

PHASE AND MORPHOLOGY FORMATION OF Na DOPED PMN THIN FILMS PREPARED BY MODIFIED SOL-GEL METHOD

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Na doped lead magnesium niobate $Pb(Mg_{1/3}Nb_{2/3})O_3$ (Na-PMN) thin films of 100 nm thickness were prepared by modified sol-gel route with niobium precursor. Na-PMN films were deposited from sol derived using tartaric acid modified polymerizable complex method by mixing of Nb-tartarate (Pechini) complex with Na, Pb and Mg acetates at 80°C with molar ratio of Na : Pb : Mg : Nb = 1/2 : 1 : 1/3 : 2/3 on Pt/Al₂O₃ substrates by spin-coating method. In Na doped PMN film the perovskite $Pb(Mg_{1/3}Nb_{2/3})O_3$ phase (65 vol. %) and a small amount of pyrochlore $Na_2Nb_8O_{21}$ phase were revealed after sintering at 650°C. In the microstructure of 2-layered Na-PMN/Pt/Al₂O₃ thin film, with ~9.5 nm of roughness, the bimodal particle distribution was observed with small spherical particles of pyrochlore phase and larger sponge-like particles of the perovskite phase. The smallest visible spherical particles (~30 nm) and mutually interconnected particles (~125 nm) were found in TEM and AFM micrographs.

INTRODUCTION

Perovskite relaxor lead magnesium niobate $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) thin films are of considerable interest in various dielectric, optical, sensors and microelectromechanical system (MEMS) applications [1]. PMN thin films have been prepared by mixed-oxide route and deposited on different substrates by pulsed laser deposition (PLD) [2, 3]. PMN-based films are doped and mixed with other perovskite structured ferroelectrics $PbTiO_3$ (PT) and $PbZrO_3$ (PZ) or oxides PbO , ZrO_2 and TiO_2 to obtaining specific properties [3]. PMN-PT (70/30) thin films have been deposited by PLD method [4] or RF magnetron sputtering [5, 6].

The chemical solution deposition (CSD) process, as sol-gel with compositional control has been used for the preparation of perovskite oxide thin films, deposited by spin-coating method [7]. To prevent the rapid hydrolysis in alkoxide sol-gel method, some ligands such as acetic acid were replaced [8, 9] by Pechini modifying the solution precursors with polymer species, which play more important roles in sol-gel processing of oxide films [10, 11]. Citric acid based Ti and Nb precursors are highly stable polymerizable complexes for the preparation of calcined powders PMN-PT [12, 13]. The precursor solutions of niobate ceramics have been prepared using the tartaric acid modified Pechini complex (PC) method with ethylenediaminetetraacetic acid (EDTA) [14-16].

The (1-x)PMN-(x)PT thin films, with $x=0-0.5$, were prepared by PC process and deposited by spin-coating on quartz and Pt/Ti/SiO₂/Si substrates [17]. From references results that it is very difficult to obtain pure perovskite PMN phase in these films. Depending on the processing conditions, a second pyrochlore phase reduces dielectric properties of the films. At low contents of PT, the PMN-PT films are composed of a large portion of pyrochlore phase and a small portion of perovskite phase. As the $PbTiO_3$ mole fraction increased, the pyrochlore phase of PMN-PT film decreased [18]. Although 0.57PMN-0.43PT films with pure perovskite phase have been obtained using polyvinylpyrrolidone (PVP) as modifier and lead nitrate in sol-gel process [19]. The pyrochlore phase as the intermediate product during perovskite crystallization, was not detected in the films with 0.25 - 1.0 PVP addition and sintered at 460 - 650°C. The parasitic pyrochlore phase dominated at low temperature (< 550°C) and it can be completely removed at annealing temperatures as high as > 700°C. In addition, the development of phase and particle morphology in PMN-PT [8, 20-22] sol-gel prepared ferroelectric thin films depend on the type of substrates and film thickness (200 - 800 nm). The main problem in PC method prepared (1-x)PMN-(x)PT films, with $x=0, 0.1, 0.35$ and 0.5, on a Pt/Ti/SiO₂/Si substrate was the occurrence of the parasitic pyrochlore phase at $x=0$, whereas the pure perovskite phase at $x=0.5$ and 600°C in a lead-rich atmosphere was

found [17]. While the film with nearly single perovskite phase had a dense and uniform microstructure, the film with a large portion of pyrochlore phase showed very porous and non-uniform plate-like morphology. It is not only there reason of the different particle growth mechanism in both phases, but also the differences in the volatility of Pb component during annealing process. In ref. [23], Na-doped PMN-Pb(In_{1/2}Nb_{1/2})O₃ (PIN) (70/30) thin films 5 wt. % of sodium were prepared by mixed-oxide route and deposited at 650°C by PLD. Note that the addition of 3.5 - 5 wt. % sodium into PMN film on Pt/Al₂O₃ sol-gel preparation procedure was not used.

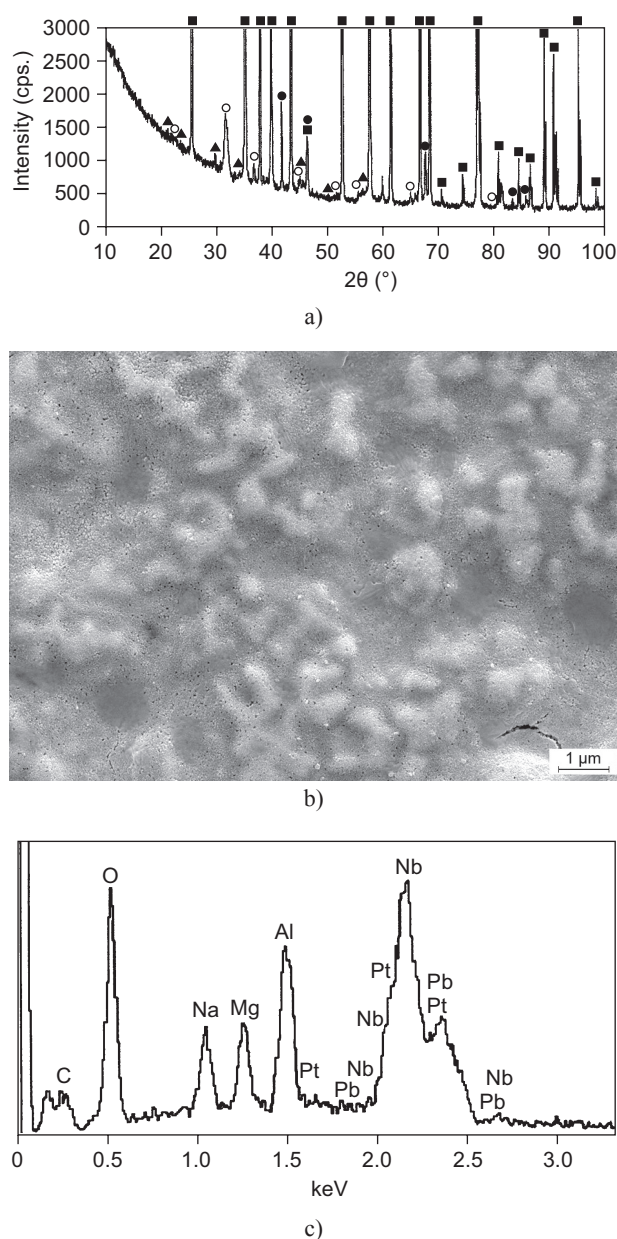


Figure 1. 2-layered Na-PMN thin film deposited on Pt/Al₂O₃ substrate after sintering at 650°C; a) XRD diffractogram (○ - perovskite (pv) Pb(Mg_{1/3}Nb_{2/3})O₃ phase, ▲ - pyrochlore (py) Na₂Nb₈O₂₁ phase *n* - Al₂O₃ substrate and ● - Pt); b) SEM micrograph; c) EDX analyse

In this work, the Na doped PMN thin films were prepared by modified sol-gel method using mixing of polymeric Nb-tartrate complex with Na, Pb and Mg acetates at molar ratio of Na:Pb:Mg:Nb = 1/2:1:1/3:2/3, spin-coating method onto Pt/Al₂O₃ or Pt/SiO₂/Si substrates and sintering at 650°C. The effect of novel Na doping, Nb-tartrate using and applying stabilizer solution in sol-gel process on the phase composition and particle morphology of Na-PMN thin films after sintering at 650°C was investigated.

EXPERIMENTAL

Preparation of Pechini-type polymerizable Nb-complex

The niobium precursor solution for Na-PMN thin film has been prepared by modified Pechini-type polymerizable complex (PC) method [24]. The niobium (V) chloride was dissolved in ethanol and precipitated with ammonium NH₃(aq) to prepare hydrated niobium oxide. The Nb-tartrate-ethylene glycol complex was formed by a reaction of Nb₂O₅.xH₂O with tartaric acid (TA) and H₂O₂. The obtained solution was dried at 80°C and dissolved in ethylene glycol (EG) (the molar ratio of EG/TA = 5.5).

Preparation of Na-PMN sol

Na-PMN precursor solution (sol) was prepared by modified sol-gel method using Pechini method and stabilizer solution [24, 25]. Sodium carbonate, lead acetate trihydrate and magnesium hydroxycarbonate 4[MgCO₃]·Mg(OH)₂·5H₂O were dissolved separately at 80°C in acetic acid. The solutions were dehydrated at 105°C/2 h and after cooling to 80°C, they were mixed with the Nb-tartrate-ethylene glycol complex to obtain sol with molar ratio of Na:Pb:Mg:Nb = 1/2:1:1/3:2/3. Finally, the basic sol was diluted and stabilized with stabilizer solution (n-propanol:1,2-propanediol equals 10:1) to 1.0 M final concentration [26]. The resulting 3.5 wt. % Na doped PMN sol was transparent and remained stable at room temperature for two months.

Preparation and characterization of Na-PMN thin films

The platinumized alumina wafers were used as substrates with Pt (50 nm) layer (sputtered as a bottom electrode). Pt/Al₂O₃ substrates were spin-coated with the Na-PMN sol precursor at 2000 rpm for 30s followed by calcining at 400°C for 5 min. The above coating-pyrolysis process cycle was repeated twice to obtain the 1 and 2-layered thin films. Finally, films were crystallized via sintering at 650°C for 1 hour in air to form the perovskite structure of Na-PMN thin films.

The phase composition of Na-PMN thin films was determined by the X-ray diffraction analysis (XRD, Philips X' Pert Pro) using CuK_α radiation. The volume fraction of the perovskite (pv) phase in the thin film pv [vol. %] can be calculated as a ratio of the intensities of XRD diffraction peaks from the reflection of (110) plane of pv phase (I_{pv}) and reflection of (222) plane of pyrochlore (py) phase (I_{py}) according to Equation (1), respectively [27].

The surface and cross-section microstructures of 1-2 layered Na-PMN thin films were characterized using a scanning electron microscopy (SEM, Jeol-JSM-7000F) equipped with an energy dispersive X-ray (EDX) analyser, atomic force microscopy (AFM, Aicon) and transmission electron microscopy (TEM, TESLA BS 500).

RESULTS AND DISCUSSION

Phase formation of Na-PMN thin film

The XRD diffractogram, SEM micrograph and EDX analyses of 2-layered Na-PMN thin film deposited on $\text{Pt}/\text{Al}_2\text{O}_3$ prepared at 650°C are shown in Figure 1a. The XRD diffractogram of Na-PMN film verifies the

presence of perovskite (pv) $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ phase (JCPDS 27-1199) with small amount of the pyrochlore (py) $\text{Na}_2\text{Nb}_8\text{O}_{21}$ (JCPDS 30-1229) phase formation. The volume fraction of the perovskite phase in Na-PMN thin film was ~ 65 vol. %. Probably it was caused by the incorporation of sodium ions into the PMN, since the Na^+ ion will substitute the lead or magnesium positions. The crystallinity size (according to Scherrer equation) in the film was around ~ 30 nm whereas pv phase had rhombohedral symmetry. The SEM surface micrograph and EDX analysis of 2-layered Na-PMN thin film deposited on $\text{Pt}/\text{Al}_2\text{O}_3$ and prepared at 650°C are shown in Figures 1b and 1c. EDX analyses showed the presence of Na, Pb, Mg and Nb elements in the film and Al, Pt from substrate. The perovskite phase formed as a result of Na doping from the amorphous Na-PMN film following the pyrochlore and perovskite crystallization. The pyrochlore $\text{Pb}_2\text{Nb}_2\text{O}_7$ and perovskite (66 %) phase formation of PMN thin film on $\text{Pt}/\text{SiO}_2/\text{Si}$ substrates deposited by sol-gel method reported in reference [17], which supports our result that around 65 % of perovskite phase is formed in Na doped PMN film of thickness 100 nm.

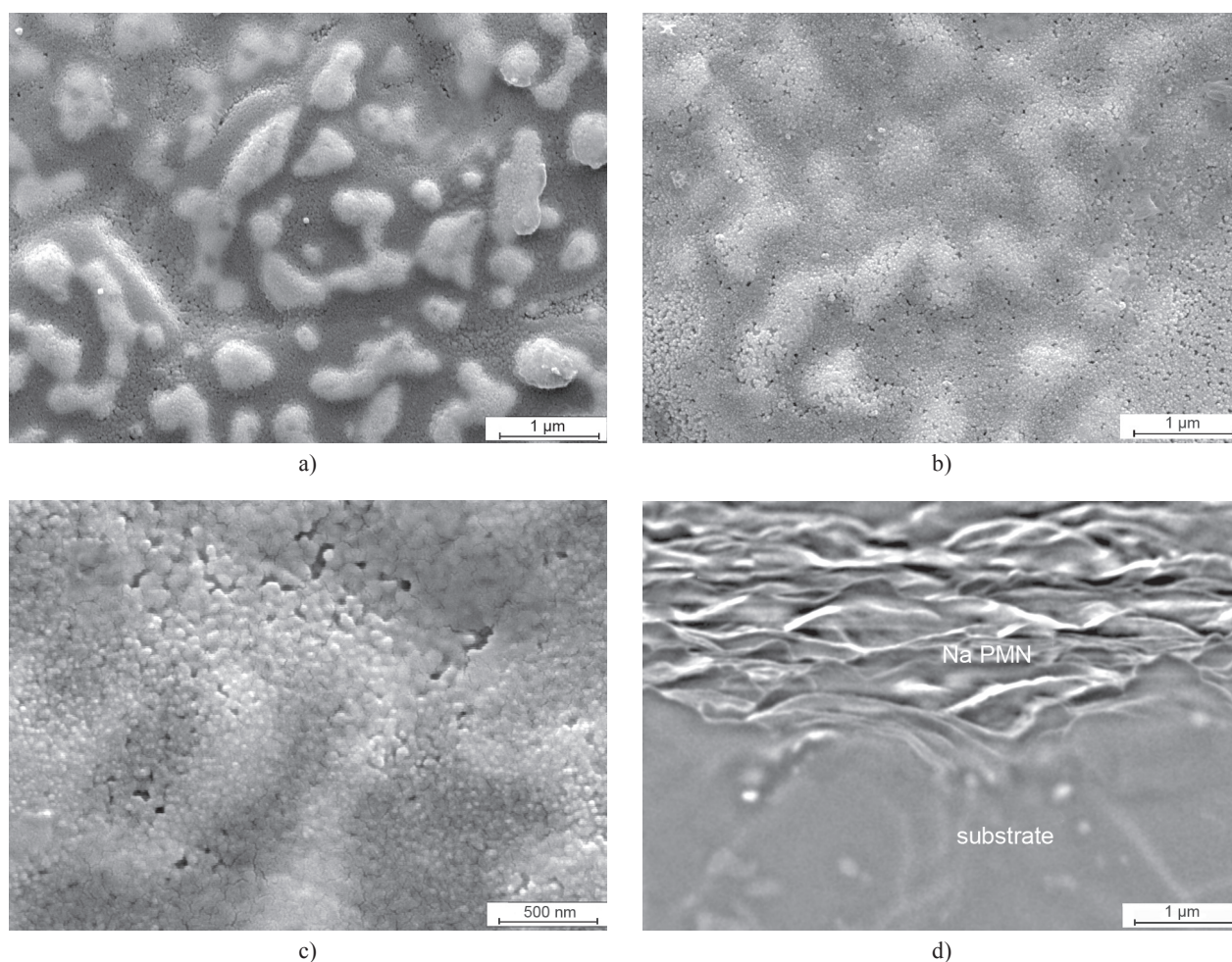


Figure 2. SEM surface micrographs of Na-PMN thin film deposited on $\text{Pt}/\text{Al}_2\text{O}_3$ substrate after sintering at 650°C ; a) 1-layer, b), c) 2-layers and d) cross-section of the 2-layered film.

Effect of pyrochlore $\text{Na}_2\text{Nb}_8\text{O}_{21}$ phase on morphology of Na-PMN thin films

SEM surface and cross-section micrographs of 1 and 2-layered Na-PMN thin film deposited on Pt/ Al_2O_3 substrate after sintering at 650°C are shown in Figure 2. The particle coalescence structures appeared in the 1-layered film, in which some sub-micron sized particles

coalesced to form particle clusters. With an increasing number of depositing layers, even more particle coalescent clusters were mutually interconnected. The microstructure of 2-layered film (Figures 2b and 2c) was characterized by a bimodal particle size distribution, containing smaller probably spherical pyrochlore $\text{Na}_2\text{Nb}_8\text{O}_{21}$ particles and larger sponge-like perovskite $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ sized particles (approx. 20 - 30 nm and 80 - 120 nm). The SEM investigation of surface revealed that the smaller particles were more prevalent on the surface and often covered larger particles. The film surface roughness (100 nm thickness) is visible from the cross-section of 2-layered thin Na-PMN film (Figure 2d). The film thickness increased with the number of layers.

Kighelman et al. [28] and Chen et al. [29] report similar phenomena for PMN thin film deposited by sol-gel, which were attributed to small particles size due to a heterogeneous nucleation. The shape of particles of the PMN-PT thin film is needle-like, square or rounded square and irregular. The clusters of fine particles were observed in the PMN-PZT film, which might be attributed to the surface pyrochlore phase [30]. The pyrochlore phase clusters were only confined to the surface of thin films, and the bulk of the film was dominantly in the perovskite phase. In the 0.5PMN-0.5PT film were observed small spherical particles (from 8 to 25 nm) that appear to be related to the perovskite phase, but in some there are more square, coarse particles that may be related to the pyramidal pyrochlore phase. It can be concluded that the thermal treatment represents a very important step in promoting the formation of the perovskite phase

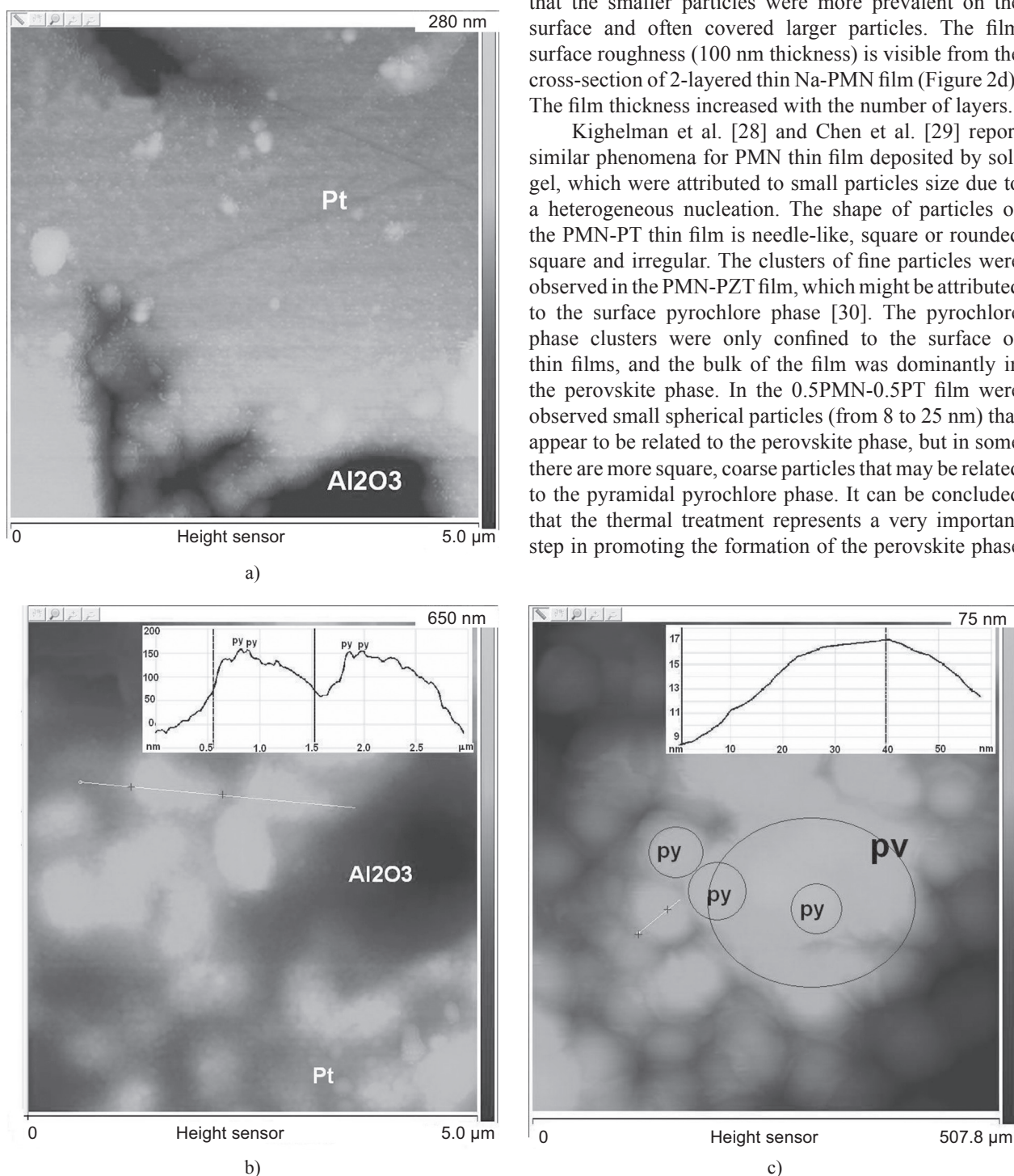


Figure 3. 2D AFM topography micrographs of (a) Pt/ Al_2O_3 substrate and (b, c) 2-layered Na-PMN thin film deposited on Pt/ Al_2O_3 substrate after sintering at 650°C and cross-lines; b) and c) over scan areas of $5 \times 5 \mu\text{m}^2$ and $500 \times 500 \text{nm}^2$, respectively.

formation as opposed to the pyrochlore phase [17]. The triangular perovskite particles of size ~ 150 nm consisted the microstructure of PMN film with thickness of 200 nm [17] and Na doped PMN-PIN film with thickness of 380 nm [23] have been obtained by PLD method. The surface morphology of Na-doped film exhibits a porous microstructure and the particle size is approximately 30 - 50 nm (smaller particles) and 100 - 150 nm (bigger particles) [23].

The atomic force microscopy (AFM) surface topography micrographs of the Pt/Al₂O₃ substrate and

2-layered Na-PMN thin film deposited on Pt/Al₂O₃ substrate are shown in Figures 3 and 4. In the 2D (Figure 3a) and 3D (Figure 4a) AFM surface topography micrograph, the Pt particles in Pt layer were observed. The root mean square roughness (R_q) over scan areas of 5×5 μm^2 of platinumized substrate was ~ 5.7 nm. (The value of average roughness (R_a) = 4.1 nm). The 2D AFM micrographs and AFM section-lines (over scan areas of 5×5 μm^2 and 500×500 μm^2 , respectively) (Figure 3b, c) of Na-PMN films showed the film roughness and particle shape are comparable with SEM surface micrographs in Figure 2b, c. The root mean square roughness (R_q) over scan areas of 5×5 μm^2 was found to be ~ 9.5 nm. (The value of average roughness (R_a) = 8.9 nm). The root mean square roughness of PMN-PT film was approximately 5.9 nm [31] and 8.9 nm [32]. From analysis of the 2D and 3D topography of Na-PMN film results that probably the spherical pyrochlore (py) Na₂Nb₈O₂₁ particles (10-20 nm) were uniformly dispersed on larger sponge-like perovskite (pv) Pb(Mg_{1/3}Nb_{2/3})O₃ particles (80-120 nm)

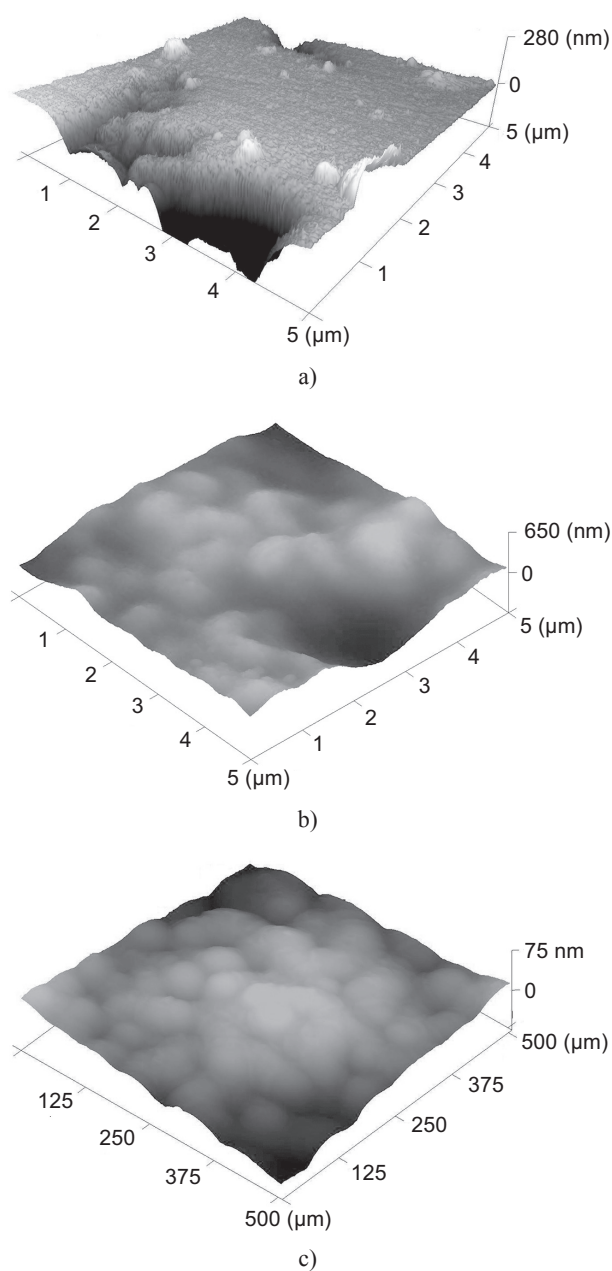


Figure 4. 3D AFM topography micrographs of: a) Pt/Al₂O₃ substrate and (b, c) 2-layered Na-PMN thin film deposited on Pt/Al₂O₃ substrate after sintering at 650°C and cross-lines; b) and c) over scan areas of 5×5 μm^2 and 500×500 μm^2 , respectively.

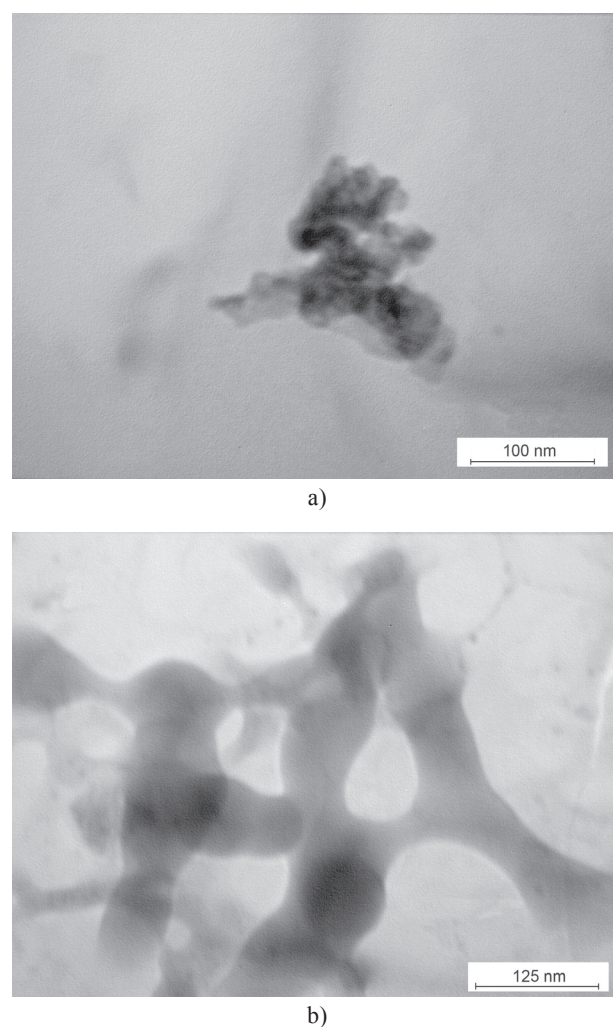


Figure 5. TEM micrographs of 2-layered Na-PMN thin film deposited on Pt/Al₂O₃ substrate after sintering at 650°C: a) particles of the pyrochlore Na₂Nb₈O₂₁ phase, b) particles of the perovskite Pb(Mg_{1/3}Nb_{2/3})O₃ phase.

(Figures 3b, c and 4b, c). In the 2D and cross-line AFM surface topography micrographs of Na-PMN film, small spherical probably pyrochlore nanoparticles on round particles of PMN-matrix (~80 - 100 nm) (pv) were found with clearly visible Pt particles from Pt layer and holes in the Al₂O₃ substrate. Similar the small spherical pyrochlore particles (from 8 to 25 nm) were observed using AFM in the PMN-PT (50/50) film prepared by the PC method [17].

TEM micrographs of particles in 2-layered Na-PMN thin film deposited on Pt/Al₂O₃ substrate after sintering at 650°C are shown in Figure 5. The smallest visible spherical particles (~30 nm) can be identified as the pyrochlore Na₂Nb₈O₂₁ phase (Figure 5a) and the perovskite spherical Pb(Mg_{1/3}Nb_{2/3})O₃ (Figure 6b) particles (~125 nm) are mutually interconnected as a result of the sintering. The average particle size is in the agreement with crystallite size obtained from the XRD analysis and AFM method.

CONCLUSIONS

Perovskite Na doped PMN thin films were prepared by the sol-gel route via tartaric acid modified polymerizable complex method with molar ratio of Na:Pb:Mg:Nb = 1/2:1:1/3:2/3 and deposited by spin-coating method on Pt/Al₂O₃ substrates.

From the XRD diffractogram resulted that the perovskite Pb(Mg_{1/3}Nb_{2/3})O₃ phase (65 vol. %) and pyrochlore Na₂Nb₈O₂₁ phase were formed in 2-layered Na-PMN thin film after sintering at 650°C.

In the microstructures of the 2-layered Na-PMN thin film surfaces, the perovskite and pyrochlore phase particles on film cross-sections (100 nm thickness) were observed. The morphology of 2-layered Na-PMN/Pt/Al₂O₃ thin films with ~9.5 nm of roughness was represented by the bimodal particle size distribution with small spherical particles probably of the pyrochlore phase (~20 - 30 nm) and larger sponge-like particles of the perovskite phase (~80 - 120 nm). From TEM and AFM micrographs was estimated that the average particle size is ~30 nm for spherical particles and ~125 nm for mutually interconnected round particles.

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