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Deposition and characterization of $La_2Ti_2O_7$ thin films via spray pyrolysis process

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Abstract

Thin films of $La_2Ti_2O_7$ have been deposited on fused silica and Si substrates by a spray pyrolysis method using ethylene glycol solution of La(III)-Ti(IV)-citrate complexes as starting material and O_2 as a carrier gas. The composition, crystal structure and morphology of the films are studied.

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Keywords: Citrates; Deposition; Lanthanum titanates; Spray pyrolysis; Thin films

1. Introduction

Being a ferroelectric at room temperature, $La_2Ti_2O_7$ exhibits high Curie-temperature and excellent piezoelectric and electrooptic properties. This makes it a strong candidate for a variety of applications in electrical and optical devices. $La_2Ti_2O_7$ thin films attract special attention as a possible component in the non-destructive readout ferroelectric random access memory (NDRO FRAM) devices.

Various techniques for $La_2Ti_2O_7$ films deposition are proposed, e.g. metaloorganic deposition combined with spin-coating followed by pyrolysis at 450 °C and final annealing at 650–850 °C [1], sol–gel technique [2–4], sequential deposition of La and Ti under a beam of atomic oxygen [5], pulsed laser ablation [6], and others [7]. Sol-gel process combined with dip-coating has been used for preparation of Eu^{3+}-doped $Gd_2Ti_2O_7$ films [8]. Single phase films, ~0.4 μm in thickness, with randomly oriented morphological grains of 60–80 nm are produced on Si(100) substrate after heating at 750 °C [1]. Epitaxial orthorhombic and monoclinic films are obtained on $SrTiO_3$(110) substrate by the MBE-method [5]. Nanocrystalline YVO_4:Ln^{3+} (Ln = Eu, Dy, Sm, Er) phosphor films have been prepared via sol–gel lithography [9]. Sol–gel process is also used for fabrication of silica spheres coated with YVO_4:Eu^{3+} [10], Y_2O_3:Eu^{3+} [11] or $Gd_2Ti_2O_7$:Eu^{3+} [12] films.

In some of our previous works it was demonstrated that thin, stoichiometric, phase homogeneous, highly crystalline layers can be prepared by spray pyrolysis deposition using ethylene glycol solution of citric complexes of the respective metals as starting material. The method is working rather well for preparation of monometallic oxide films [13,14] and is tested successfully for certain bimetallic oxide layers [15–18]. A phase homogeneous final product, however, was not obtained applying this route for synthesis of $YFeO_3$ [19] and $YAlO_3$ [20]. In the latter case, an orthorhombic modification as well as some other phases was registered along with the cubic $YAlO_3$. In La_2O_3–TiO_2 system a number of phases with different composition and structure exist depending on the actual oxygen content: La_2TiO_5, $La_2Ti_2O_7$, $La_2Ti_3O_9$, $La_{2/3}TiO_{3-X}$ and $La_2O_3 \cdot nTiO_2$ (most often $n = 4.5$ but compounds with $n = 1$, 1.5, 2, 6 were also prepared) [21]. X-ray data for phases containing Ti(III, IV) are also reported (see JCPDS 13–0505, 48–0480, 80–2476, 81–1582). It is of interest to examine the capabilities of producing single-phase films in such a

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potentially multiphase system (as La–Ti–O one) by the proposed spray pyrolysis method using the respective citric complexes as starting material.

In the present paper a spray pyrolysis procedure for $La_2Ti_2O_7$ films deposition is described and some properties of the obtained films are reported.

2. Experimental

2.1. Materials

Anhydrous citric acid (CA, extra pure), $La(NO_3)_3{\cdot}6H_2O$ (LAB), $Ti[OCH(CH_3)_2]_4$ (Merck) and ethylene glycol (EG, p.a.) were used to perform the present study. The exact content of La in the nitrate was determined complexometrically.

Optical grade silica glass and Si(100) (usually $20 \times 10 \times 2$ mm^3) were used as substrates. Before the film deposition the silica glass substrates were treated successively with trichlorethane, *i*-propanol, ethanol and acetone in an ultrasonic bath for 10 min in each solvent. Si(100) substrates were cleaned with trichlorethane (5 min), acetone (2 min), distilled water (1 min), ethanol (5 min), conc. H_2SO_4 + 30% H_2O_2 (volume ratio 3:1, 5 min), distilled water (2 min), 10% HF (1 min) in ultrasonic bath and dried in flow of dry N_2.

2.2. Preparation of the initial solution

The CA was dissolved in EG at 40 °C and $La(NO_3)_3{\cdot}6H_2O$ and $Ti[OCH(CH_3)_2]_4$ were added at stirring so as the mole ratio La^{3+}:Ti^{4+}:CA:EG = 1:1:10:40 to be adjusted. The due measures were taken to prevent the Ti^{4+} hydrolysis. The so prepared system was agitated at (120 ± 3) °C in a thermostatic heated vessel for 30 min. It was shown [22] that under the conditions described mixed-metal La(III)-Ti(IV) citric complexes were formed. Their typical composition is $LaTi[HCit(ROH)_2RCitRHCit^{4-}]_{0.5}[HCit(ROH)_2RCitRCitROH^{4-}]_{0.5}(CitROH^{3-})\cdot 0.4HROH\cdot 5H_2O$, where $R = (CH_2)_2$, HCit = $CH_2COOC(OH)COOCH_2COO$, Cit = $CH_2COOC(O)COOCH_2COO$. Before spraying the solution was diluted with EG or with water (the complex is stable enough and no hydrolysis is observed after adding of water up to volume ratio water/EG solution of citric complex = 20).

2.3. Films deposition

The deposition was carried out by means of the device described in [13] using a pneumatic nebulizer with a nozzle diameter of 0.5 mm. Oxygen was used as a carrier gas (flow rate of 1 dm^3/min) to avoid the creation of a reduction atmosphere (by the products of thermal decomposition of the complex organic components) which could cause production of Ti(III) containing products ($LaTiO_3$, etc.) and/or compounds with oxygen deficiency ($La_{2/3}TiO_{3-X}$). The silica glass substrates were heated at 350 ± 20) °C and the Si ones at (250 ± 20) °C; they were placed 20 cm apart from the nozzle. The pulverization procedures were performed at an angle of 45° for 30 s with a time interval of 5 min between the spraying cycles. The film thickness depends on the solution concentration and the diluent's nature; it could easily be controlled by the number of the spray procedures keeping constant other experimental conditions (the substrate temperature, gas flow rate, etc.). After the deposition, the samples were annealed at 750 °C in static air or in a flow of air, slightly enriched with O_2 for 2 h.

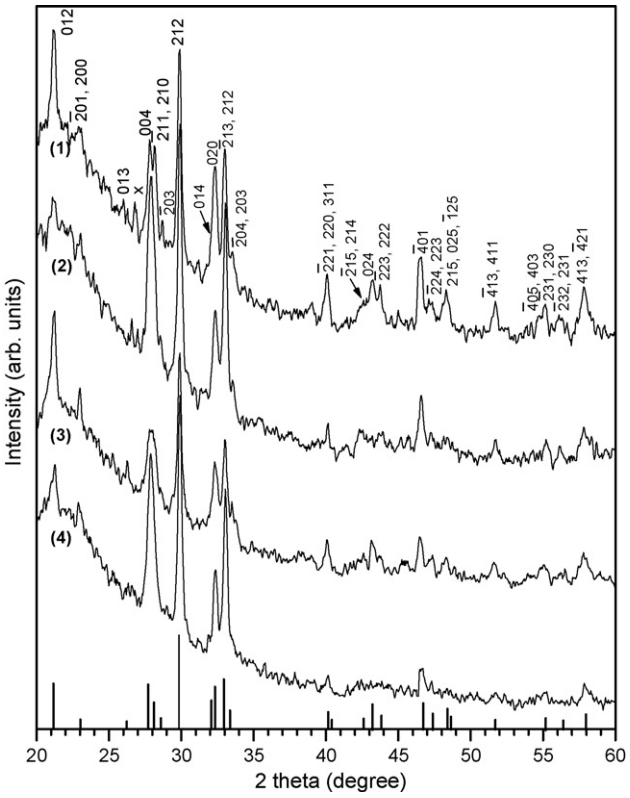

Fig. 1. X-ray diffractograms of films, prepared on silica glass substrates from initial solution diluted with: (i) EG: 1:9, annealed in static air (1); 1:19, annealed in air (2) and in O_2-enriched air flow (3); (ii) H_2O (1:19), annealed in O_2-enriched air flow (4). The reflexes (on the abscise axis) and Miller indices of $La_2Ti_2O_7$ according to JCPDS 81-1066 are shown; (x) unidentified reflection.

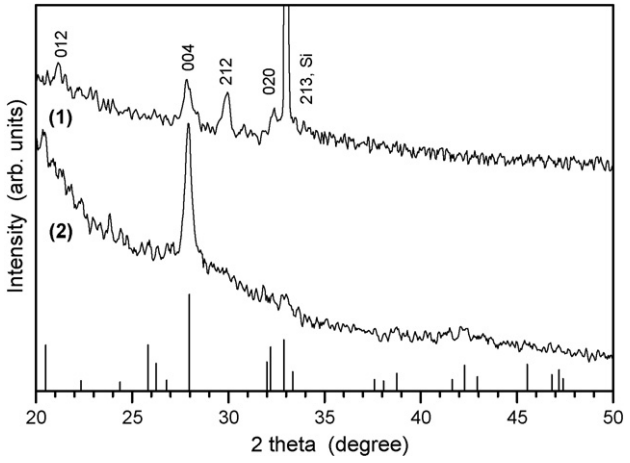

Fig. 2. X-ray diffractograms of films, prepared on Si(100) substrates from initial solution diluted with H_2O 1:19, substrate size 20 mm × 20 mm (1) and 1:9, substrate size 6 mm × 4 mm (2), both annealed in O_2-enriched air flow. The reflexes (on the abscise axis) and Miller indices of $La_2Ti_2O_7$ according to JCPDS 81-1066 are shown.