

INFLUENCE OF PREPARATION CONDITIONS ON THE MICROSTRUCTURE AND OPTICAL PROPERTIES OF LiNbO₃ THIN FILMS

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Thin films of Er³⁺/Yb³⁺: LiNbO₃ were deposited on sapphire (0001) substrates using a spin-coating process. A deposited solution was prepared by a non-aqueous sol-gel method using 2-methoxyethanol, metallic lithium, niobium(V) ethoxide and erbium and ytterbium acetates. Two starting compositions of LiNbO₃ solution (1:1 or congruent) were tested in order to minimize the present of secondary (Er/Yb)NbO₄ phases. The effect of different temperature (800°C or 1000°C) and different used atmosphere (air or oxygen) during the films crystallization was also investigated. Rapid annealing (at 1150°C with the heating rate 55°C·s⁻¹) was also tested and its influence on secondary phases crystallinity and luminescence of Er³⁺/Yb³⁺: LiNbO₃ was established. The thin films were characterized by X-ray diffraction analysis, scanning electron microscopy and photoluminescence spectroscopy.

INTRODUCTION

Lithium niobate belongs to the group of the most important crystalline materials. This ferroelectric material with the Currie temperature of 1150°C is mostly used in acousto-optic devices, optical waveguides, non-linear optics and pyroelectric sensors [1]. Lithium niobate is not a natural material; its monocrystals are grown from a melt using the Czochralski method. The prepared monocrystals have congruent stoichiometry – Li_{0.941}Nb_{1.012}O₃ [2, 3]. The epitaxial thin films of LiNbO₃ have been prepared by several methods, e.g. radio frequency (RF) sputtering, pulsed laser deposition (PLD) or sol-gel deposition [4-6]. Compared to others sol-gel methods have the advantage of low cost and possibility to change the stoichiometry of precursor mixture. In comparison with the PLD, the sol-gel deposition does not usually have a problem with the presence of secondary phases such as LiNb₃O₈ and Li₃NbO₄ [7]. Additionally, the crystallization temperature after the sol-gel deposition is lowered because of the high reactivity of sol-gel precursors and then lithium losses at high temperature are minimized. Solutions are mainly deposited on sapphire (0001) substrates that have been proved as the most appropriate for the epitaxial growth of LiNbO₃ because of appropriate crystal structure and thermal properties [8, 9].

The most widely used sol-gel method for LiNbO₃ thin film preparation is based on alkoxide solution deposition. The mixed solution of LiNb(OR)₆ is prepared by the reflux of individual alkoxides. Firstly, primary alkoxides of Li and Nb (mainly ethoxides) were used [8, 10] as well soluble starting compounds. However, the high moisture sensitivity demands controlled hydrolysis and manipulation under inert atmosphere. Alternatively, less hydrolyzing derivatives of 2-methoxyethanol are applied [11]. The hydrolysis is suppressed due to a less ionic bond between metal and oxygen (the alkoxide chain is longer and contains additional oxygen atom). Moreover, 2-methoxyethanol sterically hinders a metal center as a bidentate ligand [12].

In this work, the thin films of Er³⁺/Yb³⁺ doped LiNbO₃ were synthesized using a non-aqueous sol-gel method using the 2-methoxyethanol derivatives of Li and Nb. Ytterbium and erbium cations were doped in the concentration of 0.5 at. % each. The films were deposited on sapphire (0001) substrates using the spin-coating technique. Based on our previous experience, LiNbO₃ thin films preparation led to the formation of minor (Er/Yb)NbO₄ secondary phases. The XRD intensity of these phases is very low and the diffraction maxima appear as shoulders at optionally present LiNbO₃ (001) reflection. Therefore researchers do not pay attention even if the phases are present at XRD patterns. Our

goal was to study the influence of stoichiometry and crystallization process on the presence of (Er/Yb)NbO₄ and its impact on luminescence properties. Firstly an initial composition of LiNbO₃ solution with different Li/Nb ratio was used (1:1 or congruent ratio). Then different thermal treatments of films were utilized. Two crystallization temperatures (800°C or 1000°C) and two atmospheres (air or oxygen atmosphere) were tested. Further, a rapid annealing with the heat ramp 55°C·s⁻¹ was used and its influence on secondary phases presence, as well as, on the luminescence properties was proven. The c-orientation of the LiNbO₃ films and the presence of the possible secondary phases were examined by XRD measurement. The influence of the thermal treatment on photoluminescence spectra within the range of 1440 – 1600 nm was also determined. The microstructure of LiNbO₃ was analyzed by scanning electron microscopy. Neither the starting Li/Nb stoichiometry nor the temperature (or the atmosphere) of crystallization had significant effect on the solubility of Er³⁺ in LiNbO₃ phase (respectively on the presence of secondary Er/Yb-Nb-O phases). This work showed the considerable influence of rapid annealing on the luminescence properties in the IR range.

EXPERIMENTAL

Preparation of solutions

Due to their high water sensitivity, the manipulation with starting materials as well as with intermediates was done either in a glove box or in an apparatus under argon atmosphere. Starting solution of lithium was prepared using metallic lithium in a reaction with 2-methoxyethanol. For the niobium(V) 2-methoxyethoxide synthesis, niobium(V) ethoxide was used. 2-methoxyethanol was utilized also as a solvent in both solutions. All reactions were proceeded under reflux at the boiling temperature of 2-methoxyethanol (125°C) for 2 hours. Both single – metal 2-methoxyethoxides were mixed in an appropriate ratio and the mixed LiNb(OR)₆ solution was heated under inert atmosphere for 2 hours at the temperature of 125°C. Also, erbium and ytterbium acetates were added before this final reflux. The acetates were thermally dehydrated at 200°C [13, 14] before their use in the non-aqueous solution and they were added with the concentration of 0.5 at. % to the LiNbO₃ stoichiometry. All deposited solutions were of 0.3 M metal concentration.

Thin films deposition

Sapphire (0001) substrates (CRYTUR, spol. s.r.o.) were cleaned using several organic solvents and the “piranha” oxidizing agent - (the mixture of H₂SO₄ and H₂O₂ in the molar ratio 1:3). The coater WS-650SZ-6NPP/LITE (Laurell Technologies Corporation) with

the 650 controller unit was utilized at the spin coating. The parameters of the spin coating were fixed (based on our previous experience) – the rotation time at the maximal speed (30 s), acceleration and deceleration speed (400 min⁻²), spin speed (4000 min⁻¹) and the volume of deposited solutions per a substrate area (50 µl).

All samples were prepared by a multiple coating-decomposition process (each layer was heated at 500°C in air for 1 min after deposition). Finally, the samples were crystallized either at 800°C or 1000°C for 1 hour in air or oxygen atmosphere. Some samples were treated with rapid annealing (RA) at the temperature of 1150°C with the rate of 55°C·s⁻¹. The annealing was performed in the Solaris 75 Rapid Thermal Processing device. During the annealing, the oxygen flow of 2 sccm was maintained. The rapid annealing was used for samples with or without previous crystallization. All heat treatment procedures are summarized in Figure 1.

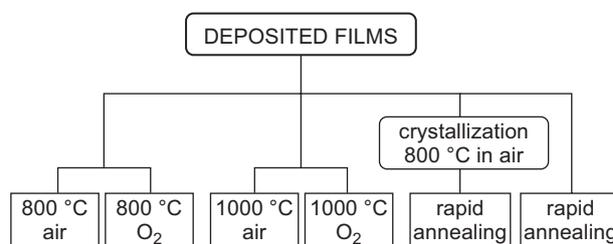


Figure 1. Scheme of final crystallization.

Characterization methods

X-ray powder diffraction (XRD) data were collected at room temperature with an X'Pert PRO θ - θ (PANanalytical) powder diffractometer with parafocusing Bragg-Brentano geometry using the CuK α radiation. Data evaluation was performed in the software package HighScore Plus using PDF2 database.

The photoluminescence (PL) spectra of the prepared thin films were collected within the 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, double monochromator SDL-1 (LOMO) was used. 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 of the luminescence spectra were transformed to the base level and, after subtraction of the baseline, they were normalised with the help of reference samples.

The film topology was characterized by scanning electron microscope (SEM) type Vega 3 LMU (TESCAN) equipped with EDS analyser INCA 350 (Oxford Instruments). The scans were collected in the regime of secondary electrons.

RESULTS

The solubility of Er^{3+} and Yb^{3+} ions in the LiNbO_3 phase is limited to very low content and is probably depending on both the preparation process and the form of LiNbO_3 (mono- or polycrystalline) [15-17]. Whether Er^{3+} doped LiNbO_3 was grown as a congruent crystal or was prepared by Er^{3+} implantation into a LiNbO_3 congruent crystal, Er^{3+} ions can enter into vacant Li^+ positions formed in the congruent structure. Therefore we tried to compare the use of different Li/Nb ratio in the thin films preparation and to establish the influence on the formation of $\text{Er}^{3+}/\text{Yb}^{3+}$ secondary phases.

LiNbO_3 thin films crystallized at 800°C in air with Li/Nb ratio 1:1 or with the congruent composition of 0.94:1.01. The XRD pattern of the samples is presented in Figure 2. Intensive reflections of LiNbO_3 (006) and a sapphire substrate (0001) are dominant, no secondary phases of the Li/Nb phase equilibria (i.e. Li_3NbO_4 or LiNb_3O_8) are present. The insets of the Figure 2 show enlarged interval $32.5 - 37^\circ 2\theta$ where the diffraction peaks of the ErNbO_4 and YbNbO_4 phases can be found. The phases have monoclinic crystal structure [18]; however, in the matrix of (006) oriented LiNbO_3 , maximal (and only) diffraction is matched for (200) and (002) reflection (instead of the (-121) diffraction in a not oriented phase). The peaks are broaden by different layer spacing in the ErNbO_4 and YbNbO_4 phases caused by different Er^{3+} and Yb^{3+} radius [18]. The intensity of this diffraction is about 0.5 % of the LiNbO_3 (006) diffraction; nevertheless, the quantification of the phase content is complicated due to the oriented structure. There are also visible peaks belonging to other LiNbO_3 orientation – (104) and (110). The peak intensity differs only very slightly in the samples with different Li/Nb ratio and,

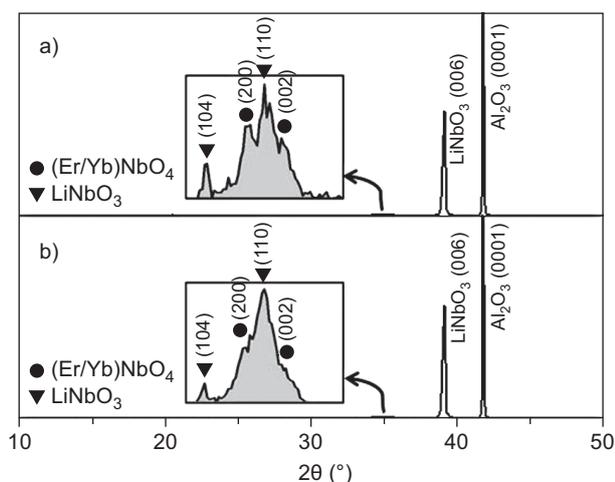


Figure 2. The XRD patterns of $\text{Er}^{3+}/\text{Yb}^{3+}$ doped LiNbO_3 thin films with different starting Li/Nb ratio: a) 1:1, b) 0.94:1.01. The inset pictures enlarge the pattern around $35^\circ 2\theta$ where the reflections of $(\text{Er}/\text{Yb})\text{NbO}_4$ or LiNbO_3 are marked by ● or ▼, respectively.

in comparison with the (006) LiNbO_3 intensity, it stays almost unchanged. It means that the change of LiNbO_3 stoichiometry does not influence the solubility of Er^{3+} and Yb^{3+} ions in the LiNbO_3 polycrystalline oriented structure. It could be caused by the Er^{3+} dissolution mechanism that was presented for the Er^{3+} diffusion after electron beam evaporation [15]. The authors supposed the formation of Er/Nb mixed oxide in the first step of diffusion. This phase then serves as a reservoir for Er^{3+} ions diffusion into a monocrystal. Contrary, in our polycrystalline samples, the Er/Nb oxide (or Yb/Nb oxide) probably stays stable and the dissolution in LiNbO_3 is suppressed.

As in the case of phase composition, the change of the starting Li/Nb stoichiometry did not have significant effect on the emission properties. Luminescence spectra in the 1450-1650 nm interval are presented in Figure 3. There are visible bands of the erbium ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ emission: the most intensive bands at around 1530 nm and 1484 nm and further weaker bands at 1519, 1543 and 1559 nm. Although, the content of ErNbO_4 phase is low, compared to the $\text{Er}^{3+}/\text{LiNbO}_3$ substitution level, the Er^{3+} in the form of ErNbO_4 influences the luminescent properties significantly. We can notice some luminescence characteristics of Er^{3+} in the form of ErNbO_4 [19] (comparing with monocrystalline $\text{Er}^{3+}/\text{LiNbO}_3$) – band shoulders at 1519 and 1536 nm and also increased intensity in the 1485 nm region even if it can be also caused by poorly developed crystal structure of the Er^{3+} containing phases.

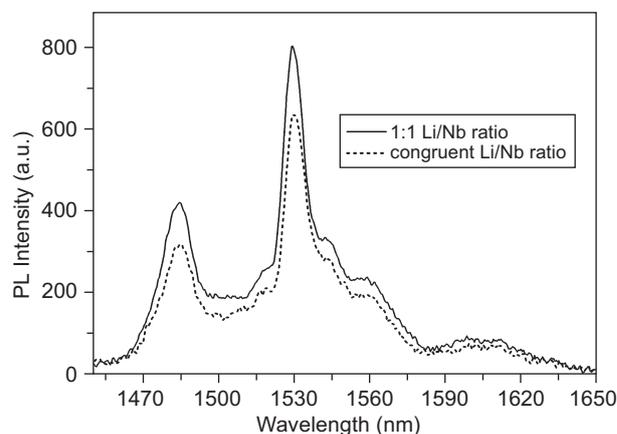


Figure 3. Luminescence spectra of $\text{Er}^{3+}/\text{Yb}^{3+}$: LiNbO_3 thin films heated with the different starting Li/Nb ratio.

For the samples with 1:1 composition, we further studied the impact of different annealing temperatures and also of altered crystallization atmospheres. We compared the crystallization at 800 or 1000°C and in air or in pure O_2 . The used atmosphere did not have any significant impact on the phase composition or on the luminescence properties (XRD and PL not presented). Both measurements showed weakly improved crystallinity after the use of higher temperature (independently on the atmosphere)

– the intensity of secondary phases reflection is slightly increased and, similarly, the LiNbO₃ phase diffraction peaks were weakly developed. The intensity and the structure of luminescent bands were almost unchanged, according to the marginal change in the crystallinity of the thin films.

Finally, we used rapid annealing to establish the influence on the phase composition and on IR emission spectra. We prepared two sets of samples – firstly, a pre-crystallized film (at 800°C in air) + rapidly annealed at 1050°C (with the heating rate 55°C·s⁻¹) and, secondly, a directly rapidly annealed sample without the previous crystallization. The phase composition was not changed but the intensity of all secondary phases reflection (whether of ErNbO₄/YbNbO₄ phases) or of minor LiNbO₃ reflections was further enhanced after rapid

annealing – see Figure 4. This effect is best visible when two insets of Figure 4 (in the interval 32.5 - 37° 2θ) are compared. The photoluminescence behaviour was influenced considerably by the rapid annealing (whether with or without the pre-crystallization). In Figure 5, the increased intensity of the erbium ⁴I_{13/2} → ⁴I_{15/2} emission in the entire interval is visible (in comparison with the not rapidly annealed sample). The intensity of the 1530 nm band and its full width at half maximum (FWHM) of 4 - 5 nm are the evidence of improved crystallinity with improved Er³⁺ crystal positions - obviously in both

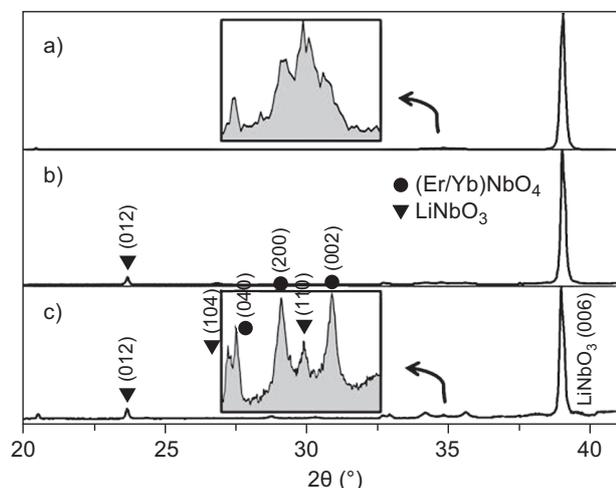


Figure 4. The XRD patterns of Er³⁺/Yb³⁺ doped LiNbO₃ thin films with different crystallization procedure: a) 800°C in air, b) rapid annealed, c) 800°C in air + rapid annealed. The inset pictures enlarge the pattern around 35° 2θ where the reflections of (Er/Yb)NbO₄ or LiNbO₃ are marked by ● or ▼, respectively.

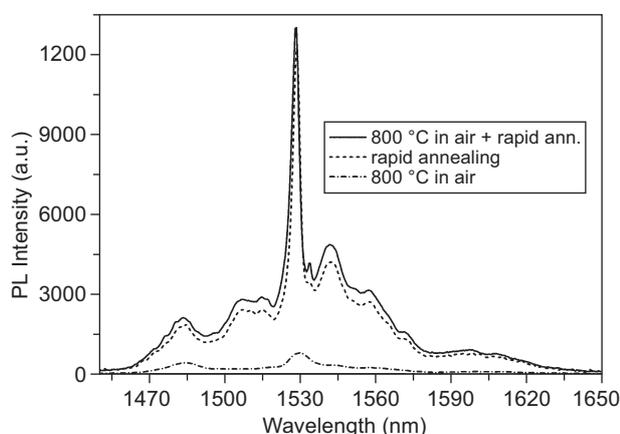


Figure 5. Luminescence spectra of Er³⁺/Yb³⁺: LiNbO₃ thin films with the different heat treated (800°C, rapid annealing with or without previous crystallization).

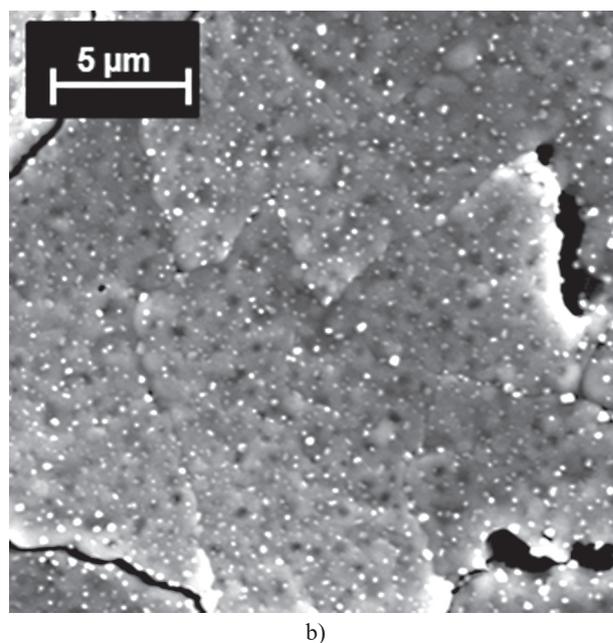
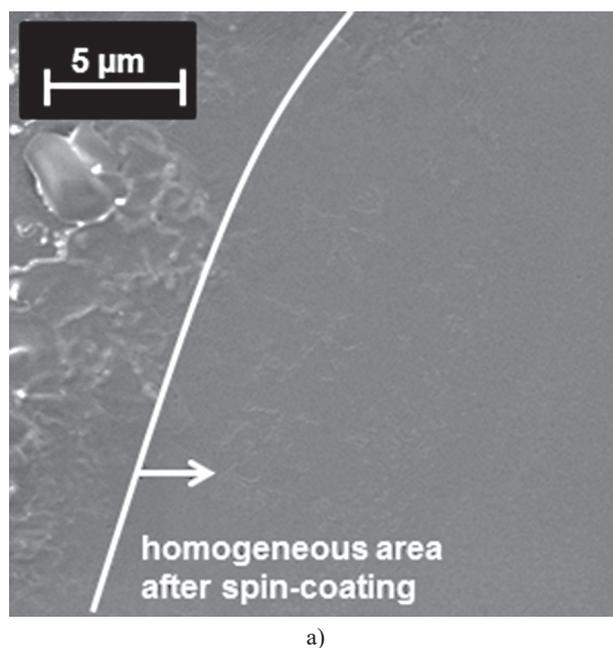


Figure 6. SEM pictures of Er³⁺/Yb³⁺: LiNbO₃ thin films a) rapid annealing without previous crystallization b) rapid annealing with previous crystallization (800°C, air). Magnification for both pictures – 5 000×.

phases containing Er^{3+} - LiNbO_3 or ErNbO_4 . The spectra also contain some above described characteristics of ErNbO_4 emission and the measurement demonstrates that the presence of erbium niobate phase does not have deteriorating influence on the ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ emission.

Despite negligible impact of the pre-crystallization on the final photoluminescence properties, the microstructure of the pre-crystallized layer was considerably destroyed. In Figure 6, we can compare both rapidly annealed layers at the magnification of $5000\times$. The pre-crystallized layer probably has higher difference in the thermal expansion coefficient in comparison with the sapphire substrate and therefore it worse overcomes the rapid thermal treatment. Nevertheless, the rapid annealing can be successfully used for the enhancement of the films structure and so for the improvement of the photoluminescence properties.

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CONCLUSION

C-oriented films of $\text{Er}^{3+}/\text{Yb}^{3+}$: LiNbO_3 were prepared using the spin coating of 2-methoxyethoxide solutions. In order to minimize the presence of $(\text{Er}/\text{Yb})\text{NbO}_4$ secondary phases, different Li/Nb starting ratio (1:1 or the congruent ratio) was used. The use of the congruent ratio did not enhance the solubility of Er^{3+} or Yb^{3+} ions. Further, various crystallization temperatures (800°C or 1000°C), atmospheres (air or O_2) and crystallization techniques (conventional and rapid annealing) were examined. Neither crystallization temperatures or atmospheres influenced the $(\text{Er}/\text{Yb})\text{NbO}_4$ presence and the luminescence properties of Er^{3+} ions. By contrast, the

use of rapid annealing at 1150°C significantly improved the luminescent properties of the layers. The increased intensity of the 1530 nm band and its narrow FWHM (4 - 5 nm) demonstrate that the crystallinity of layers is significantly improved. In addition, the influence of crystallization at 800°C (inserted before the rapid annealing) did not enhance the luminescent properties and did not have influence on the presence of the secondary phases. In terms of microstructure and possible use of $\text{Er}^{3+}/\text{Yb}^{3+}$: LiNbO_3 films for wave guiding applications, the rapid annealing is better to apply directly after spin coating without any pre-crystallization.

REFERENCES

1. Arizmendi L.: Phys. Status Solidi A. 201, 2 (2004).
2. Lerner P., Legras C., Dumas J.P.: J. Crys. Growth. 3-4, 231 (1968).
3. Svaasand L.O., et al.: J. Crys. Growth. 22, 3 (1974).
4. Hirano S.-i., et al.: J. Crys. Growth. 237-239, 3 (2002).
5. Meek P.R., Holland L., Townsend P.D.: Thin Solid Films. 141, 2 (1986).
6. Shibata Y., et al.: J. Appl. Phys. 77, 4 (1995).
7. Tan S., et al.: J. Appl. Phys. 79, 7 (1996).
8. Hirano S., Kato K.: Adv. Ceramic Mater. 3, 5 (1988)
9. Won, D.H., Hur N.H., No K.: Japan. J. Appl. Phys. 35, 1A (1996).
10. Kaufherr N., Eichorst D.J., Payne D.A.: J. Vac. Sci. Technol. A. 14, 2 (1996).
11. Eichorst D.J., Payne D.A.: Mater. Res. Soc. 773 (1988).
12. Hubert-Pfalzgraf L.G.: J. Coord Chem. Rev. 178-180, 967 (1998).
13. Hussein G.A.M.: Powder Technol. 108, 285 (2001).
14. Hussein G.A.M. et al.: Powder Technol. 103, 156 (1999).
15. Baumann I., et al.: Appl. Phys. A. 64, 1 (1997).
16. Nekvindova P., et al.: Opt. Mater. 34, 4 (2012).
17. Cajzl J., et al.: Scr. Mater. 68, 9 (2013).
18. Zhang D.L., et al.: J. Am. Ceram. Soc. 90, 9 (2007)
19. Jakeš V. et al.: J. Sol-Gel Sci. Technol. (not accepted yet).