

## HIGH DIELECTRIC PERMITTIVITY IN LITHIUM SODIUM LANTHANUM TITANATE

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Lanthanum lithium titanate with the perovskite structure is one of the most conductive known ion oxides [1]. It has prospects in the development of lithium batteries and as a solid electrolyte [2]. The development of materials with a giant dielectric constant on the base of perovskites is particularly interesting [3, 4]. It is known, that materials with a giant dielectric permittivity have been widely investigating due to potential applications in the microelectronic industry. This phenomenon is also shown in literature for polycrystalline samples of  $\text{La}_{0.67}\text{Li}_{0.25}\text{Ti}_{0.75}\text{Al}_{0.25}\text{O}_3$  ( $\epsilon \geq 1000$ ), where titanium is partially substituted by aluminum. In this case the high dielectric constant associated with grain boundary effects in the ion-conducting material, described by a barrier layer capacitor [5]. Named effects are mainly related to a lithium ions transport through the structural conduction channels, formed by oxygen ions and A-site perovskite cations (lanthanum and substituting ions) [6]. Number of A-site structural vacancies alongside with channels dimensions define contribution of mobile lithium ions to ion conductivity and low-frequency polarization. Channels can be “widened” by substitution of the A-site with large cations or ions, causing a reduce in conductivity activation energy, on the other hand in this case the number of vacancies and lithium mobility decreases [7, 8].

In the presented work we synthesized partially substituted in Li-position  $\text{La}_{0.5}\text{Li}_{0.5-x}\text{Na}_x\text{TiO}_3$  ( $0 \leq x \leq 0.5$ ) perovskites and studied dielectric properties of obtained materials.

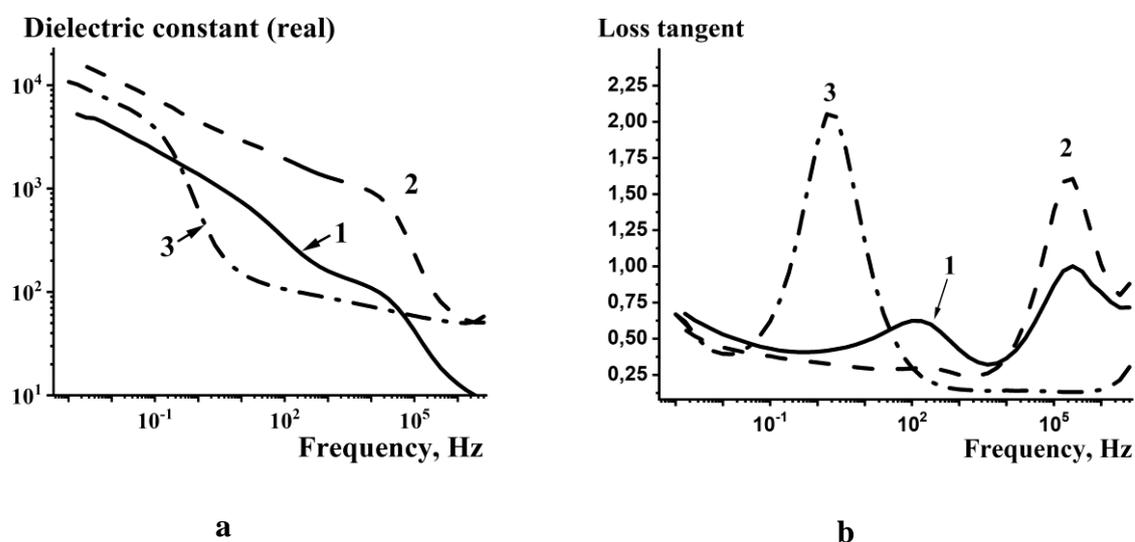
Solid-state reaction technique was used for synthesis of ceramic samples. As initial reagents were used dried  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{La}_2\text{O}_3$  and  $\text{TiO}_2$ . Mixtures of the reagents were calcined in the air for 4 h at  $1100^\circ\text{C}$ . Calcinated powders were pressed into pellets, pellets were sintered for 6 h at  $1300\text{--}1330^\circ\text{C}$  depending on Na content.

XRD patterns showed that unit cell volume increases with the increase in x for  $\text{La}_{0.5}\text{Li}_{0.5-x}\text{Na}_x\text{TiO}_3$  system, solid solutions are formed at temperatures higher than  $1100^\circ\text{C}$ . SEM investigations showed that sodium addition leads to the reduction of a grain size of  $\text{La}_{0.5}\text{Li}_{0.5-x}\text{Na}_x\text{TiO}_3$  solid solutions ceramics from 4.7 to 3  $\mu\text{m}$  for  $x = 0.1$  and 0.4 respectively. The size reduction can be the result of the partial segregation of  $\text{Na}^+$  ions near the grain boundaries [9-11]. Densification of  $\text{Na}^+$  also hinder the mass transport, hence smaller grains are formed [12]. It is important to note, that the adsorption of oxygen at the grain boundaries is stimulated by pores in the ceramic. That means that porous samples are better in surface acceptor states forming, compared to samples with the common density values. And it was shown [13], that sodium containing materials have lower density caused by the melting temperature difference between lithium and sodium carbonates [14].

Complex impedance of obtained ceramics was measured, results were processed using Zview software. The real part of the impedance for all samples  $\text{La}_{0.5}\text{Li}_{0.5-x}\text{Na}_x\text{TiO}_3$  increases with increase of Na containment.

Frequency spectra of electric modulus imaginary part for the samples demonstrate 3 dispersion regions: a region of the sample-electrode interface polarization (low frequencies), intermediate region representing processes in grain boundaries, high frequency region related to charge carrier relaxation in grains. At the room temperature the main contribution to electrical properties of  $\text{La}_{0.5}\text{Li}_{0.5-x}\text{Na}_x\text{TiO}_3$  ( $0 \leq x \leq 0.1$ ) in the frequency range  $10^{-1} \leq f \leq 10^7$  Hz is made by intermediate and high frequency regions. In the case of  $\text{La}_{0.5}\text{Li}_{0.5-x}\text{Na}_x\text{TiO}_3$  with  $0.2 \leq x \leq 0.4$  contributions of all regions are comparable and for the samples with  $0.45 \leq x \leq 0.5$  low and high frequency regions are determinative. The observed dependency is an aftermath of the substitution Li to Na. Na ions causes many effects, leading to conductivity reduction: decrease in concentration of mobile charge carriers; reduction in the number of vacant A sites, that are a pathway for ion motion; increase of the contribution of the grain boundary resistance in the total resistance. Despite these facts the charge transport takes a place up to  $x \leq 0.3$ , but conductivity is found to decrease after sodium content increases above  $x = 0.2$ . The maximum value of electric modulus imaginary part for grain boundary increases coherent with the sodium concentration ( $0 \leq x \leq 0.4$ ) due to the limited mobility of Li ions.  $\text{La}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  doesn't contain Li ions, ion conductivity is mostly absent, material becomes dielectric.

Dielectric constant and dielectric loss versus frequency for  $\text{La}_{0.5}\text{Li}_{0.5-x}\text{Na}_x\text{TiO}_3$  samples at room temperature are presented in the **figure 1a, 1b** respectively. Samples with  $x = 0, 0.1$  have high dielectric constant values  $\epsilon' > 10^4$  at frequencies below 10 Hz, further increase of sodium containment ( $x > 0.2$ ) decreases the maximum value of the dielectric constant. Two relaxation peaks on the curve of dielectric loss tangent for the named samples indicate coexistence of two phases: rhombohedral  $R-3c$  and tetragonal  $P4/mmm$ . At the same time the dielectric loss decreases with increasing sodium concentration due to reduced Li mobility.



**Fig. 1.** Dielectric constant (a) and dielectric loss tangent (b) of  $\text{La}_{0.5}\text{Li}_{0.5-x}\text{Na}_x\text{TiO}_3$  at  $x = 0$  (1), 0.1 (2), 0.2 (3).

In summary, it has been shown that solid solutions are formed at temperatures higher than  $1050^\circ\text{C}$ . Ceramic sample  $\text{La}_{0.5}\text{Li}_{0.4}\text{Na}_{0.1}\text{TiO}_3$  has maximum value of dielectric constant and, as it was said, this fact is the aftermath of two competing processes influencing the

lithium ions movement: sodium provokes an increase in unit cell volume, a decrease of conductivity activation energy, but also sodium ions replaces mobile Li ions and fill A-site vacancies, that are conduction channels for lithium.

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