Influence of composition nonstoichiometry and ordering effects on the properties of ferroelectric ceramics based on lead magnoniobate

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Abstract. The effects of violation of the stoichiometry of lead magnoniobate in the preparation of compositions \((1-x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3 - x\text{PbMg}_{1/2}\text{Nb}_{1/2}\text{O}_{2.75}\) with a step of 0.1 and \(0\leq x\leq 1\) have been studied by X-ray diffraction methods. Differences in the unit cell parameters of the ferroelectric ceramic samples of the composition under study were found. It was shown that the effect of ordering of different types of atoms in the cells, leading to the formation of a superstructure and a doubling of the lattice period, was not observed in any of the samples. Measurements of the dielectric constant of the synthesized samples and the tangent of the dielectric loss angle showed a violation of the Curie-Weiss law, which indicates the diffusion of the phase transition.

1. Introduction

The development of production and research of nanocrystalline materials and structures [1-5] is primarily associated with the potentially unique prospects of their use in electronic engineering. However, the realization of this perspective requires a deep understanding of the essence of physical phenomena and careful development of the physical foundations of the corresponding technological processes for their production and purposeful control of their properties [6-8]. The possibility of using nanocrystalline materials and structures in various technological processes makes it necessary to purposefully control their functional properties. The solution of these problems requires the development of the physical foundations of the corresponding technological processes for obtaining ceramic materials with desired functional properties.

Relaxor ferroelectrics [1, 8], discovered more than half a century ago, are of great interest to researchers today as highly promising functional materials in the form of single crystals, ceramics, and thin films due to the unique set of their properties.

Among oxide perovskites of complex composition \(A_3B'B_{x}O_9\), lead magnoniobate \(\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3\) (PMN), which is still a traditional model object for studying relaxor properties, is of great interest to researchers. In lead magnoniobate, the superstructure of the period doubling of the perovskite cell was found in regions up to 30 Å by the methods of electron, X-ray and neutron diffraction [6-8].

Of course, single crystals, which, as a rule, have high characteristics, are very expensive and unique in preparation, and their use is often limited due to the appearance of defects during their processing. The undoubted advantage of ceramic materials in comparison with single-crystal materials is their...
availability, practicality, and the identity of the functional properties observed in them during the transition to the nanocrystalline state in comparison with single crystals.

In the synthesis of PMN-based solid solutions, the main problem is associated with the presence of the pyrochlore phase simultaneously with the perovskite phase in the samples. This phase is piezoelectrically inactive and its presence leads to low values of the piezoelectric parameters of ceramic elements.

The $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ component was chosen because ordering in the B-sublattice of differently charged $\text{Mg}$ and $\text{Nb}$ atoms with doubling of the periods of the perovskite cell is possible [6,8,9].

2. Materials and methods

2.1. Fabrication of samples and X-ray structural studies
Ferro-ceramic samples were synthesized from a mixture of $\text{PbO}$, $\text{MgO}$, and $\text{Nb}_2\text{O}_5$ oxides selected in appropriate proportions corresponding to the compositions $(1-x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3 - x\text{PbMg}_{1/2}\text{Nb}_{1/2}\text{O}_{2.75}$, where $x$ varied from 0 to 1 with a step of 0.1. The synthesis of the samples was carried out according to the usual ceramic technology for 3 hours at a temperature of 890°C. It should be emphasized that both the synthesis and sintering of the samples were carried out under almost completely identical conditions, which excludes the possibility of the influence of changes in the conditions of the technological process on the properties of the ceramic [7,8].

After each stage of the synthesis, X-ray structural studies were carried out on an URS-50 IM X-ray diffractometer using $\text{Cu}k\alpha$ - radiation with $\text{Cu}k\alpha_1$ filtration by a nickel filter. Lines with $h^2 + k^2 + l^2 = 14$ (321) and 24 (422) were recorded, the measurement accuracy was 0.003 Å in the first case and 0.001 Å in the second.

2.2. Investigation of dielectric properties of samples
Measurements of the dielectric constant of the obtained samples and the tangent of the dielectric loss angle were carried out at the frequency of the measuring field $f = 1$ kHz in the range of temperatures from 25 to 150°C with the heating rate of the samples $\nu = 1$ °C / min. The temperature dependences of the electrical capacity (C) and electrical conductivity (G) of the samples were measured. The calculation of the required values was carried out according to the formulas:

$$\varepsilon = \frac{4\pi h}{S} C$$

(1)

$$\tan\delta = \frac{G}{\omega C}$$

(2)

where $\varepsilon$ is the dielectric constant, $\tan\delta$- tangent of the dielectric loss angle, $h$ and $S$- thickness and surface area of the sample, $C$ and $G$ - measured electrical capacity and electrical conductivity of the sample, $\omega = 2\pi f$, where $f = 1$ kHz.

3. Experimental results and discussion
It was found from the diffraction patterns that, for the selected synthesis and sintering mode, compounds of a perovskite-like type and ideally cubic cell are formed in all compositions. The indexing of the X-ray diffraction patterns showed differences in the cell parameters of the studied compositions with different values of $x$. The obtained results on the cell parameters in the compositions of nonstoichiometric PMN for two types of diffraction reflections of the type (321) and (422) are presented in table 1.

For compositions with $x$ changing from 0 to 0.5, in addition to the perovskite phase, reflections of impurity phases, pyrochlore and two modifications of $\text{Nb}_2\text{O}_5$, were recorded on the diffraction patterns. From the relative intensities of the lines, it was found that the impurities are concentrated mainly on the surfaces of the samples.
Table 1. Cell parameters ($a_{\text{per}}$) in nonstoichiometric PMN compositions for two types of diffraction reflections, type (321) and (422).

| Compositions | $a_{\text{per}}$ (321), Å | $a_{\text{per}}$ (422), Å |
|--------------|----------------------------|---------------------------|
| (1-x)PbMg$_{1/3}$Nb$_{2/3}$O$_3$ - xPbMg$_{1/2}$Nb$_{1/2}$O$_{2.75}$ |                         |                           |
| x = 0.0      | 4.041(3)                   | 4.044(1)                  |
| x = 0.1      | 4.045(3)                   | 4.047(1)                  |
| x = 0.2      | 4.054(3)                   | 4.049(1)                  |
| x = 0.3      | 4.048(3)                   | 4.048(1)                  |
| x = 0.4      | 4.054(3)                   | 4.049(1)                  |
| x = 0.5      | 4.054(3)                   | 4.050(1)                  |
| x = 0.6      | 4.064(3)                   | 4.052(1)                  |
| x = 0.7      | 4.059(3)                   | 4.049(1)                  |
| x = 0.8      | 4.052(3)                   | 4.049(1)                  |
| x = 0.9      | 4.048(3)                   | 4.047(1)                  |
| x = 1.0      | 4.048(3)                   | 4.047(1)                  |

A careful examination of the obtained diffraction patterns of the samples did not reveal any superstructural reflections for all the studied sample compositions, which indicates the absence of the effect of ordering atoms of different types in the B-sublattice leading to a doubling of the unit cell parameters.

Table 2. Values of the dielectric constant ($\varepsilon$) and tangent of the dielectric loss angle ($\tan\delta$) at temperatures $T = 25^\circ C$ and $50^\circ C$.

| Compositions | $T=25^\circ C$ | $T=50^\circ C$ |
|--------------|----------------|----------------|
| (1-x)PbMg$_{1/3}$Nb$_{2/3}$O$_3$ - xPbMg$_{1/2}$Nb$_{1/2}$O$_{2.75}$ | $\varepsilon$ | $\tan\delta$ | $\varepsilon$ | $\tan\delta$ |
| x = 0.0      | 6406           | 0.2055         | 4404           | 0.0342         |
| x = 0.1      | 4449           | 0.0676         | 3483           | 0.0238         |
| x = 0.2      | 3854           | 0.1329         | 3030           | 0.1160         |
| x = 0.3      | 4777           | 0.0512         | 3650           | 0.0441         |
| x = 0.4      | 1948           | 0.1113         | 2059           | 0.2595         |
| x = 0.5      | 10535          | 0.1842         | 9210           | 0.1885         |
| x = 0.6      | 7237           | 0.2938         | 6769           | 0.3446         |
| x = 0.7      | 7631           | 0.0881         | 5949           | 0.0786         |
| x = 0.8      | 8267           | 0.0719         | 6233           | 0.0516         |
| x = 0.9      | 6624           | 0.1777         | 5580           | 0.1951         |
| x = 1.0      | 4460           | 0.0635         | 3536           | 0.0497         |

As is known, lead magnoniobate belongs to the class of ferroelectric relaxors [3,4,10-13]. For all samples, it was found that the Curie-Weiss law is not fulfilled, which indicates a smearing of the phase transition. It is generally accepted that in the case of ferroelectrics with a diffuse phase transition, instead of the usual Curie-Weiss law $1/\varepsilon = (T-T_0)/C_w$, one should use the formula $1/\varepsilon = A + B(1-T/T_0)^m$,
where $A$ and $B$ are some constants, $T_o$ Curie temperature, and $m$ takes on different values from 1.5 to 2.0. For lead magnoniobate, it is usually assumed that $m = 2$. From the temperature dependences $\varepsilon(T)$ at temperatures from 25 to 150°C, the values of the Curie temperature, of constants $A$ and $B$ were obtained by calculation. The values of these parameters are given in tables 2 and 3.

### Table 3. The values of the A and B constants and Curie temperature for different compositions.

| Compositions | $A$, $\times 10^{-4}$ | $B$, $\times 10^{-8}$ | $T_o$, °C |
|--------------|----------------------|----------------------|----------|
| $(1-x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ |                     |                      |          |
| $-x\text{PbMg}_{1/2}\text{Nb}_{1/2}\text{O}_{2.75}$ |                     |                      |          |
| $x = 0.0$    | 0.376355             | 1.523466             | -58.26   |
| $x = 0.1$    | 1.964185             | 3.096179             | -3.68    |
| $x = 0.2$    | 0.612425             | 3.028753             | -48.53   |
| $x = 0.3$    | 1.870444             | 3.515499             | +0.98    |
| $x = 0.4$    | 2.544109             | 7.887078             | -15.78   |
| $x = 0.5$    | 0.935968             | 2.134559             | +22.07   |
| $x = 0.6$    | 1.384200             | 2.972646             | +31.70   |
| $x = 0.7$    | 1.236226             | 2.657120             | +8.40    |
| $x = 0.8$    | 1.069574             | 2.442676             | +2.32    |
| $x = 0.9$    | 1.433186             | 2.951184             | +12.31   |
| $x = 1.0$    | 2.102110             | 3.865964             | +6.50    |

The calculated Curie temperature turned out to be significantly different for different sample compositions, which once again confirms the dependence of the ceramic properties on stoichiometry [14].

### 4. Conclusions

Analysis of the currently available experimental data on the study of the effect of deviations of the oxygen content from stoichiometric one on the physical properties of samples with the perovskite structure does not give an accurate picture of the observed changes in the structure and properties. An experimental study of the synthesis of nonstoichiometric compositions $(1-x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3 - x\text{PbMg}_{1/2}\text{Nb}_{1/2}\text{O}_{2.75}$ ($0 \leq x \leq 1$, $\Delta x=0.1$) shows that the formation of the perovskite phase most likely corresponds to the effects characteristic of nanocrystalline materials. In the course of the study, it has been found that the properties of the obtained ferroelectric ceramics based on lead magnoniobate substantially depend on the stoichiometry. In ceramics, a structure with a predetermined ratio of magnesium and niobium is not realized; some of these substances contribute the formation of the perovskite structure, and some are released in the form of impurity phases. A diffuse phase transition was observed in the synthesized samples.

Thus, the studies of the nature and conditions of the formation of the structural and electromagnetic properties of ceramic samples with substitutions of different-valence magnesium and niobium ions in the B-sublattice and deviations from stoichiometry in oxygen are promising both in terms of determining the relationship and mutual influence of structural parameters on physical properties, and in connection with the urgent need to create promising functional materials and control their characteristics.

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