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Al-DOPED LANTHANUM-LITHIUM TITANATE WITH HIGH DIELECTRIC CONSTANT

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$La_{0.67}Li_xTi_{1-x}Al_xO_3$ ceramics (x = 0.05, 0.10, 0.15, 0.20, 0.25, 0.30) were synthesized with the use of Al_2O_3 and an aqueous solution of $Al(NO_3)_3$ as an aluminium source. In both cases, the ceramics preserve a high dielectric constant $\varepsilon \sim 10^5$. It was found that the single-phase $La_{0.67}Li_xTi_{1-x}Al_xO_3$ perovskite structure is formed at temperatures above 1200 °C. It was shown that the use of $Al(NO_3)_3$ allows simplifying the synthesis: reduction in the sintering temperature by 20 °C, Li loss and, as a result, an increase in the density of ceramics. Ceramics $La_{0.67}Li_{0.15}Ti_{0.85}Al_{0.15}O_3$ with a maximum density higher than 85 % were sintered at about 1280 and 1300 °C of with the use of $Al(NO_3)_3$ and Al_2O_3 respectively. Frequency spectra of imaginary parts of impedance and electrical modulus demonstrate two dispersion regions that refer to processes in the ceramic grains' boundaries and ceramic grains. Ceramic samples synthesized using $Al(NO_3)_3$ solutions tend to exhibit higher dielectric constants than those synthesized using Al_2O_3. At a frequency of 100 Hz, the dielectric constant for ceramics synthesized using $Al(NO_3)_3$ aqueous solution is 70600, whereas that for ceramics synthesized using Al_2O_3 is 44300. Obtained materials are useful for microelectronics, energy storage and harvesting devices.

Keywords: Li-containing, aluminium nitrate, microelectronics, perovskite, solid-state reaction technique.

INTRODUCTION. Materials based on lithium-containing perovskites with a high dielectric constant ($\varepsilon > 1000$) have been developed for use in microelectronics to address the challenge of miniaturizing electronic circuits [1]. They are used in the field of microelectronics, in the development of thermostable components of electronics [1], solid energy storage (Multi-Layer Ceramic Capacitors) [2], solar energy [3], electrochemical devices, and deep mining and space technology [4]. These materials are of both scientific and practical interest due to the high effective dielectric constant resulting from the relaxation of mobile lithium ions [5]. The authors of [6, 7] investigated the substitution of La and Ti ions by Li and Al ions in the $La_{2/3}Li_xTi_{1-x}Al_xO_3$ system to improve its electrical characteristics. Depending on the sintering conditions, the resulting perovskites can crystallize in either orthorhombic or rhombohedral syngony. The $La_{2/3}Li_xTi_{1-x}Al_xO_3$ materials with orthorhombic syngony form solid solutions in the concentration range x = 0.15–0.30, and exhibit a high dielectric constant [8]. However, there is a lack of research on the crystal structure and dielectric properties of this material at concentration ranges of x less than 0.15 and more than 0.3.

The conventional method of preparing powders for ceramic material production involves roasting a mechanically crushed mixture of metal oxides and carbonates in specific proportions [9]. However, this process introduces pollutants from abrasive materials during grinding, which negatively affect dielectric properties. The solid-state reaction, a diffusion-controlled process, requires a uniform distribution of each substance to produce a fully reacted and homogeneous product. The prolonged calcination at high temperatures and precise atmospheric control needed for the mechanically ground mixture results in the loss of volatile components, such as lithium. Additionally, achieving good density requires very high sintering temperatures.

Numerous studies have been dedicated to the development of $La_{2/3-x}Li_{3x}TiO_3$ LLTO-based materials; however, they typically focus solely on the properties of the resulting perovskites, neglecting the study of chemical transformations that occur during synthesis. As a result, further enhancement of synthesis and material characteristics is impeded. The present study represents a pivotal point in investigating the chemical transformations that occur during the synthesis of LLTO-based perovskites and aims to improve the synthesis process for further research.

The goal of this study is to explore phase formation during the synthesis of $La_{0.67}Li_xTi_{1-x}Al_xO_3$-based solid solutions using the solid-state reaction technique with the incorporation of Al_2O_3, as well as to reduce sintering temperature and minimize Li loss during solid-state synthesis. The use of an aqueous solution of $Al(NO_3)_3$ as an aluminum source should decrease the sintering temperature while ensuring a more uniform distribution of aluminum in the material, thus preventing the accumulation of Al in localized conglomerates that can occur with solid Al_2O_3.

EXPERIMENT AND DISCUSSION OF THE RESULT. The following initial reagents were used for the synthesis of $La_{0.67}Li_xTi_{1-x}Al_xO_3$ (x = 0.05, 0.10, 0.15, 0.20, 0.25, 0.30) solid solutions: stoichiometric amounts of dried Li_2CO_3 (Merck 99.99%), La_2O_3 (Aldrich 99.99%), TiO_2 (Aldrich 99%), and Al_2O_3 (Merck 99.99%) or an aqueous solution of $Al(NO_3)_3$ as the source of aluminium. Li_2CO_3 was dried at 300 °C, La_2O_3 at 800° C, Al_2O_3 and TiO_2 at 600 °C. Mixed powders were ground in an agate mortar with isopropyl alcohol (or alcohol and the solution of $Al(NO_3)_3$) and calcined in air for 4 h at 1200 °C.

X-ray powder diffraction was performed using a DRON-4-07 diffractometer (Cu Kα radiation, 40 kV, 20 mA) for the analysis of phases formed during the synthesis. The unit cell parameters of the samples were calculated using the Le Bail procedure [8] and the FullProf software. In order to determine intermediate phases during synthesis, isothermal heat treatment was carried out in the temperature range from room temperature (RT) to 1200 °C during 2 h (crucibles with the diameter D = 3 cm and height h = 2 cm). The change in the phase composition was studied in the temperature range 20–1200 °C by method X-ray phase diffraction (XRD) analysis using DRON-4-07

CuKα-radiation; 40 kV, 20 mA). SiO_2 and Al_2O_3 were used as external standards (for 2Θ and intensity).

The heat treatment of powders was carried out. After grinding, the powders were compressed into tablets under the pressure of 500 kg/cm² (50 MPa). The materials sintered in the temperature range of 1270–1320 °C depending on the Li and Al contents (the heating rate was 200 °/h). The tablets were sintered for 6 hours and cooled to the room temperature at a cooling rate of 200 °/h.

To carry out the measurements of the dielectric properties metal electrodes were applied on the end faces of sintered cylindrical samples with a diameter of 8 mm and a thickness of 2 mm. Impedance spectroscopy measurements were performed using a 1260 Impedance / Gain phase Analyzer (Solartron Analytical).

It was shown that single-phase $La_{0.67}Li_xTi_{1-x}Al_xO_3$ perovskites were formed at temperatures above 1200 °C (Fig. 1.). Using XRPD analysis intermediate phases during solid-state reaction technique were determined.

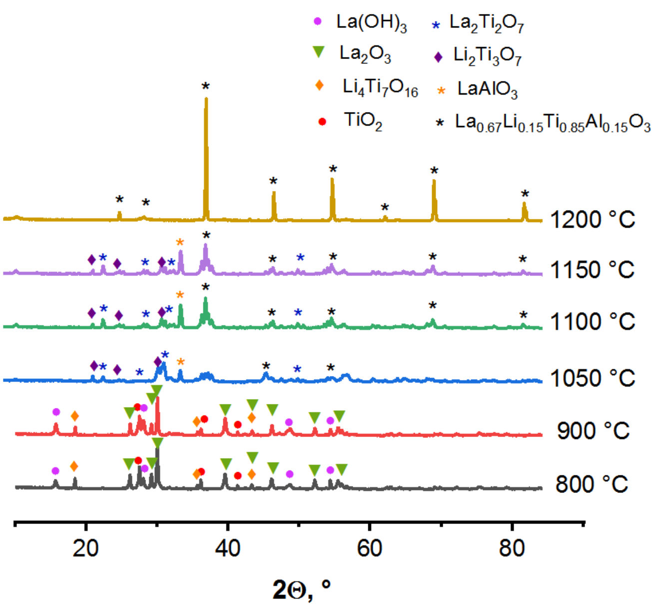

Fig. 1. XRPD patterns for $La_{0.67}Li_{0.15}Ti_{0.85}Al_{0.15}O_3$ solid solution at different calcination temperatures. Intermediate phases are marked with symbols.

The processes of mechanical mixing and adsorption of moisture from the air by lanthanum oxide at room temperature lead to the formation of hydroxide:

$$La_2O_3 + 2H_2O \xrightarrow{20-300\,^{\circ}C} 2\,La(OH)_3 \quad (1)$$

Increase in temperature to 300–400 °C leads to reactions of lanthanum hydroxide and carbon dioxide from the air, lanthanum dioxycarbonate forms:

$$2\,La(OH)_3 + CO_2 \xrightarrow{300-400\,^{\circ}C} La_2O_2CO_3 + 3\,H_2O \quad (2)$$

In the temperature range of 500-600 °C lithium carbonate interacts with titanium oxide:

$$Li_2CO_3 + TiO_2 \xrightarrow{500-600\,^{\circ}C} Li_2TiO_3 + CO_2\uparrow \quad (3)$$

Lanthanum dioxycarbonate decomposes and lanthanum titanate interacts with titanium oxide at a temperature of about 900 °C. Di- and trititanates forms

$$La_2O_2CO_3 \xrightarrow{600–900\ °C} La_2O_3 + CO_2\uparrow \quad (4)$$

$$Li_2TiO_3 + TiO_2 \xrightarrow{650–900\ °C} Li_2Ti_2O_5 \quad (5)$$

$$Li_2Ti_2O_5 + TiO_2 \xrightarrow{750–900\ °C} Li_2Ti_3O_7 \quad (6)$$

Lanthanum and titanium oxides interact in the temperature range of 800–1000 °C to form lanthanum dititanate:

$$La_2O_3 + 2TiO_2 \xrightarrow{800–1000\ °C} La_2Ti_2O_7 \quad (7)$$

At temperatures above 1000 °C lanthanum aluminate and lanthanum titanate perovskites form:

$$La_2Ti_2O_7 + TiO_2 \xrightarrow{1000–1100\ °C} 3La_{2/3}TiO_3 \quad (8)$$

$$La_2O_3 + Al_2O_3 \xrightarrow{1000–1100\ °C} 2LaAlO_3 \quad (9)$$

Onwards lithium-lanthanum titanate and lanthanum titanate-aluminate form at 1100–1200 °C:

$$(1\text{-}1{,}5y)\ La_{2/3}TiO_3 + 1{,}5y\ Li_2TiO_3 \xrightarrow{1100–1200\ °C} \xrightarrow{1100–1200\ °C} La_{(2/3\text{-}y)}Li_{3y}TiO_3 \quad (10)$$

$$(1\text{-}3z)\ La_{2/3}TiO_3 + 3z\ LaAlO_3 \xrightarrow{1100–1200\ °C} \xrightarrow{1100–1200\ °C} La_{(2/3+z)}Ti_{(1\text{-}3z)}Al_{3z}O_3 \quad (11)$$

$La_{2/3}Li_xTi_{1-x}Al_xO_3$ solid solutions were obtained by the interaction of the phases obtained by reactions (10) and (11).

$$zLa_{(2/3\text{-}y)}Li_{3y}TiO_3+yLa_{(2/3+z)}Ti_{(1\text{-}3z)}Al_{3z}O_3 \xrightarrow{1100–1200\ °C} (z+y)La_{2/3}Li_{3yz/y+z}Ti_{1\text{-}(3yz/y+z)}Al_{3yz/y+z}O_3 \rightarrow$$
$$\rightarrow (z+y)\ La_{2/3}Li_xTi_{1\text{-}x}Al_xO_3, \text{where } x = 3yz/(y+z) \quad (12)$$

The unit cell parameters were determined from the XRPD patterns using a rapid whole-pattern profile-matching Le Bail procedure. $La_{0.67}Li_xTi_{1-x}Al_xO_3$ (where $0.15 \le x \le 0.3$) solid solutions synthesized with the use of Al_2O_3 and $Al(NO_3)_3$ aqueous solution materials have a rhombohedral perovskite-related structure (space group R-3c, № 167).

Fig. 2 shows the dependencies of the relative density of ceramics on the sintering temperature at x = 0.15. For $La_{0.67}Li_{0.15}Ti_{0.85}Al_{0.15}O_3$ synthesized using the solution of $Al(NO_3)_3$ as the aluminium source, the relative density of ceramics is higher and is achieved at lower temperatures compared to the synthesis using Al_2O_3. The maximum density is 89 % and 87 % for the use of $Al(NO_3)_3$ and Al_2O_3 respectively. Dependencies have maxima at about 1280 and 1300 °C. Higher porosity of materials at high sintering temperatures can be associated with Li loss.

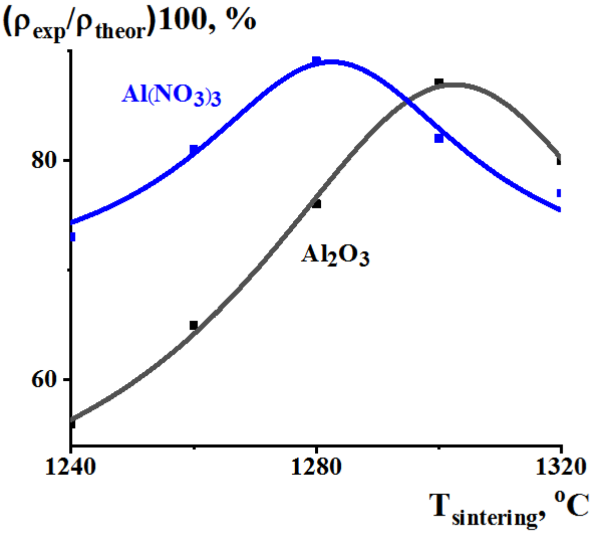

Fig. 2. Dependencies of relative density on sintering temperature for $La_{0.67}Li_{0.15}Ti_{0.85}Al_{0.15}O_3$ ceramic samples at x = 0.15 synthesized using Al_2O_3 and an aqueous solution of $Al(NO_3)_3$ as the aluminium source.

Sintering temperatures depending on the x content in ceramic samples are presented in

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Fig. 3. Temperatures rise with increasing Al content. The use of $Al(NO_3)_3$ aqueous solution instead of Al_2O_3 leads to a decrease in the sintering temperature. The decrease is 18–24 °C.

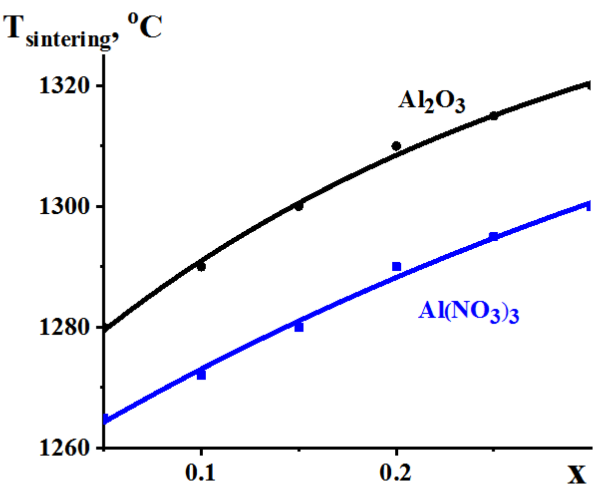

Fig. 3. Dependencies of sintering temperatures on x content for $La_{0.67}Li_xTi_{1-x}Al_xO_3$ ceramic samples synthesized with the use of $Al(NO_3)_3$ aqueous solution and Al_2O_3.

Using impedance spectroscopy there are three semicircles on the complex impedance diagram at room temperature for $La_{0.67}Li_xTi_{1-x}Al_xO_3$ ceramic samples synthesized with the use of $Al(NO_3)_3$. Three semicircles in the Cole-Cole plots show three relaxation mechanisms, which may be attributed to grain, grain boundary, and electrode polarization. Frequency spectra of imaginary parts of impedance and electrical modulus also demonstrate three dispersion regions (**Fig. 4**), covering the frequency band at least up to 10 MHz. The low-frequency region (up to 10 Hz) refers to processes in the sample/electrode area, the middle-frequency area (up to 1 kHz) refers to processes within the ceramic grains' boundaries, and the high-frequency region refers to the relaxation of charge carriers in ceramic grains [10].

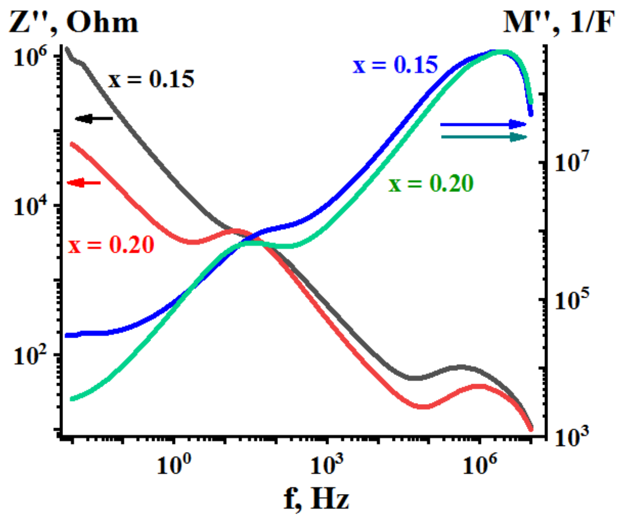

Fig. 4. Frequency spectra of imaginary part of impedance and electrical modulus, for $La_{0.67}Li_xTi_{1-}xAlxO_3$ at x = 0.15 and x = 0.20 for ceramic samples, synthesized using aqueous solution of $Al(NO_3)_3$.

It can be noted, that the maximum value of the electrical modulus slightly increased after increasing the Al content for both regions.

Dielectric constants spectra for $La_{0.67}Li_{x-}Ti_{1-x}Al_xO_3$ at x = 0.20 were determined (**Fig. 5**). Regardless of the synthesis method ceramic samples demonstrate high values of dielectric constant. The dielectric constant of the ceramics synthesized using $Al(NO_3)_3$ solutions is generally higher. At the frequency of 100 Hz dielectric constant is 70600 and 44300 with the use of $Al(NO_3)_3$ aqueous solution and Al_2O_3 respectively.

A notable feature of the obtained spectra is the presence of a flat region, which will determine the operating band of the microelectronics components based on the presented ceramics. Bandwidth (± 15 % of ε') is 256 and 764 Hz for the ceramics synthesized using $Al(NO_3)_3$ and Al_2O_3, respectively.

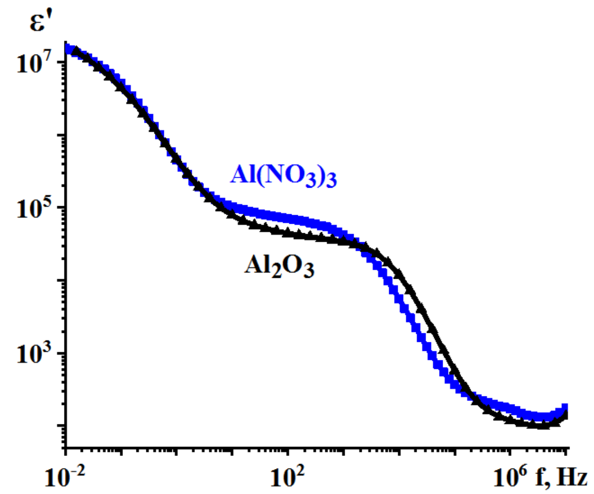

Fig. 5. Spectra of dielectric constant real parts for the $La_{0.67}Li_xTi_{1-x}Al_xO_3$ ceramics at x = 0.20 synthesized using Al_2O_3 and $Al(NO_3)_3$ aqueous solutions as aluminium sources.

CONCLUSIONS. $La_{0.67}Li_xTi_{1-x}Al_xO_3$ ceramics were synthesized by solid-state reaction technique with the use of Al_2O_3 and the aqueous solution of $Al(NO_3)_3$ as a source of aluminium. It was shown that intermediate phases during the solid-state reaction technique were $La(OH)_3$, $La_2O_2CO_3$, Li_2TiO_3, $Li_2Ti_2O_5$, $Li_2Ti_3O_7$ and $La_2Ti_2O_7$. It was found, that the use of the $Al(NO_3)_3$ solution allows to reduce the sintering temperature, to extend the operation time of sintering furnaces, reduces the loss of volatile elements and slightly increases the dielectric constant of the ceramic material. Dielectric constant spectra have a flat region with a width of 256 and 764 Hz for the use of Al_2O_3 and $Al(NO_3)_3$ respectively.

Relaxation processes within the ceramic grains boundaries and the ceramic grains determine the dielectric properties of $La_{0.67}Li_xTi_{1-x}Al_xO_3$ ceramics according to the three observed regions on the spectra of electric modulus and impedance.

DECLARATION OF COMPETING INTEREST. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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ТИТАНАТ ЛАНТАНУ-ЛІТІЮ, ЛЕГОВАНИЙ АЛЮМІНІЄМ, ЩО ХАРАКТЕРИЗУЄТЬСЯ ВИСОКОЮ ДІЕЛЕКТРИЧНОЮ КОНСТАНТОЮ

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Керамічні матеріали на основі $La_{0,67}Li_xTi_{1-x}Al_xO_3$ було синтезовано методом твердофазних реакцій з використанням оксиду Al_2O_3 та нітрату алюмінію $Al(NO_3)_3$. В обох випадках кераміка характеризується високими значеннями діелектричної проникності ε ~ 10^5. Встановлено, що за температури понад 1200 °C утворюється однофазний твердий розчин $La_{0,67}Li_xTi_{1-x}Al_xO_3$ зі структурою перовськіту. Використовуючи рентгенофазовий аналіз, було встановлено фазові перетворення, які відбуваються під час твердофазного синтезу. Показано, що проміжними фазами під час твердофазного синтезу були $La(OH)_3$, $La_2O_2CO_3$, Li_2TiO_3, $Li_2Ti_2O_5$, $Li_2Ti_3O_7$ та $La_2Ti_2O_7$. Використання як вихідного реагенту нітрату алюмінію дозволяє спростити технологію синтезу, знизити температури спікання, втрати летких компонентів та збільшити щільність кераміки порівняно з матеріалами, синтезованими з використанням оксиду алюмінію. Було показано, що тверді розчини $La_{0.67}Li_{0.15}Ti_{0.85}Al_{0.15}O_3$, синтезовані з використанням оксиду та нітрату алюмінію як вихідних реагентів, характеризуються максимальною щільністю керамічних зразків за температур 1280 і 1300 °C відповідно. Матеріали, отримані з використанням нітрату алюмінію, характеризуються вищим значенням діелектричної проникності та ширшим частотним діапазоном, де зміна діелектричної проникності не перевищує 15 % порівняно з матеріалами, що отримані з використанням оксиду алюмінію. Одержані матеріали можуть бути перспективними для використання їх у мікроелектроніці, пристроях накопичення та збирання енергії.

Ключові слова: літій-вмісний, нітрат алюмінію, мікроелектроніка, перовськіт, твердофазний синтез.

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