

X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF EUROPIUM NIOBATE THIN FILM PREPARED BY CHEMICAL SOLUTION DEPOSITION

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Abstract

Transparent europium niobate EuNbO_4 (ENO_F) thin film (~ 100 nm) was prepared by sol-gel/spin-coating process on alumina substrates with PbZrO_3 (PZ) interlayer and annealing at 1000°C . The X-ray diffraction (XRD) analyses verified the formation of the monoclinic M- EuNbO_4 and tetragonal T- $\text{EuNb}_5\text{O}_{14}$ phases in ENO precursor and ENO_F film. The surface morphology of powder precursor and microstructure of film were investigated by SEM analyses. Surface chemistry was investigated by X-ray photoelectron spectroscopy (XPS). The XPS demonstrated two valence states of Eu ($\text{Eu}^{3+}/\text{Eu}^{2+}$) in powder precursor as nanophosphor for lighting and display technologies. Eu concentration (at. %) decreases from 10 % in the precursor to 2 % in the film considering the substrate contains C, Al, Si, Pb, and Zr elements (40 %) at Nb (6 %) and O (52 %). The single valence state of Eu^{3+} was confirmed in ENO film designed for the application in environmental electrolytic thin-film devices.

Keywords: sol-gel, thin films, EuNbO_4 , microstructure, Spectroscopy, XPS

INTRODUCTION

Lanthanide niobates (LnNbO_4) have been attracting interest due to their excellent and interesting properties in the fields of luminescence, ionic conductivity, photocatalytic activity, magnetic properties, and crystal structures [1]. Ferroelastic LnNbO_4 is being researched for diverse applications, according to their individual properties [2]. The investigative fields of LnNbO_4 include proton-conducting solid oxide fuel cells, microwave dielectric materials, and shape memory materials [2]. Europium niobate EuNbO_4 (ENO) ceramics and film have possessed mixed types of conduction processes, including protonic, ionic, and electronic conduction which is determined by fabrication conditions, and these materials are promising for sensors, solid fuel cell electrolytes, and high-temperature proton conductors [1,3-5]. The excellent material mechanical properties of EuNbO_4 imply that ENO is a promising thermal barrier coating [2]. It also possesses excellent photoluminescence properties. ENO is a material with high potential in optoelectronics as a light emitter [5]. Microwave dielectric EuNbO_4 ceramics are widely used in GPS antenna technology, dielectric waveguide circuits, radar, and wireless communication devices [6]. For ENO, there are two crystalline forms, the low-temperature M-phase isostructural with a monoclinic form of the fergusonite and the T-phase corresponding to tetragonal scheelite [7,8].

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X-ray photoelectron spectroscopy (XPS) of element core levels is among the most prominent methods applicable for chemical bonding characterization in complex compounds [9-11]. Niobates are characterized by a set of binding energies (BE) related to the maxima of Nb 3d and O 1s lines. The valence state of europium and the Eu 3d core-level XPS spectra of $\text{Eu}_m\text{Nb}_x\text{O}_y$ compounds and Eu_2O_3 thin film were studied [12-14]. The splitting of the 3d core level in 3+ and 2+ states interpreted Cho et al. as a consequence of Eu 4f6 and Eu 4f7 final state configurations [15,16]. The ENO compounds seem to be interesting due to the possible existence of the mixed-valence state of Eu ions.

In this work, we prepared EuNbO_4 (ENO) precursor by sol-gel method. XPS measurements have been done to investigate the chemical composition and bonding state of ENO phosphor powder. We also report the surface chemistry of ENO thin film prepared by spin-coating and annealed at 1000°C. We have performed a more detailed investigation of the chemical state of the Eu (Eu^{3+} and Eu^{2+}) in ENO.

EXPERIMENTAL

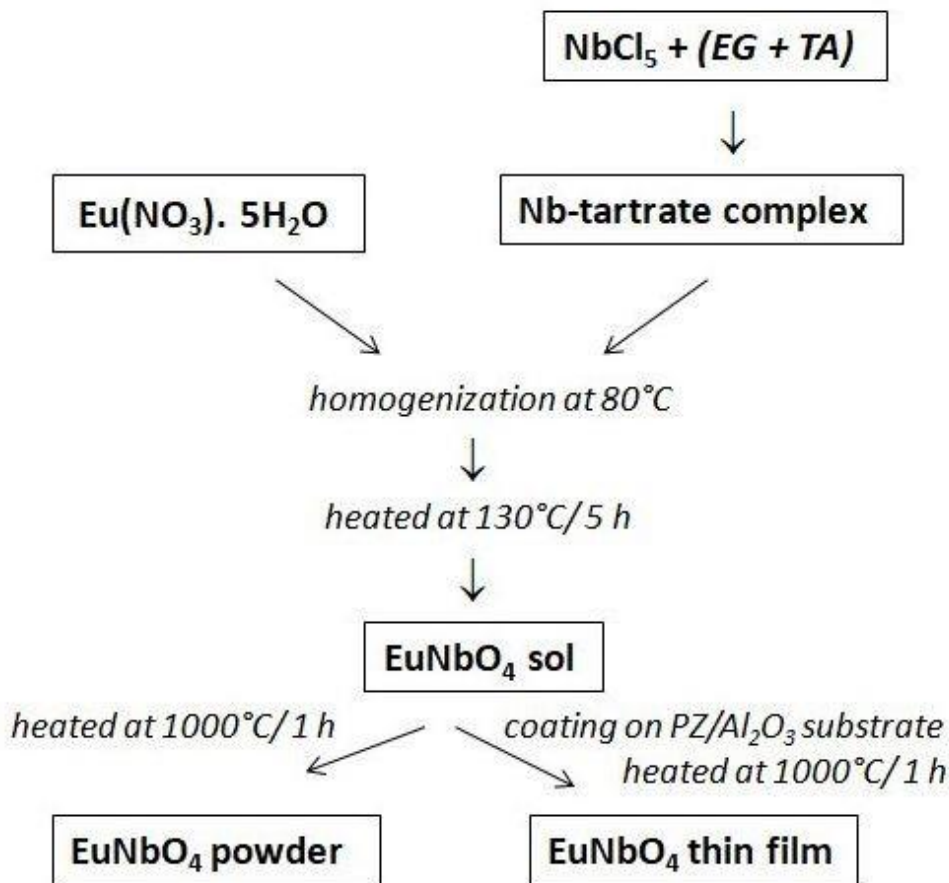
EuNbO_4 (ENO) precursor was prepared by the sol-gel method [17] according to Scheme 1. The sol precursor was synthesized from $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and Nb-tartrate complex in solvent ethylene glycol (EG) with a molar ratio of $\text{Ln}/\text{Nb} = 1/1$. After homogenization at 80°C, the solution was stirred and heated at 130°C for 5 hours with the formation of transparent viscous sol. The ENO powder precursor was annealed at 1000°C for 1 hour in the air. The Nb-tartrate complex was synthesized by polymer complex method (modified with tartaric acid (TA) instead of citric acid), where NbCl_5 was dissolved in ethylene glycol and mixed with chelating agent (tartaric acid) at molar ratio $\text{TA}:\text{EG} = 3:1$.

We repeated a similar sol-gel process for the fabrication of thin film. Basic (0.5 M) ENO sol was diluted in stabilization solution (n-propanol). The Al_2O_3 substrate was spin-coated with PbZrO_3 (PZ) sol precursor at 2000 rpm for 30 s (PZ interlayer with ~50 nm thickness) followed by drying at 110°C for 3 min and calcining at 400°C for 3 min. The coating cycling was repeated three times to obtain three layers of the thin film. EuNbO_4 thin film (~100 nm) was prepared from the ENO sol precursor synthesized in the stoichiometric ratio and deposited on PZ/ Al_2O_3 substrate. The final ENO_F film was annealed at 1000°C for 1 hour in the air [17]. The PbZrO_3 (PZ) sol was prepared by the sol-gel method [17]. The basic precursors, lead acetate trihydrate and zirconium acetylacetonate were dissolved separately at $T = 80^\circ\text{C}$ in acetic acid in two closed flasks. The solutions were dehydrated at 105°C/2 h and after cooling to 80°C they were mixed in the required ratio of $\text{Pb}:\text{Zr} = 1:1$. By polycondensation of the formed lead zirconyl acetate precursor, after adding a hydrolyzing agent (ethylene glycol, H_2O , and $\text{NH}_3(\text{aq})$) and the temperature of 80°C, a sol was formed.

The phase compositions of precursor and film were determined by X-ray diffraction analysis (XRD), (a model X'Pert Pro, Philips, The Netherlands) using CuK_α radiation. The surface of ENO powder and film microstructures were characterized using a scanning electron microscope (SEM), (a model JSM-7000F, Jeol, Japan) equipped with an energy dispersive X-ray (EDS) analyzer link ISIS (Oxford, UK).

The surface chemical composition of the samples was analyzed by X-ray photoelectron spectroscopy (XPS). Photoelectron spectroscopy was performed using an XPS instrument (SPECS) equipped with PHOIBOS 100 SCD and a non-monochromatic Al/Mg twin X-ray source. The survey surface spectrum was measured at 70-eV transition energy and high-resolution spectra at 50 eV, at room temperature. All spectra were acquired at a basic pressure of 2×10^{-9} mbar with AlK_α excitation at 10 kV (100 W). The data were analyzed by SpecsLab2 CasaXPS software (Casa Software Ltd). The spectrometer was

calibrated against silver (Ag 3d). All samples showed variable degrees of charging due to their insulating nature. The energy scale has been calibrated by normalizing the C 1s line of adsorbed adventitious hydrocarbons to 285.0 eV. The processing of the measured spectra includes subtraction of X-ray satellites and Shirley-type backgrounds [18]. The peak positions and areas were evaluated by asymmetrical Gaussian-Lorentzian curve fitting. The XPS spectra of Nb, O, and Eu were compared with NIST XPS Database and data published in the literature. The relative concentrations of the different chemical species were determined after normalization of the peak areas to their photoionization cross-sections, calculated by Scofield [19].



Scheme 1. Preparation route for the ENO powder and ENO_F thin film.

RESULTS AND DISCUSSION

The structures of ENO precursor and ENO_F thin film (after annealing at 1000°C) were studied by the XRD diffractometry and determined different polymorphs (Fig. 1). The XRD patterns verified the formation of monoclinic (M) and tetragonal (T) phases, which

correspond to $\text{T-EuNb}_5\text{O}_{14}$ (JCPDS 26-0632), M-EuNbO_4 (22-1099) in ENO, Fig. 1 shows XRD patterns of the substrate, interlayer, and thin films annealed at 1000°C . XRD analyses verified the formation of the monoclinic ZrO_2 phase (83-0944) and PZ as interlayer on substrate Al_2O_3 and phases: $\text{T-EuNb}_5\text{O}_{14}$ (main phase) and M-EuNbO_4 in ENO_F film.

The particle morphology of the ENO precursor was investigated by SEM (Fig. 2). After annealing at 1000°C , the spherical particle coarsened to the size of about 50-80 nm, and cuboidal 100-150 nm in ENO was observed (Fig. 2(a)). Using the SEM/EDS, local point-by-point probing made it possible to define the position and qualitative composition of such EuNbO_4 analyzed in ENO powder at 1000°C . The Eu/Nb atomic ratio was approximately 1.0. In Fig. 2(b), the surface morphology of the film was affected by the introduction of the Eu element resulting in a strong effect on surface roughness ($\text{EuNb}_5\text{O}_{14}$ particles).

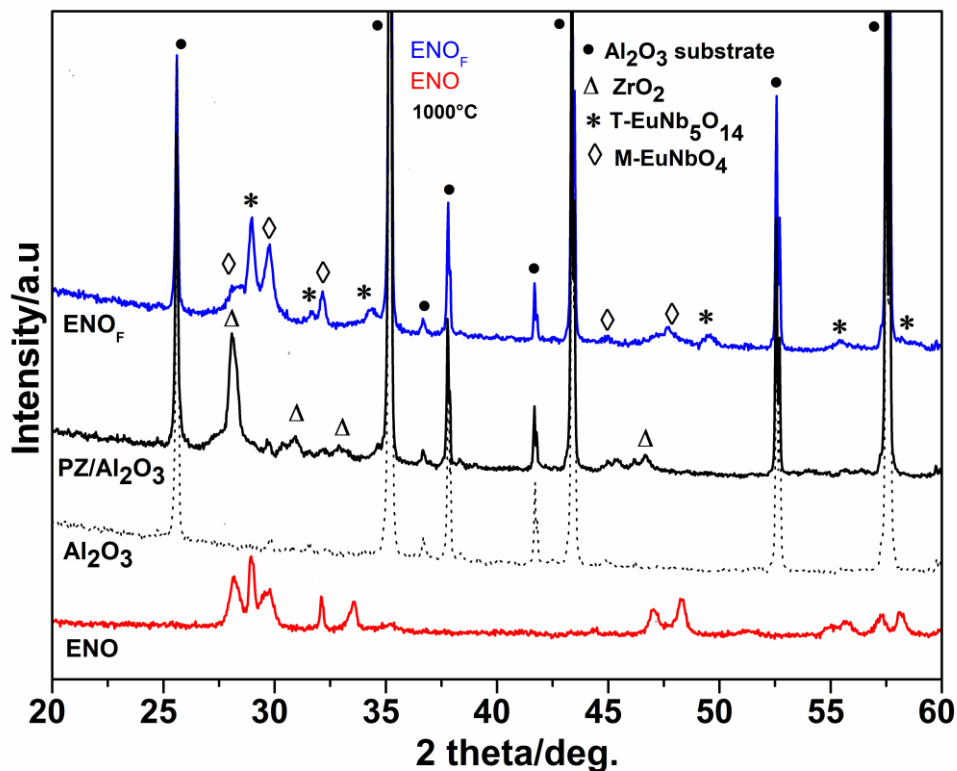


Fig. 1. XRD patterns of EuNbO_4 (ENO) precursor and ENO_F thin film on Al_2O_3 substrate with PbZrO_3 (PZ) interlayer after annealing at 1000°C .

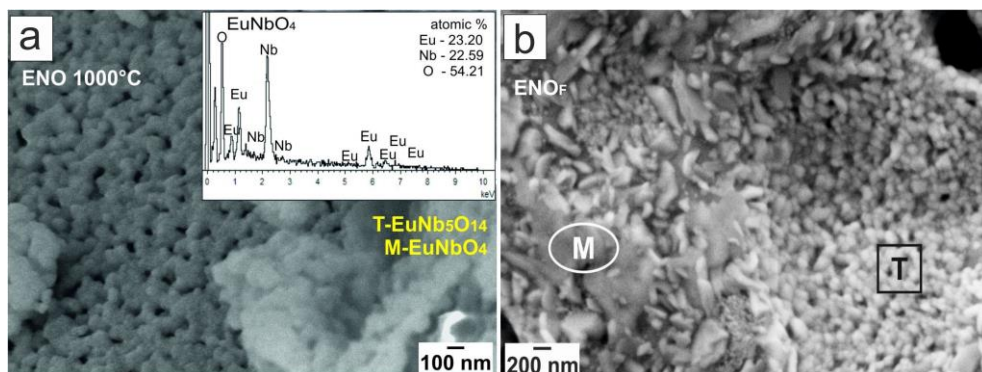


Fig. 2. SEM surface microstructures of (a) ENO precursor and (b) ENO_F thin film.

The XPS was employed to evaluate the surface chemical composition and the oxidation states of individual elements in the powder and thin film. The XPS spectrum of EuNbO₄ powder in a wide energy range is shown in Fig. 3(a). Besides carbon, no foreign impurities were found in samples. The survey XPS scans commonly showed Eu 3d, Eu (Auger), Eu 4d, O 1s, C 1s, Nb 3d, and Nb 3p peaks. Fig. 3(a) also presents all peaks related to the ENO: Eu 3d between 1120 (3d_{5/2}) and 1190 eV (3d_{3/2}), Nb 3p at 367 (3p_{3/2}) and 382 eV (3p_{1/2}), Nb 3d at 207 (3d_{5/2}) and 209 eV (3d_{3/2}). Peaks related to oxygen (O 1s) bonds were observed at around 530 eV and peaks corresponding to O KLL Auger's line at 973 eV were identified for niobate [20,21]. The XPS survey spectra of ENO_F thin film, substrate Al₂O₃ and PZ interlayer in a wide energy range are shown in Figs. 3(b,c,d). Spectra indicate elements Al, Si from substrates, Pb, Zr, from interlayer, Eu, Nb from the film, C, and O on the film surfaces.

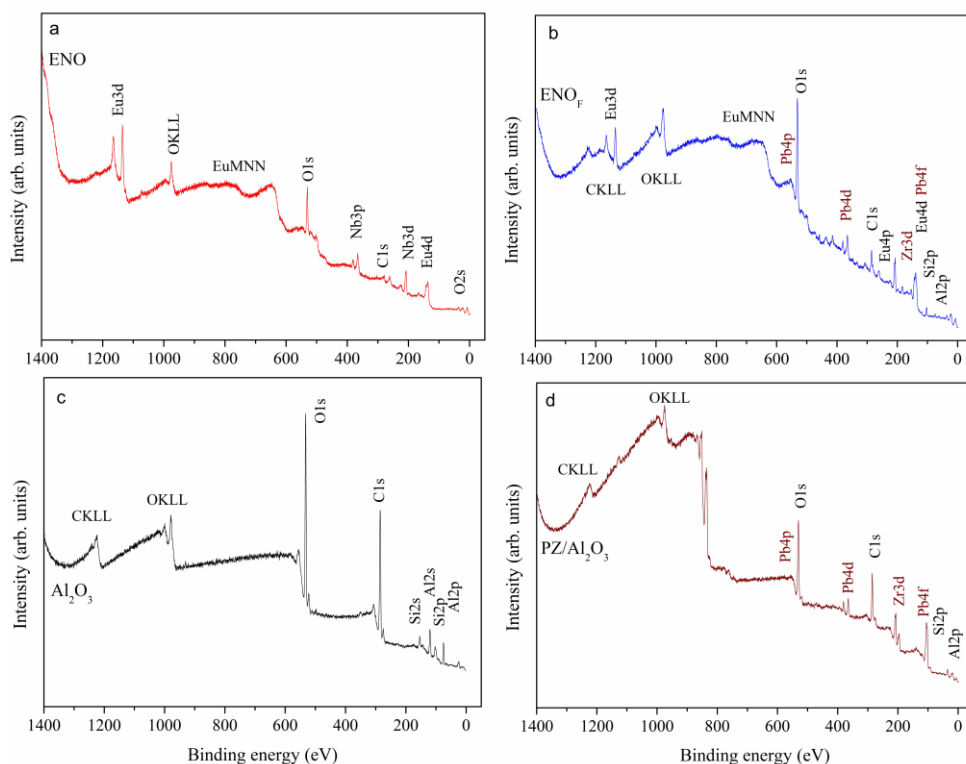


Fig.3. XPS survey spectra of (a) EuNbO_4 (ENO) precursor, (b) ENO_F thin film, (c) Al_2O_3 substrate, and PZ interlayer.

The Eu 3d core-level XPS spectra of EuNbO_4 powder and thin film and deconvoluted spectra are shown in Figs. 4 and 5. In Fig. 4, the features of $\text{Eu } 3d_{5/2}$ and $\text{Eu } 3d_{3/2}$ are fitted with combined Gaussian-Lorentzian functions which reveal 3+ state of Eu (at binding energy 1134.2 eV) with a satellite peak corresponding to 2+ state (1127.1 eV) for $\text{Eu } 3d_{5/2}$ core level, whereas fitting of $\text{Eu } 3d_{3/2}$ shows the presence of 3+ state (1164.2 eV) and satellite peak at 1154.5 eV (2+) [12-14]. Cho and Oh [15] labeled prominent peaks as 3+ due to the trivalent $3d^4f^6$ configuration (from bulk) while they labeled other weaker peaks located at a lower BE than the main peak as 2+, which corresponds to the divalent $3d^4f^7$ configuration (from the surface). The contents of Eu^{3+} and Eu^{2+} states were 9 at.% and 1 at.%, respectively in the ENO powder and 2 at.% of Eu^{3+} in the ENO film (Tabs. 1 and 2). The presence of Eu^{2+} states may induce oxygen vacancies in Eu_2O_3 [22].

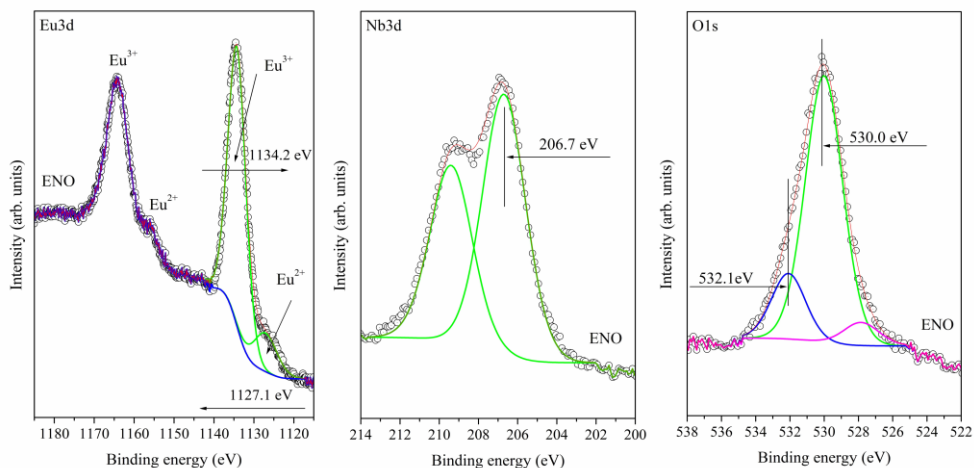


Fig. 4. HR XPS spectra of Eu 3d, Nb 3d, and O 1s and deconvolution peaks for EuNbO_4 (ENO) precursor.

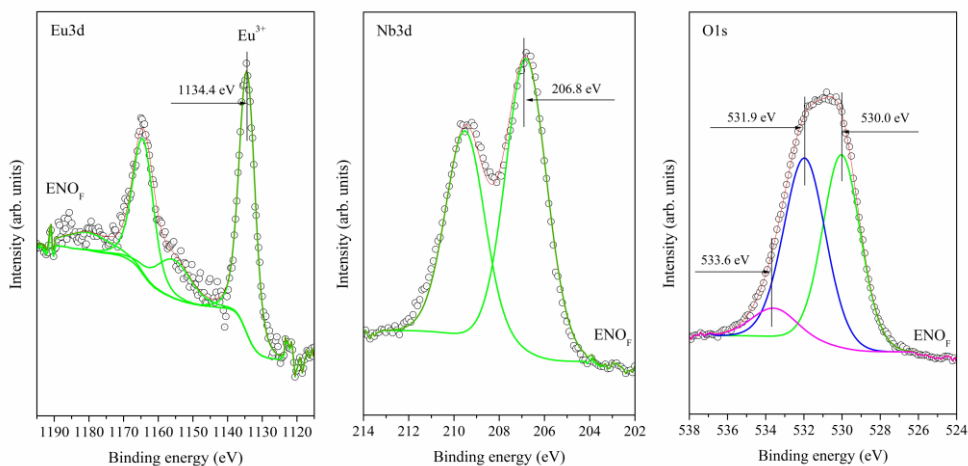


Fig. 5. HR XPS spectra of Eu 3d, Nb 3d, and O 1s and deconvolution peaks for ENO_F thin film.

The High-resolution XPS spectrum of the Eu 3d core level for the ENO_F film is shown in Fig. 5. The doublet at 1134.4 and 1164.2 eV can be attributed to Eu^{3+} $3d_{5/2}$ and $3d_{3/2}$ core levels, respectively. The analysis of peak positions and binding energies in the XPS spectra in the region corresponding to the $3d_{5/2}$ and $3d_{3/2}$ core levels of Eu ion (2 at. %) confirms that Eu characterizes a single Eu^{3+} oxidation state. The peaks of Nb^{5+} 3d centered at 206.7 and 209.5 eV can be assigned to $3d_{5/2}$ and $3d_{3/2}$ states, respectively. The deconvoluted spectrum of O 1s verifies triplet at 527.8, 530.0, and 532.1 eV. The main intense peak centered at 530.0 eV is attributed to the Eu-O and Nb-O in ENO powders [10]. The oxygen ions in the films are bonded to the Eu^{3+} ions. From Tabs. 1 and 2, Eu

concentration (at. %) decreases from 10 % in the precursor to 2 % in the film considering the substrate contains C, Al, Si, Pb, and Zr elements (40 %) at Nb (6 %) and O (52 %).

Tabs. 1 and 2 represent a comparison of Eu, Nb, and O relative concentrations (at.%) in EuNbO_4 precursor (Tab. 1) and ENO_F thin film (Tab. 2). The Nd/Nb/O ratio was determined to be 0.7:1.0:4.1 (in precursor) and 0.3:1.0:8.9 (in film). The carbon C 1s is an impurity (C-C and C=O bonds).

Tab. 1. Surface relative concentration (at. %) of EuNbO_4 powder after annealing at 1000°C for 1 hour.

Element	C 1s (hydrocarbons +CO ₃ ²⁻)		O 1s			Eu 3d (3d _{5/2} , 3d _{3/2})		Nb 3d (3d _{5/2} , 3d _{3/2})
Conc. (at. %)	9		66			11		16
Bond	C-H	C=O	Eu MNN	Nb-O Eu-O	non lattice			
Conc. (at. %)	7	2	3.7	51.4	10.9			
Conc. (at. %)	-		73			10		17
			4	57	12	1	9	
BE (eV)	285.0	289.8	527.8	530.0	532.1	1127.1 1157.1 (Eu ²⁺)	1134.2 1164.2 (Eu ³⁺)	206.7 209.4 (Nb ⁵⁺)
Eu:Nb:O = 0.7:1.0:4.1						Δ = 30 eV		Δ = 2.7 eV

Tab. 2. Surface relative concentration (at. %) of EuNbO_4 film after annealing at 1000°C for 1 hour.

Elem.	C 1s (adventitious hydrocarbons)		O 1s			Eu 3d 3d _{5/2} 3d _{3/2}	Nb 3d 3d _{5/2} 3d _{3/2}	Pb 4f 4f _{7/2} 4f _{5/2}	Zr 3d 3d _{5/2} 3d _{3/2}	Al 2p	Si 2p
Conc. (at. %)	20		52			2	6	2	2	6	10
Bond	C-H	C-O	Nb- O Eu-O	Eu, Nb- O	OH ⁻						
Conc. (at. %)	13	7	23	24	5						
BE (eV)	285.0	286.8	530.0	531.9	533.6	1134.4 1164.4 (Eu ³⁺)	206.8 209.5 (Nb ⁵⁺)	138.5 143.3 PbO	182.2 184.6 ZrO ₂	74.5	102.6
Eu:Nb:O = 0.3:1.0:8.9						Δ = 30 eV	Δ = 2.7 eV	Δ = 4.87eV	Δ = 2.4eV		

CONCLUSIONS

X-ray photoelectron spectroscopy (XPS) results demonstrate the existence of Eu^{3+} and Eu^{2+} ions in the EuNbO_4 precursor. The $\text{Eu } 3d_{5/2}$ peak consists of strong features characteristic of Eu^{3+} (1134.2 eV) with electron configuration ($4f^5$) and Eu^{2+} (1127.1 eV) with electron configuration ($4f^6$). The molar concentration of Eu^{3+} in ENO was higher (9.0 at.%) than Eu^{2+} (1.0 at.%).

The XPS revealed one valence state of Eu (Eu^{3+}) in the thin film. The relative concentration of Eu on the surface of ENO (10.0 at.%) precursor was higher than thin film (2 at.%). Presently, europium niobates have been observed with XPS, and further accumulation of experimental results is beneficial for the design of new effective electrolytic materials.

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