Lead ferroniobat ceramic and films structures manufacture features and dielectric characteristic

S H Alikhadjiev\textsuperscript{1}, M A Kazaryan\textsuperscript{2}, A V Pavlenko\textsuperscript{1,3} and P S Plyaka\textsuperscript{3,4}

\textsuperscript{1} Southern federal university, 105/42 B Sadovaya str., Rostov-on-Don, 344006, Russia
\textsuperscript{2} P.N. Lebedev Physical Institute of Russian Academy of Sciences, 53 Lenin ave., Moscow, 119991, Russia
\textsuperscript{3} Southern Scientific Center of Russian Academy of Sciences, 41 Chekhova str., Rostov-on-Don, 344006, Russia
\textsuperscript{4} E-mail: pavelsp08@gmail.com

Abstract. Lead ferroniobat lithium doped ceramic samples have been prepared and investigated. Ceramic high quality has confirmed by obtained structural and electro physical properties. The attempt to thin films synthesis by deposition in a capacitive radiofrequency discharge from ceramic target is described; MgO substrate and pure oxygen ambient have been used. Synthesized films structure properties have been investigated, X-ray pattern with lead ferroniobat weak peak and cross-section SEM-image are presented.

1. Introduction
Lead ferroniobat (PFN) is a representative of the class of materials called "multiferroics" [1]. Its rather high values of the Neel and Curie temperatures make PFN a very interesting object from an applied point of view [2]. PFN have great perspectives for UHF and sensor technique [3], especially in thin film form [2, 4]. A series of papers is devoted to growth and characterization of lead ferroniobat thin films, but achieved structural properties are not high yet [5, 6], even when one uses specially prepared substrate [7]. Almost all PFN thin films have been prepared by pulsed laser depositions [4 - 6], film parameters are critical to substrate temperature and ambient oxygen pressure [5].

Thin films deposition technology in oxygen capacitive radiofrequency discharge is well known [7, 8], one stage film synthesis is realized in high energies electron beam influence discharge region [9]. Electron beams transmit energy to deposited film and increase atoms mobility, facilitating to dislocations reduction. Barium-strontium titanate [8], barium-strontium niobate [10], bismuth ferrite [7] and other thin films have just been successfully synthesized on MgO simple substrate and demonstrated high quality structure and electro physical parameters.

Attempt to fabricate PFN thin films by discharge sputtering deposition from specially prepared ceramic target is the aim of presented work. Target technology and properties have been also investigated.

2. Experimental part
The ceramic targets of 38 mm in diameter have been synthesized by the method of solid-state reactions from the high-purity oxides PbO, Fe\textsubscript{2}O\textsubscript{3} and Nb\textsubscript{2}O\textsubscript{5} using two-stage annealing with intermediate milling at temperatures \(T_1=1123\) K for 4 hours \((r_1=r_2)\). At each temperature the
synthesized products were sintered at \( T_{\text{sint}} = 1373 \) K for 2 hours. 1 mass % lithium carbonate has been added at synthesis stage for lithium doping.

X-ray powder diffraction patterns were recorded on DRON-3 diffractometer in the Bragg–Bretano geometry with filtered CuK\( \alpha \) radiation. The dielectric spectra were investigated using Aglient E4980A LCR meter in the temperature and frequency ranges of 300–500 K and 20 Hz–2.0 MHz, respectively. Piezoelectric constants have been measured by YE2730A d33 meter.

For thin film depositions we have chosen technology based on ceramic target sputtering in capacitive radiofrequency discharge without using magnetron [8]. Film rising and crystallizations occurred in pure oxygen, RF power, initial substrate temperature, substrate-target distance and oxygen pressure varied and for the best films sample were equals to 240 W, 460 °C, 12 mm and 0.38 Torr respectively.

3. Results and discussion

The analysis of experimental results evidences the obtaining of high-density, impurity-free samples of the PFNL ceramics (the relative density, \( \rho_{\text{rel}} > 95\% \)), which enables one to consider them as reliable and trustworthy. The microstructure of the surface and ceramic cleavages, presented in Figure 1, were studied in detail by microanalysis.

![Figure 1. PFN+Li₂CO₃ target microstructure fragments. The markers in fragments are 10 µm](image)

The deep etching of the surface allowed assessing the grain size (~10–20 µm) and their shape (polyhedrons). Fractures in the cleavage occurred mostly along grains and, to a lesser extent, along their boundaries. The character of the cleavage and the features of the etching likely indicate the closeness of the strengths of intergrain boundaries and the grains themselves.

Investigated PFN ceramic permittivity has demonstrated variance absence until 400 K temperature. Measured piezoelectric constants had the next values: \( |d_{31}| = 82 \) pQ·N\(^{-1}\), \( d_{33} = 230 \) pQ·N\(^{-1}\), and \( Q_M = 262 \). Obtained results confirm enough high material quality. Ceramic dielectric parameters plots are presented in Figure 2. The well defined, frequency independent \( \varepsilon'(T) \) maximum at \( T = 367 \) K is indicative of the fact that it is just the temperature which is \( T_C \).
Figure 2. PFNL ceramic temperature dependences of relative permittivity $\varepsilon'$ (top) and dielectric loses $\tan \delta$ (bottom) for lot of frequencies in the range of $10^2 \div 10^6$ Hz

Obtained thin film samples were not convincing enough. X-ray pattern example is presented in Figure 3. As can be seen lead ferroniobat thin film reflex is smaller than MgO substrate peak. The major well-known difficulty in lead containing material film sputtering is lead volatility. Lead evaporation from target and deposited film surfaces results in a thin films violation. A lot of high intensity atomic lead spectral lines have been observed in discharge plasma during PFNL thin films deposition. Grown films composition investigation confirmed the lead deficiency. To prevent lead evaporation losses we plan to change ceramic target technology.

Figure 3. Synthesized thin films X-ray pattern

Electron microscope investigations by FE-SEM Zeiss SUPRA 25 of deposited on substrate film
chipping demonstrated monolithic structure layer on substrate surface. Results are presented in the figure 4 and confirmed suboptimal technology regimes. As can be seen monolithic layer has thickness equal to 127 nm, but it is covered by loose layer with 17 nm thickness. Thin films growth rate was about 4 nm/sec, thus only films layer, formed during last 4 minutes, is non monolithic. Evaporation of lead and oxygen can result in top layer structure defects. Works on PFN thin film radiofrequency discharge sputter depositions optimal regimes will be continued, the main efforts will be focused on film deposition final stage including pressure rising and RF power changing.

Figure 4. PFNL thin film on MgO substrate cross-section SEM-image

4. Conclusions
Obtained lead ferroniobat ceramic samples have demonstrated high ferroelectric characteristics. The main measured electro physical parameters are presented. An encouraging result has been reached in lead ferroniobat thin film on MgO substrate deposition. Film samples have X-ray reflex corresponding to perovskite crystal structure and basically monolithic layer.

Acknowledgments
This study was supported by the Ministry of Education and Science of the Russian Federation (the base and project parts of state order: no. 3.1246.2014/K) and the Russian Foundation for Basic Research (project no. 150805711 A)

References
[1] Lente M H, Guerra J D S, De Souza G K S, Fraygola B M, Raigoza C F V, Garcia D and Eiras J A 2008 Phys. Rev. B. 78 5421-5425
[2] Gao X S, Chen X Y, Yin J, Wu J, Liu Z G and Wang M 2000 Journal of Materials Science. 35 054109
[3] Zvezdin A K, Loginov A S, Meshkov G A and Pyatakov A P  2007 Proc. Rus. Academy of Sci. Phys. [Izvestiya Rossiyskoy Akademii Nauk. Fizika – in Russian] 71/1 1604
[4] Peng W, Lemée N, Karkut M, Dkhil B, Shvartsman V V, Borisov P, Kleemann W, Holc J, Kosec M and Blinc R 2009 Appl. Phys. Lett. 94 012509
[5] Wei Z, Shu Ya W and XiangMing C 2013 Chinese Science Bulletin 58 27 3398-3402
[6] Yan L, Lia J and Viehland D 2011 Journal of Materials Research 23 3 663-670
[7] Mukhortov V M, Golovko Y I and Yuzyuk Y I 2009 Advances in Phys. [Uspekhi Fiziki – in Russian] 52/8 856
[8] Mukhortov V M, Golovko Yu I, Tolmachev G N and Mashchenko A I 1999 Rus. J. App. Phys. 44/12 1477
[9] Schulze J, Heill B G, Luggenhölscher D, Mussenbrock T, Brinkmann R P and Czarnetzki U 2008 J. Phys. D: Appl. Phys. 41/4 042003

[10] Tolmachev G N, Kovtun A P, Zakharchenko I N, Aliev I M, Pavlenko A V, Reznichenko L A and Verbenko I A 2015 Phys. Solid State 57/10 2106