

Polyethylene glycol (PEG) used in the preparation of (Er³⁺/Yb³⁺):LiNbO₃ waveguides

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Abstract. LiNbO₃ co-doped with Er³⁺ and Yb³⁺ belongs among the most promising materials in photonics. In the form of thin films on a suitable substrate, it can be used as an active waveguide. Only few articles have been published concerning the deposition of such thin layers using a sol-gel method. Our aim was to test polyethylene glycol (PEG) as a water-soluble polymer in solutions to be deposited by spin-coating on sapphire substrates. Two heat treatment regimes were tested after single layers were deposited. Photoluminescence in a range of 1450–1650 nm was measured and the final films exhibited emission spectra with 6 local maxima. The deposited (Er³⁺/Yb³⁺):LiNbO₃ films were also characterized by m-line spectroscopy. In the NIR range, the films behaved as one-mode waveguides. This non-hydrolytic sol-gel method based on PEG thus represents one of few methods applicable in LiNbO₃ waveguiding films preparation.

1. Introduction

Due to its extraordinary spectrum of physical properties, LiNbO₃ is one of the most widely used dielectric materials [1]. Besides, LiNbO₃ is a very important material in optics and photonics – whether pure or doped with d- or f-ions [2]. Co-doping with Er³⁺ and Yb³⁺ ions results in the additional photoluminescence of the LiNbO₃ material. The energy of the radiative transition ⁴I_{13/2} → ⁴I_{15/2} of erbium f-electrons (1450–1650 nm with a maximum of 1530 nm) is well applicable in the so called third telecommunication window. (Er³⁺/Yb³⁺):LiNbO₃ in the form of a waveguide can be then employed as an amplifier or switcher. To prepare a waveguiding structure, various techniques are used – either the modification of a LiNbO₃ single crystal or the deposition of LiNbO₃ thin film. In the single crystals, a waveguide can be created by doping ions to the surface layer – e. g. high-energy ion implantation or high-temperature diffusion [3, 4]. To deposit (Er³⁺/Yb³⁺):LiNbO₃ thin films, physical (e. g. Pulsed Laser Deposition or Liquid Phase Epitaxy) [5, 6] or chemical methods belonging to the sol-gel family [7] are used.

The sol-gel method is generally a cost-effective procedure that is able to transfer elemental homogeneity from a solution up to a solid sample. Thin films can be deposited by spray drying, spin- or dip-coating using either pre-hydrolysed sols (hydrolytic alkoxide methods) or homogeneous solutions (chelation or polymeric processes). Lithium niobate in the form of thin films has been prepared with several methods [7, 8]; however, high demands on microstructure quality cause that



very few articles describe the preparation of thin layers able to guide actually an optical signal [9, 10]. We were successful previously with the use of polyvinylpyrrolidone (PVP) as a chelating and anti-stress agent at the deposition of waveguiding ($\text{Er}^{3+}/\text{Yb}^{3+}$): LiNbO_3 layers [11, 12]. Microstructure is not the only limitation for waveguiding properties. Films must also be of sufficient thickness and have high refractive index contrast with a substrate for an optical signal guiding. This can be limiting in a sol-gel method compared to the physical methods of films deposition. However, PVP can overcome this problem and layers with a thickness over 1 μm can be prepared [13]. Not so in the case of LiNbO_3 – the presence of the highly hydrolyzing Nb^{5+} ion does not allow for the preparation of solutions concentrated sufficiently to produce films of a thickness over 1 μm . In spite of all these factors, our ($\text{Er}^{3+}/\text{Yb}^{3+}$): LiNbO_3 films were proven as active waveguides and therefore we decided to continue in testing of another water-soluble polymer – polyethylene glycol (PEG).

Based on our previous study, we tested one- and two-step decomposition regime after each layer deposition. After crystallization, the films were characterized with the aim to test its effect on luminescent and waveguiding properties of prepared ($\text{Er}^{3+}/\text{Yb}^{3+}$): LiNbO_3 structures.

2. Experimental

The preparation of a $\text{Li}^{\text{I}}/\text{Nb}^{5+}/\text{Er}^{\text{III}}/\text{Yb}^{\text{III}}$ solution was carried out in an anhydrous and inert Ar atmosphere. First, $\text{Nb}(\text{OC}_2\text{H}_5)_5$ (STREM Chemicals; 99.9 %) was dissolved in 2-methoxyethanol (2-ME; Sigma-Aldrich; anhydrous; 99.8 %) and refluxed at 125 °C for 1 hour. Then, polyethylene glycol (PEG; Sigma-Aldrich; $M_w \sim 200$ g/mol; purity not specified) was added to the Nb(V) solution and further refluxed at 125 °C for 1 hour. Finally, lithium acetate (Sigma-Aldrich; 99.5 %), erbium acetate (Sigma-Aldrich; 99.9 %) and ytterbium acetate (Sigma-Aldrich; 99.9 %) were added and the solution was refluxed at 125 °C for another 1 hour. Prior to the preparation, the acetates were thermally dehydrated at 200 °C [14-16]. $\text{Er}(\text{Ac})_3$ and $\text{Yb}(\text{Ac})_3$ were added in a concentration of 0.5 at% each with respect to the LiNbO_3 stoichiometry. The final $\text{Li}^{\text{I}}/\text{Nb}^{5+}/\text{Er}^{\text{III}}/\text{Yb}^{\text{III}}$ solution had a metal concentration of 0.6 mol/L and the molar ratio of Li:Nb:PEG:2-ME was equal to 1:1:1:15.

The films were prepared by spin-coating on sapphire (0001) substrates (sized 1.5 cm $\times$ 1.5 cm). The coater WS-650SZ-6NPP/LITE with the 650 controller unit was utilized for the spin-coating (Laurell Technologies Corporation). The optimized deposition parameters were: rotation at 5000 rpm for 30 s and the volume of the injected solution 55 μL ; a total of 5 layers were deposited on each substrate. The heat treatment of each deposited layer was performed in one-step (700 °C/10 min in air) or two-steps regime (350 °C/10 min in air and 700 °C/10 min in air). The preparation and names of thin films samples are summarized in Table 1.

Table 1. The names and heat treatment condition of prepared thin films.

	PEG-1S	PEG-2S
PEG molecular mass (g/mol)	200	200
number of deposited layer	5	5
heat treatment in air	one-step (700 °C/10 min)	two-step (350 °C/10 min and 700 °C/10 min)

Thermal behavior of deposited solutions was studied by differential thermal analysis (DTA) and thermogravimetric analysis (TG) using the SetSys Evolution equipment (Setaram). The DTA and TG data were measured in a range of 20–800 °C with a heating rate of 5 °C/min in air. The phase composition of the prepared samples was determined by XRD. The device used was Bruker-AXS D2 Phaser powder diffractometer with the parafocusing Bragg–Brentano geometry using the CoK_α radiation. Data were evaluated in the software package HighScore Plus. The film morphology was characterized by atomic force microscopy (AFM) using Ntegra Spectra (NT-MDT). The surface scans were performed in a tapping (semi-contact) mode. Cantilevers with a strain constant of 1.5 kN m^{-1}

equipped with a standard silicon tip with curvature radius lower than 10 nm was used for all measurements.

The photoluminescence spectra of the prepared thin films were collected within a range of 1440–1600 nm at room temperature. A semiconductor laser POL 4300 emitting at 980 nm was used for the excitation of electrons. The luminescence radiation was detected by a two-step-cooled Ge detector J16 (Teledyne Judson Technologies). To scoop specific wavelengths, a double monochromator SDL-1 (LOMO) was used. A synchronous detection technique was implemented by chopping the laser beam at a modulation frequency of about 35 Hz and by employing a lock-in amplifier (EG&G 5205). For the evaluation, all luminescence spectra were transformed to the base level and normalized to a standard sample – an $\text{Er}^{3+}/\text{Yb}^{3+}:\text{LiNbO}_3$ monocrystalline sample. Transmission spectra were collected in a range of 300–1800 nm using two different equipments. In a range of 300–1100 nm, a fiber spectrometer Avaspec-3648 (Avantes) was used. In a wavelength range of 600–1800 nm, the transmission was measured by a single grating spectrometer MDR 23 with tungsten lamp. The spectra measured by the two spectrometers were linked up at 600 nm. The film thickness was determined by a UV-vis reflectance spectrometer Avaspec-3648 (Avantes). Waveguiding properties were measured by m-line mode spectroscopy using the Metricon Prism Coupler device. Our measurement was done using a prism with an effective range of refractive index from 1.55 to 2.45 (for 633 nm) at operating wavelengths of 633, 964, 1311 and 1552 nm in the TE polarization.

3. Results and discussion

Based on DTA/TG measurement (Figure 1), we suggested the thermal treatment of deposited layers. The first endothermic step between 20 °C and 130 °C belongs to the evaporation of 2-methoxyethanol. The following two exothermic processes (in this case with no significant mass change) can be assigned to the decomposition of present organics – acetates, 2-methoxylesters of acetic acid and PEG. As in the case of PVP, we decided to compare one- and two-step heating at 700 °C and 300 °C/700 °C, respectively.

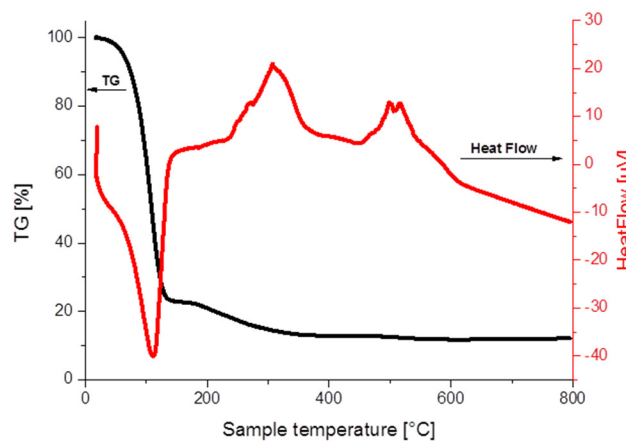


Figure 1. DTA/TG measurement of the $\text{Li}^{+I}/\text{Nb}^{+V}/\text{Er}^{+III}/\text{Yb}^{+III}$ precursor solution.

Figure 2 shows X-ray diffraction patterns of the prepared films. The measurement is presented only in a range of 20–47° without the dominating sapphire (0001) reflection at 48.7°. The LiNbO_3 reflections were indexed according to the PDF 00-020-0631; the reflections of the sapphire substrate are marked by *. Prepared films were polycrystalline with no secondary phase detectable. The films exhibited the preferential orientation of LiNbO_3 along the (006) plane; however, also other reflections were present – (012), (104), (110) and (113). In comparison with our previous sol-gel prepared LiNbO_3 films [11, 12], the described disorientation is more significant; however, this phenomenon does not have any major influence on the waveguiding ability of thin films (as described below).

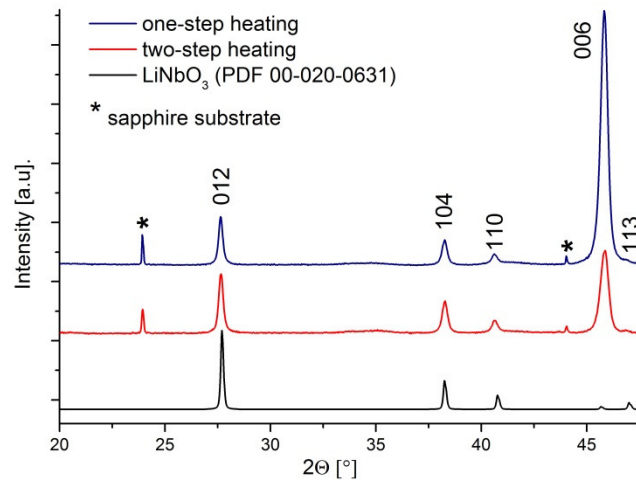


Figure 2. XRD patterns of thin films prepared using different heat treatment of deposited layers. A simulated pattern of LiNbO_3 using PDF 00-020-0631 is also presented. (for a black white version: in the legend, the order from top to bottom is the same as the order of lines in the picture)

The photoluminescence spectra were measured in a wavelength range of 1440–1650 nm where the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition of Er^{3+} ions is located. Figure 3 presents the emission spectra of both samples (the intensity was normalized to a standard $\text{Er}^{3+}/\text{Yb}^{3+}:\text{LiNbO}_3$ monocrystalline sample). The heat treatment used did not have any influence on the structure of the spectra, only a slight difference in the intensity is visible. In both cases, the most intense band is placed at 1530 nm, other distinguishable bands are placed at 1485 nm, 1510 nm, 1543 nm, 1558 nm (and one broad band around 1600 nm). Such energy separation of emission spectrum is indicative of a proper crystal surrounding of Er^{3+} ions and of overall good crystallinity of the LiNbO_3 phase. In comparison with the sole other published $\text{Er}^{3+}/\text{Yb}^{3+}:\text{LiNbO}_3$ thin film prepared using a sol-gel method [17] (besides our articles using PVP), the clear bands position in the emission spectra is comparable to monocrystalline thin films [3].

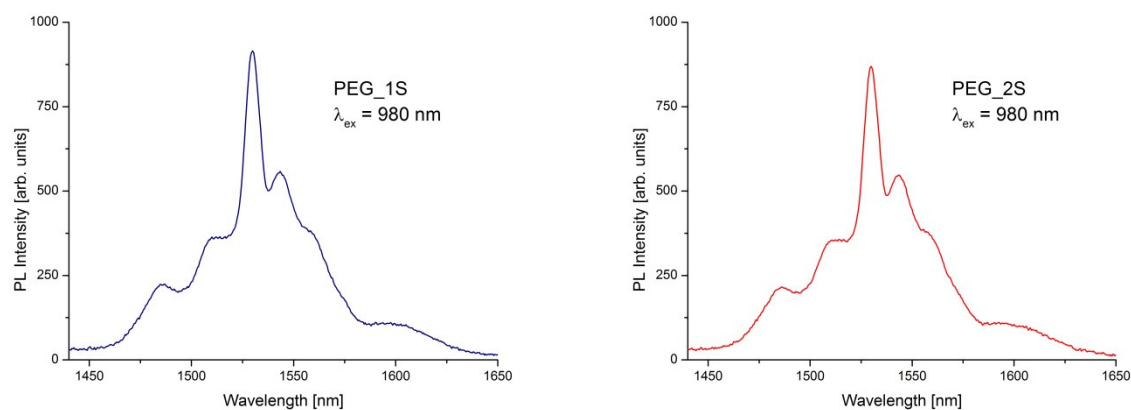


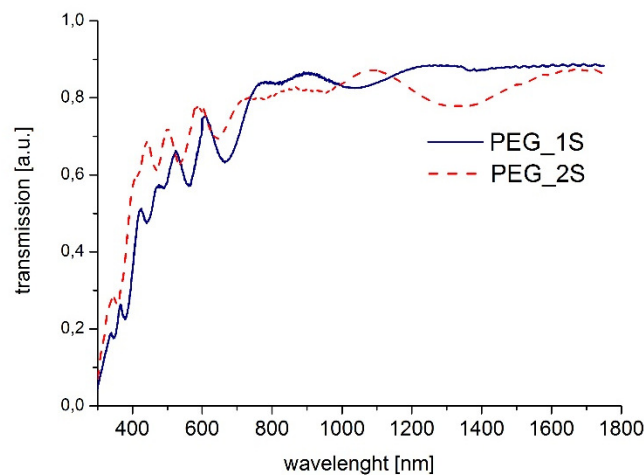
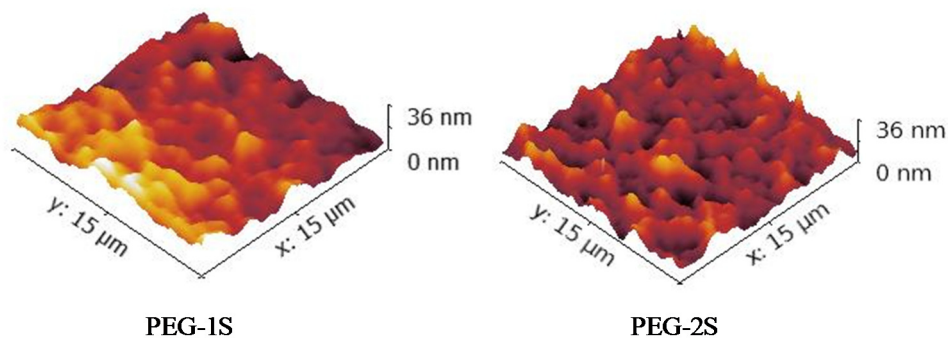
Figure 3. Photoluminescence emission spectra excited using a 980 nm laser measured at room temperature. The intensity was normalized to a standard $\text{Er}^{3+}/\text{Yb}^{3+}:\text{LiNbO}_3$ monocrystalline sample.

Regarding the waveguiding properties of prepared thin films, m-line spectroscopy was performed at the following wavelengths: 633 nm, 964 nm, 1311 nm and 1552 nm. Table 2 summarizes the number of modes guided by both samples.

Table 2. The summary of optical modes guided, and the thickness and roughness of prepared films.

Sample	Wave propagation (number of modes)				Thickness [nm]	R_a [nm]
	633 nm	964 nm	1311 nm	1552 nm		
PEG-1S	0	1	1	1	771	3.29
PEG-2S	0	1	1	1	743	3.98

In accordance with our previous experience with polycrystalline LiNbO_3 thin films, the waveguiding ability disappears at shorter wavelengths where an optical signal is probably dispersed and attenuated by grains with a size comparable to the wavelengths used. This assumption can be supported by transmittance spectra in the VIS and NIR region (Figure 4) where the interaction of a film with the light is increased when wavelength decreases. The roughness and thickness of the films was comparable - Table 2 (taking into account the precision of the roughness determination using AFM images). The AFM images of both samples are presented in Figure 5. Contrary to monocrystalline samples, the waveguiding ability in polycrystalline LiNbO_3 samples is strongly driven by microstructure; thickness is a minor, but not legible, parameter [18]. In any case, one-mode $\text{Er}^{3+}/\text{Yb}^{3+}:\text{LiNbO}_3$ active waveguides were prepared.

**Figure 4.** Transmission spectra of both prepared films measured in a spectral range of 300–1800 nm.**Figure 5.** AFM images of prepared thin films. The calculated roughness is presented in Table 2.

4. Conclusions

We present $\text{Er}^{3+}/\text{Yb}^{3+}:\text{LiNbO}_3$ waveguiding thin films deposited by the spin-coating of solutions based on polyethylene glycol. Two different heat treatments of deposited layers were applied and the influence on the optical properties was established. Irrespective to the treatment used, one-mode waveguides were prepared. These results, together with our previous films prepared with another water-soluble polymer – PVP, are promising for the development of active waveguide technology based on LiNbO_3 material. Especially the high homogeneity of dopant ions, demonstrated here by photoluminescence spectra, is crucial in testing new dopants. Comparing this sol-gel method with physical deposition processes, the thickness of deposited films, achievable by sol-gel methods, can with difficulty reach 1 μm without loss of suitable microstructure. On the other hand, this method represents a cost-effective and simple method applicable in LiNbO_3 thin films deposition.

Acknowledgements

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