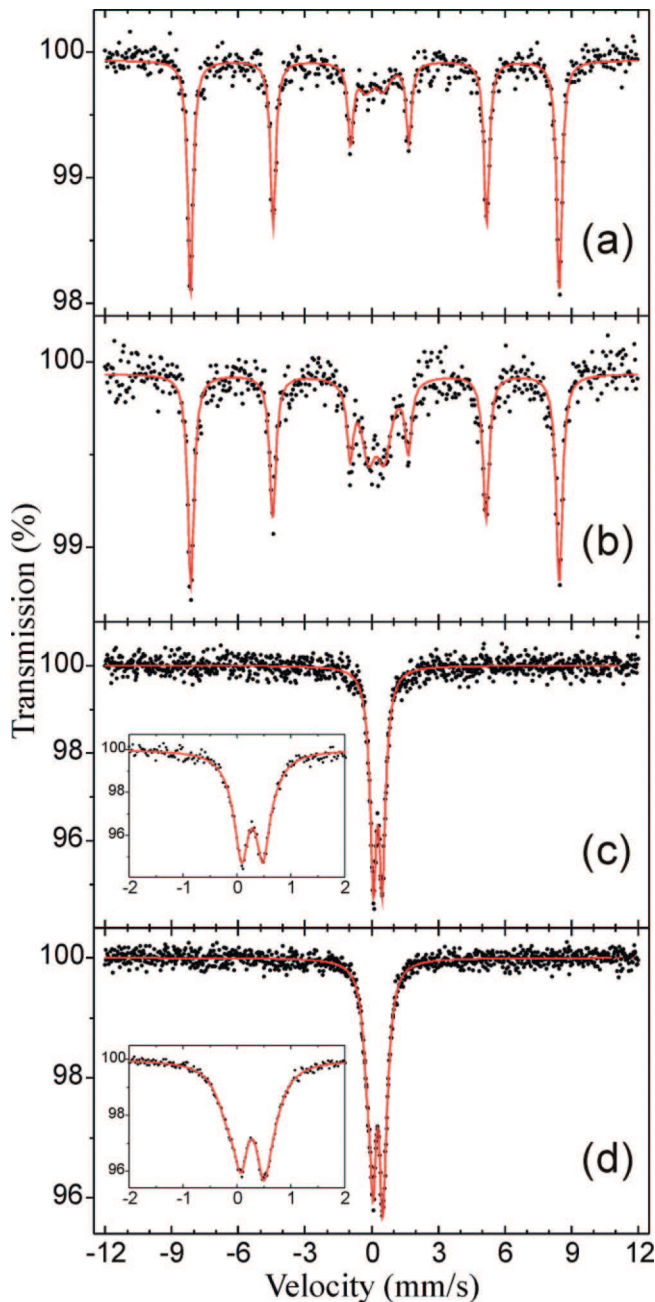


Fig. 6.  $^{57}\text{Fe}$  Mössbauer spectra: (a) PFN1 powder after homogenization of initial constituents, (b) PFN1 powder after high-energy

milling, (c) PFN2 powder after homogenization of initial constituents, (d) PFN2 powder after high-energy milling

In the case of PFN2 powders after initial homogenization of complex compounds ( $\text{FeNbO}_4$  and  $\text{PbO}$ ) the spectrum of the initial material consists of non-magnetic quadrupole doublets which correspond to  $\text{FeNbO}_4$  and FeO in the amount of 70% and 30%, respectively (Fig. 6c, Table 1).

The percentage share of the main phase ( $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$ ) being created in PFN2 after mechanical activation (together with FeO) is considerably larger than in the case of PFN1 and equals 49% and 28%, respectively. However, in PFN2 the effectiveness of transferring Fe from the base compound  $\text{FeNbO}_4$  to the main compound  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$ , after the process of high-energy milling, equals approx. 19% and is comparable for PFN1 (Fig.6d, Table 1). This is proven by the percentage share of subspectrum  $\text{FeNbO}_4$  being decreased by approx. 19%.

#### 4. Conclusions

Constituent powders functioning as initial components for obtaining a multiferroic  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  material (PFN), based on simple oxides (PFN1) and obtained on the basis of complex oxides (PFN2) were subjected to the process of high-energy milling (mechanical activation) in a “shaker”-type mill.

The presented qualitative phase analysis of PFN1 and PFN2 powders after high-energy milling confirmed partial compound synthesis of  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  phases. By comparing the two methods of PFN synthesizing it may be stated that mechanical activation in the case of a simple oxide mixture (PFN1) is equally effective as for a compound oxide mixture (PFN2).

The values of hyperfine parameters prove that apart from Fe atoms also Nb atoms occur in the perovskite layer; moreover, they point to disturbances in a homogeneous distribution of these elements in the B position of the compound.

One of the reasons why PFN powders do not undergo complete synthesis may be the lack of sufficient energy in the environment of the reaction needed for a complete conversion of the initial constituents (e.g. lack of sufficiently high temperature during the process).

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