



Perovskite lanthanum niobate and tantalate thin films prepared by sol-gel method



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ABSTRACT

Perovskite lanthanum niobate La_{1/3}NbO₃ (LN), tantalate La_{1/3}TaO₃ (LT) and La_{1/3}Nb_{0.8}Ta_{0.2}O₃ (LNT) thin films (~150 nm thickness) were prepared for the first time by sol-gel/spin-coating process on Pt/SiO₂/Si substrates and annealing at 1100 °C. The novel precursors of films were synthesized using Nb- or Ta-tartrate complexes. XRD analyses confirmed that the LT possessed a single perovskite tetragonal La_{0.33}TaO₃ phase, while LN or LNT films contained perovskite orthorhombic La_{1/3}NbO₃ or tetragonal La_{1/3}TaO₃ and traces of secondary pyrochlore LaNb₅O₁₄. The spherical and needle-like particles in heterogeneous microstructure of LN and LNT films and presence homogeneous transparent clusters of spherical nanoparticles in LT were observed.

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1. Introduction

Perovskite niobate of La_{1/3}NbO₃ (LN) and tantalate of La_{1/3}TaO₃ (LT) based on La rare-earth element represent progressive technological benefits in the form of ferroelectric ceramics and thin films for their dielectric, ferroelectric and electrolytic properties enabling application example in microelectromechanical systems (MEMS) and solid oxide fuel cells (SOFC) [1]. The structures of La_{1/3}MO₃ (M=Nb⁵⁺, Ta⁵⁺) were described by Carrillo et al. [2]. Orthorhombic structure at 25 °C is transformed to the tetragonal at 200 °C for LN and at 650 °C for LT.

Lanthanum niobate–tantalate (La_{1/3}Nb_{1-x}Ta_xO₃) is solid solution of LN and LT and therefore possesses intermediate properties, which vary with x=Ta/(Nb+Ta) ratio, from those of LN (x=0) to those of LT (x=1). Characterization of secondary pyrochlore (monoclinic LaNbO₄ and LaTaO₄) phases is still in its infancy, with most work being performed by Haugrud et al. [3]. Orthorhombic LaNb₅O₁₄ consists of two types of Nb–O polyhedra [4]. Tungsten bronze structure, where the charge balance is implemented by distinct ions like it is the case in Ag₈(Nb_{0.5}Ta_{0.5})₂₆O₆₉ [5] and La_{4.67}Ta₂₂O₆₂ [6].

The methods of niobate–tantalate thin film preparation onto different substrates are known: sputtering [7], pulsed liquid (PLD)

[8,9], physical vapor (PVD) [10] and chemical solution (sol-gel) [11,12] deposition. Perovskite (K_{0.5}Na_{0.5})_{0.96}Li_{0.04}(Nb_{0.8}Ta_{0.2})O₃ and KTa_{0.7}Nb_{0.3}O₃ films were epitaxially grown on SrTiO₃ substrates using PLD at 600 °C [8,9]. The advantages of sol-gel process are: stoichiometry control, homogeneity, low process temperature and cost. KTa_{0.65}Nb_{0.35}O₃ (KTN) films were prepared by sol-gel processing from alkoxide at 750 °C [11], while LiTaO₃ films were obtained by similar method at 1000 °C [12]. In the Pechini method, citric acid based Nb and Ta are highly stable polymeric complexes (PC) were applied for film preparation [13]. LiNbO₃ and KTN were prepared by PC sol-gel route using citrate complex at 500 and 600 °C by spin-coating technique on Si substrates [14,15]. La_{1/3}Nb_{1-x}Ta_xO₃ films were not reported and characterized in literature up to now.

In present paper, we have prepared for the first time La_{1/3}Nb_{1-x}Ta_xO₃ thin films from novel polymeric Nb and Ta-tartrate complexes (instead citrate solutions) by sol-gel/spin-coating method. We also report structural properties of LN, LNT and LT films deposited on the Pt/SiO₂/Si substrates and annealed at 1100 °C.

2. Experimental

LN, LNT and LT films were prepared by modified polymeric complex sol-gel/spin-coating method on Pt/SiO₂/Si substrates and

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annealing at 1100 °C. LNT sol precursor was prepared from $\text{La}(\text{NO}_3)_3$ and novel (Nb+Ta)-tartrate complex in solvent (ethylene glycol, EG) with molar ratio of $\text{La}/(\text{Nb}+\text{Ta})=0.33/1.0$ [16,17]. (Nb+Ta)-tartrate complex was synthesized by polymer complex method (modified with tartaric acid (TA) instead citric acid), where NbCl_5 and TaCl_5 were separately dissolved in EG and mixed with chelating agent TA at molar ratio $\text{TA}:\text{EG}=3:1$. The mole ratio of $\text{La}:\text{Nb}:\text{Ta}=0.33:0.8:0.2$. Similarly, LN(LT) sol precursors were prepared at mole ratio of $\text{La}:\text{Nb}(\text{Ta})=0.33:1.0$. All chemicals were of analytical grade and were purchased from Merck (Darmstadt, Germany). After homogenization at 80 °C the solutions were stirred and heated at 130 °C for 5 h with formation of transparent viscous yellow sols. Basic (0.5 M) sols were diluted in stabilizer solution (n-propanol). Platinized substrates (p-type silicon [100] single-crystal wafer of diameter 50 mm) to deposit the films were used. Pt (50 nm) electrode layer was sputtered as a bottom electrode. Thickness of SiO_2 layer was 1 μm . Pt/ SiO_2 /Si substrates were spin-coated with sol precursor at 2000 rpm for 30 s. Single film layer was deposited on substrate with a drying step at 110 °C for 3 min. Final LN, LNT and LT 5-layered films were annealed at 1100 °C for 30 min. The films were repeatedly prepared four times.

The thermal decomposition of gels were analyzed by differential scanning calorimetry, thermogravimetric analysis (JUPITER STA 449-F1 NETZSCH). The phase composition of films was determined by X-ray diffraction analysis (XRD), (a model X'Pert Pro, Philips, The Netherlands) using $\text{CuK}\alpha$ radiation and Raman spectra were collected by Raman spectroscopy (HORIBA BX 41TF). The surface and cross-section of film microstructures were characterized by scanning electron microscopy (SEM), (Tescan) and using focused ion beam (FIB-SEM), (Auriga Compact, Carl Zeiss Germany). Cross sections of films were cut with the focused Ga^+ ion beam.

3. Results and discussion

XRD diffractograms of films annealed at 1100 °C are shown in Fig.1. XRD analyses verified formation of perovskite orthorhombic $\text{La}_{0.33}\text{NbO}_3$ (JCPDS 35-1298), tetragonal $\text{La}_{0.33}\text{TaO}_3$ (JCPDS 42-0061) and pyrochlore orthorhombic $\text{LaNb}_5\text{O}_{14}$ (JCPDS 76-0263) phases. From XRD patterns resulted that the major components represent the perovskite $\text{La}_{0.33}\text{NbO}_3$ (in LN) or $\text{La}_{0.33}\text{TaO}_3$ (in LNT) and traces of pyrochlore $\text{LaNb}_5\text{O}_{14}$ phase were revealed in both films. Created pure $\text{La}_{0.33}\text{TaO}_3$ perovskite phase exhibits a

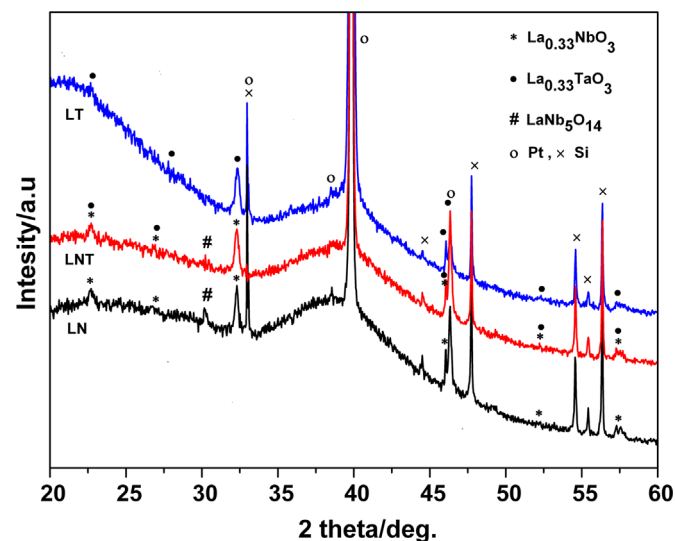


Fig. 1. XRD patterns of LN, LNT and LT thin films after annealing at 1100 °C.

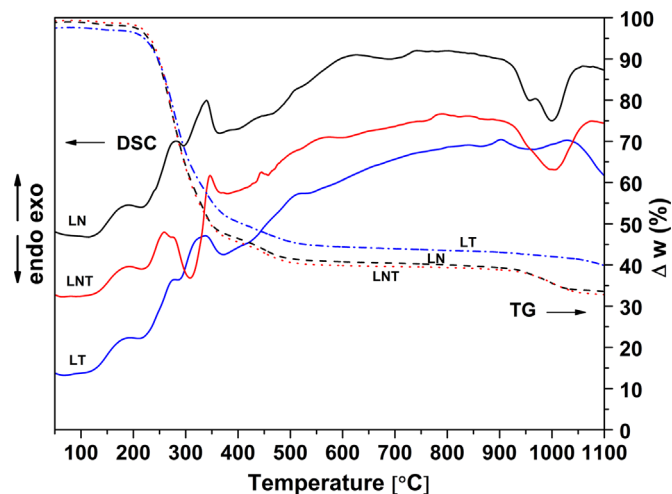


Fig. 2. DSC and TG curves of gel precursors.

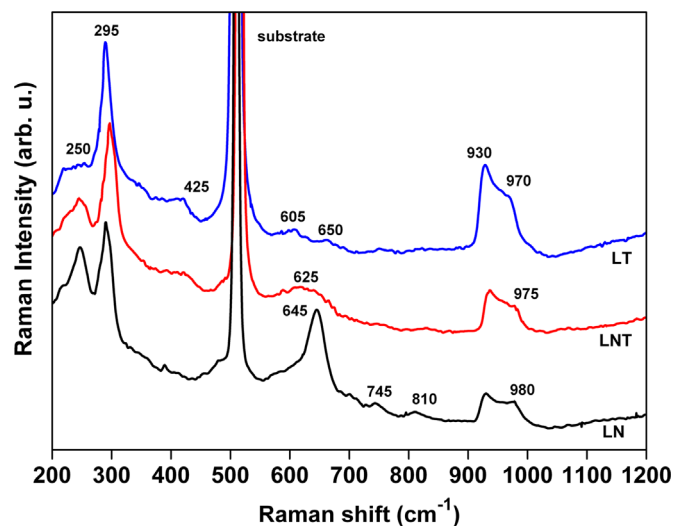


Fig. 3. Raman spectra of films after annealing at 1100 °C.

tetragonal structure in LT films. We compared the phase composition of films based on other niobates and tantalates on Si substrates. Pyrochlore $\text{K}_2\text{Ta}_2\text{O}_6$ [11] and LiNb_3O_8 [13,14] were confirmed in KTN and LiNbO_3 films at 600 °C. Pure perovskite KTN [15] and LiTaO_3 [12] films were determined at 750 and 1000 °C, respectively.

TG and DSC curves of xerogels are shown in Fig. 2. Small weight loss of 1% at temperatures up to 200 °C is due to evaporation of remaining water and EG. Exothermic peaks at 280 and 340 °C (LN), 266 and 350 °C (LNT) and 275 and 325 °C (LT) could be attributed to thermal decomposition of tartrate complexes, corresponding to weight loss of 50.0%. Up to 400 °C there is rapid mass decrease combined with endothermic peak at 320 °C (LNT). The weight losses in range of 180–400 °C represent decomposition of nitrates, free carboxylic acids, release of water from dehydration of tartrate-nitrate gels, polymerization of complexes. Formation of amorphous oxides were found above 400 °C with small exo-effect at 450 °C (LN and LNT) and 510 °C (LT). In tartrate xerogels, the peaks were observed at lower temperatures in comparison with citrate precursors [16,17]. Small exothermic peaks between 450 and 600 °C is caused by combustion of residual carbon and following crystallization of pyrochlore LaNbO_4 phase [16]. In DSC curves of LN and LNT, distinct endothermic peaks correspond at 715 and 766 °C. Formation of $\text{LaNb}_5\text{O}_{14}$ and $\text{La}_{1/3}\text{NbO}_3$ exhibit

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