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Journal of Physics and Chemistry of Solids 68 (2007) 1272–1275

JOURNAL OF
PHYSICS AND CHEMISTRY
OF SOLIDS

www.elsevier.com/locate/jpcs

Synthesis of Er-complexes for photonic applications

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Abstract

We present a new approach of introducing erbium ions onto thin surface layers of silica glass substrates based on soaking of solution of erbium complexes. Different types of Er^{3+} complexes with 2,2′-dipyridyle, 1,10-phenantroline, 8-hydroxyquinoline and ethylendiamine ligands and nitrate, thiocyanate and acetate anions were prepared. Composition of the complexes was determined by elementary analysis and by FT-IR spectroscopy. Decomposition temperature was measured by thermogravimetric analysis. Erbium doped surface layers exhibit strong photoluminescence with maximum on 1533 nm and full width at half maximum above 50 nm.

Keywords: A. Glasses; A. Optical materials; B. Chemical synthesis; D. Luminescence; D. Optical properties

1. Introduction

Rare earths (RE) doped materials are of crucial importance to photonics and are becoming to be widely deployed in solid-state lasers. To avoid unwanted pair interactions of the RE ions within the whole body of the substrate it is needed to restrict the presence of them only in the shallow surface layer; that is the localized doping is highly desirable. Er^{3+} is for this reason the most popular RE ion [1], mainly for the characteristic emission around 1550 nm (coming from the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition), which is the wavelength currently used in telecommunications [1].

We present a new approach of introducing erbium ions onto thin surface layers of glass substrates. The approach is based on soaking of solutions of erbium coordination compound (Er complexes) into porous silicate glass followed by annealing to decompose the Er-complex and to sinter the porous glass material. To achieve homogeneous distribution of erbium ions in the glass matrix the fact that the presented method utilizes two advantages: large molecules of the erbium complexes are spread in regularly located micro or nano pores of the glass. The synthesized erbium complexes should fulfill following criteria: (a) they should have large ligands (to substantially lower or even to avoid the risk of the RE clustering) with the number of donor oxygen atoms kept as low as possible (to avoid presence of the OH groups, which would shorten some of the Er^{3+} excited states lifetimes) and (b) they should allow for synthesizing in non-aqueous solutions (for the same reason as above). Moreover, the complexes should be decomposable by heating without leaving any unwonted residues.

Synthesis and properties of RE complexes were broadly studied in last decades. Syntheses of several RE complexes with 1,10-phenantroline were reported [2–4]. Synthesis of RE complex with ethylendiamine was carried out in anhydrous acetonitrile [5] as well as anhydrous tetrachlormethane [4]. Several complexes of 2,2′-dipyridile ligands were successfully synthesized in anhydrous ethanol [6]. Syntheses of 8-hydroxyquinoline complexes were reported mainly in aqueous solutions [7,8].

2. Experiments and measurements

Erbium complexes with 2,2′-dipyridyle, 1,10-phenantroline, 8-hydroxyquinoline and ethylendiamine ligands were prepared in anhydrous ethanol or isopropanol. Erbium was obtained as their oxide of 99.9% purity from Alchimica (Czech Republic). 2,2′-dipyridyl, 1,10-phenantrolin, 1,2-ethylendiamin, 8-hydroxyquinoline, and other chemicals were obtained in analytical grade from Penta (Czech Republic) and used without further purification.

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0022-3697/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jpcs.2007.01.003

Analytical grade anhydrous ethanol was obtained from Aldrich and used without further purification.

Sorption of Er complexes was performed on porous glass substrates from saturated isopropanol solution. Sorbet substrates were heated for several hours at 600 °C and then the temperature was slowly increased to 1100 °C. Temperature stability of the complexes was investigated by thermogravimetric analysis (TGA) on commercial apparatus Redcrost TG-750. The range of TGA measurements were from room temperature up to 850 °C. All TGA measurements were carried out in air. Chemical composition was estimated by elementary analysis on ELEMENTAR VARIO L3. The concentration of C, N, H and S were determined. Photoluminescence (PL) spectra were measured in the range of 1440–1650 nm with 0.5 nm steps. The semiconductor laser POL 4300 with pumping wavelength 980 nm and power density $5\,\mathrm{W\,cm^{-2}}$ was used for excitation. All measurements were carried out at room temperature. FT-IR spectroscopy was performed on commercial apparatus Nicolet 740. The potassium bromide disk technique was used for recording of the FT-IR spectra. We investigated solubility of prepared complexes in common organic solvents. Erbium nitrate was prepared by dissolving of erbium oxide in diluted nitric acid. Solution of erbium nitrate was evaporated until crystallization starts and then cools down. Crystals of erbium nitrate pentahydrate were filtered out. Erbium chloride hexahydrate was prepared in the same way.

Trinitrato-bis-(2,2′-dipyridyl) erbium (III): A solution of erbium nitrate pentahydrate (2.25 g, 5.1 mmol) in 100 ml isopropanol was treated with a solution of 2,2′-dipyridyl (2.04 g, 13.1 mmol) in 100 ml of isopropanol. Formation of insoluble complex occurred after mixing of these two solutions. The mixture was allowed to stay for 24 h and the insoluble complex was filtered out. The crystalline product was dried over P_4O_{10}. The yield was 95%. Trinitrato-bis-(1,10-phenantrolin) erbium (III): A solution of erbium nitrate pentahydrate (1.20 g, 2.7 mmol) in 100 ml isopropanol was treated with a solution of 1,10-phenantroline monohydrate (1.12 g, 6.0 mmol) in 100 ml of isopropanol. The formation of crystalline compound occurred immediately. The mixture was allowed to stay for 24 h and then the insoluble complex was filtered out. The crystalline product was dried over P_4O_{10}. The yield was 94%. Tricetato-2, 2′-bipyridyl erbium (III): A boiling solution of erbium nitrate pentahydrate (1.40 g, 3.2 mmol) in 10 ml of ethanol was treated with boiling solution of sodium acetate trihydrate (1.40 g, 10.3 mmol) in 50 ml of ethanol. The mixture was cooled down and insoluble sodium nitrate was filtered out. Filtrated solution was slowly added to a solution of 2,2′-dipyridyl (0.49 g, 3.1 mmol) in 10 ml of ethanol. The mixture was allowed to stay for 24 h and the insoluble complex was filtered out. The crystalline product was dried over P_4O_{10}. The yield was 71%. Triacetato-1,10-phenantrolin erbium (III): A boiling solution of erbium nitrate pentahydrate (1.40 g, 3.2 mmol) in 10 ml of ethanol was treated with boiling solution of sodium acetate trihydrate (1.40 g, 10.3 mmol) in 50 ml of ethanol. The mixture was cooled down and insoluble sodium nitrate was filtered out. Filtrated solution was slowly added to a solution of 1,10-phenantroline monohydrate (0.56 g, 2.8 mmol) in 20 ml of ethanol. The mixture was allowed to stay for 24 h and the insoluble complex was filtered out. The crystalline product was dried over P_4O_{10}. The yield was 70%. Trithiocyanato-tris-(1,10-phenantrolin) erbium (III): A solution of erbium chloride hexahydrate (2.45 g, 6.4 mmol) in 50 ml ethanol was treated with potassium thiocyanate (2.80 g, 28.8 mmol) in 150 ml ethanol. The mixture was cooled down to 0 °C and precipitated potassium chloride was filtered out. 1,10-phenantroline monohydrate (5.10 g, 25.7 mmol) in 100 ml of ethanol was added to filtrated solution. The mixture was allowed to stay for 24 h and precipitated crystals were filtered out. The crystalline product was dried over P_4O_{10}. The yield was 75%. Trithiocyanato-tris-(2,2′-dipyridyl) erbium (III): A solution of erbium chloride hexahydrate (2.45 g, 6.4 mmol) in 50 ml ethanol was treated with potassium thiocyanate (2.80 g, 28.8 mmol) in 150 ml ethanol. The mixture was cooled down to 0 °C and precipitated potassium chloride was filtered out. 2,2′-dipyridyl (3.50 g, 22.4 mmol) in 60 ml of ethanol was added to filtrated solution. The mixture was allowed to stay for 24 h and precipitated crystals were filtered out. The crystalline product was dried over P_4O_{10}. The yield was 71%. Trinitrato-tetrakis-(8-hydroxyquinoline) erbium (III): Erbium nitrate pentahydrate (1.33 g, 3.0 mmol) was dissolved in 600 ml of water and 8-hydroxyquinoline (1.32 g, 13.6 mmol) was dissolved in 130 ml of ethanol. Erbium nitrate solution was heated to 70 °C and alkalized by ammonia on pH ~9. The solution of 8-hydroxyquinoline was dropwise added to this vigorously stirred solution of erbium nitrate. This solution was allowed to stay for 5 h and then the precipitated complex was filtered out. Product was dried for 3 h at 110 °C. The yield was 68%. Trinitrato-tetrakis-ethylendiamin erbium (III): A solution of erbium nitrate pentahydrate (2.21 g, 5.0 mmol) in 10 ml ethanol was treated with 1,2-ethylendiamin (3.01 g, 50 mmol) in 100 ml of tetrachlormethane. The immediately formed precipitate was filtered out and washed with tetrachlormethane. This light pink crystalline solid is extremely hygroscopic. The yield was 66%.

3. Results and discussion

Syntheses of the erbium complexes are necessary to carry out in anhydrous conditions. Ethylendiamine complex of erbium is very hygroscopic and fast hydrolysis occurs in air [9]. This synthesis must be made in non-alcoholic solution because alcohol acts here as a ligand, too [9]. It is important to know the temperature stability of complexes for preparation of erbium doped glass from porous glass substrates. Erbium complexes of 1,10-phenantroline and 2,2′-dipyridyl with nitrate, and thiocyanate anions were well crystalline and thermal stable. Thermal stability and decomposition temperature of the complexes were investigated by TGA. Temperatures of complexes decomposition are summarized in Table 1. Two most stable complexes contain thiocyanate anions; decomposition is finished at temperature range 600–700 °C. Decomposition temperature range of 8-hydroxyquinoline complex is very broad, it starts at about 150 °C and is over 600 °C.

Chemical composition of prepared complexes was investigated by elementary analysis and concentrations of C, H, N and S were determined. The obtained values are in good agreement for complexes of erbium with nitrate anion. Some small disagreement between the observed and calculated value was detected for the complexes with acetate and thiocyanate anions. It is done by uncompleted exchanging of these anions with starting salts, chloride for thiocyanate and nitrate for acetate. Determination of exact composition for ethylandiamine complex was problematic due to hygroscopic behavior of this substance. The 8-hydroxyquinoline complex still contained traces of water which are difficult to eliminate without its decomposition. Table 2 gives the results from elementary analysis and their comparison with theoretical values on. Solubility of complexes was tested in several commonly used organic solvents. They are insoluble in aliphatic hydrocarbons and ethers, slightly soluble in alcohols and aromatic hydrocarbons, like toluene and xylene, and halogen derivates of hydrocarbons. The highest solubility was observed in dimethylformamide.

A broad absorption band about 3400 cm^{-1} from water was observed in all FT-IR-spectra. We observed strong absorption band on 2063 cm^{-1} from stretching of thicayanate group in thiocyanate complexes [6]. Splitting of this absorption band indicates coordinated thiocyanate group [4]. Strong absorption band at 1385 cm^{-1} indicates ionic nitrate group in nitrate complexes. We although observed absorption bands in region about 1400 and 1600 cm^{-1} which are mainly attributed to C=N and C=C stretching vibration frequencies [10]. In the case of 8-hydroxyquinoline nitrate complex we observed absorption band of ionic nitrate group at 1383 cm^{-1} and also absorption bands of coordinated nitrate group at 1319, 1466 and 1498 cm^{-1}. Absorption bands in region of 1100 cm^{-1} are related to the C–O stretching vibration energy and are largely affected with the ionic potential of the cation [8,11]. Absorption bands of C=N and C=C stretching vibration were clearly observed on this complex. In the acetate complexes, we observed strong split absorption bands of OCO unsymmetrical strain vibration in the range from 1550 to 1600 cm^{-1}. OCO symmetrical strain vibration frequency was about 1450 cm^{-1} [2].

PL are shown in Fig. 1. Maximum intensity was at 1533 nm. Higher PL intensity was observed for fabricated optical layer using complexes with 1,10-phenantroline and 8-hydroxyquinoline ligands. The sample fabricated by soaking with triacetato-1,10-phenantrolin erbium(III) exhibited the highest PL intensity. The value of FWHM (full width at half maximum) at 1533 nm is above 50 nm.

Table 1
Temperature stability of Er complexes

Complex	Starting temperature of decomposition (°C)	The final temperature of decomposition (°C)
[(2,2′-dipy)$_2$Er](NO$_3$)$_3$	200	470
[(1,10-phen)$_2$Er](NO$_3$)$_3$	300	550
[(2,2′-dipy)Er](ac)$_3$	200	500
[(8-hq)$_4$Er](NO$_3$)$_3$	150	650
[(1,10-phen)Er](ac)$_3$	200	450
[(1,10-phen)$_3$Er](SCN)$_3$	200	700
[(2,2′-dipy)$_3$Er](SCN)$_3$	220	600

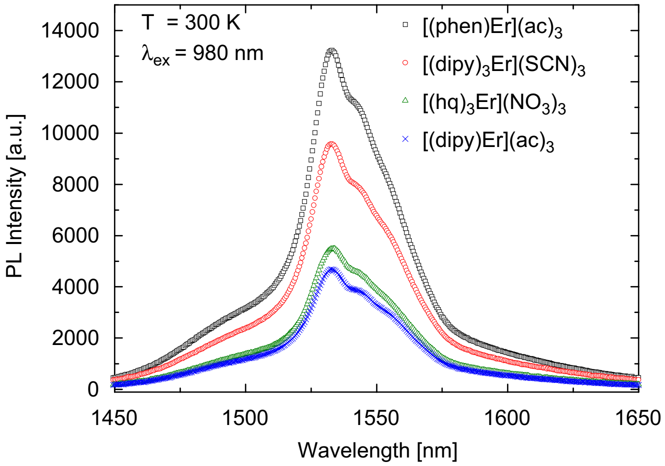

Fig. 1. Photoluminescence of erbium doped glass substrates.

Table 2
Results of elementary analysis

Complex	% N Theor.	% N Exp.	% C Theor.	% C Exp.	% H Theor.	% H Exp.	% S Theor.	% S Exp.
[(2,2′-dipy)$_2$Er](NO$_3$)$_3$	14.73	14.83	36.09	35.99	2.420	2.434	0.00	0.00
[(1,10-phen)$_2$Er](NO$_3$)$_3$	13.74	13.71	40.39	40.02	2.260	2.314	0.00	0.00
[(2,2′-dipy)Er](ac)$_3$	5.60	6.084	38.39	35.20	3.420	2.982	0.00	0.00
[(8-hq)$_4$Er](NO$_3$)$_3$	6.64	6.93	51.24	51.72	3.344	3.061	0.00	0.00
[(1,10-phen)Er](ac)$_3$	5.34	5.50	41.21	40.55	3.266	3.134	0.00	0.00
[(en)$_4$Er](NO$_3$)$_3$	25.95	23.60	16.19	14.74	5.430	5.273	0.00	0.00
[(1,10-phen)$_3$Er](SCN)$_3$	14.29	14.17	53.10	50.28	2.742	2.869	10.90	10.75
[(2,2′-dipy)$_3$Er](SCN)$_3$	15.56	13.40	48.93	38.23	2.986	2.855	11.87	12.89

4. Conclusion

A series of erbium complexes with heterocyclic ligands were prepared. These complexes were characterized by FT-IR spectroscopy and elementary analysis. Decomposition was studied by thermogravimetric analysis. Glass substrates doped by erbium complex were studied by photoluminescence measurements with pumping wavelength of 980 nm. The best result was obtained for triacetato-1, 10-phenantrolin erbium(III). The sample fabricated by soaking with triacetato-1,10-phenantrolin erbium(III) had the value of FWHM at 1533 nm above 50 nm, which is sufficient for practical utilization.

Acknowledgment

The research has been supported by the GACR project 106/05/0706 and 102/03/D041. We thank Alchimica Company for supplying the erbium oxide.

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