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Samarium as an activator in cerium dioxide

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A samarium-activated cerium dioxide with f-f luminescence under UV excitation is prepared using lithium as a co-activator and hydroxide, oxalate and nitrate of Ce(III) as precursors. The activator ions are introduced in the precursors by co-precipitation or co-crystallization respectively. Incorporation of Sm^{3+} ions in CeO_2 is obtained during thermal decomposition and simultaneous Ce(III) to Ce(IV) oxidation by heating at 800-1100 ^{o}C, after addition of lithium nitrate. The results obtained show that co-doping with lithium leads to a considerably higher efficiency of the Sm^{3+} luminescence in comparison with samples doped with samarium only. This could be explained by a lower concentration of oxygen vacancies, supposing that they act as quenching centers and that lithium ions might be located in interstitial lattice sites. Relatively strong f-f emission is observed in a wide range of wavelengths between 220 and 390 nm. The decay of the Sm^{3+} luminescence excited with the third harmonic generation pulses of a Nd-YAG laser (335 nm) is influenced to some extent by introduction of Li^+ ions. On the contrary, the luminescence spectrum does not depend on the presence of lithium.

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Keywords: Luminescence, Cerium dioxide, Samarium, Decay, Lithium co-dopant

1. Introduction

In recent years, increasing interest has been focused on cerium dioxide as an inorganic material used in fuel cells, non-linear resistors, sensor systems for the determination of CO, NO and CO_2 in exhaust gases, and as a catalyst [1-3]. Its luminescent properties have been insufficiently investigated, mainly in relation to the identification and semi-quantitative determination of rare earth elements [4,5]. In the present paper, the preparation and luminescent properties of Sm-activated CeO_2 are reported, using Ce(III) compounds as precursors and Li as a co-dopant, thus improving the efficiency of the Sm f-f - luminescence.

2. Experimental

Samarium ions were introduced in the precursors by co-precipitation with cerium (III) hydroxide, carbonate or oxalate, or by co-crystallization when using Ce(III) nitrate and formate. After addition of the $LiNO_3$ solution and drying, conversion to CeO_2 was carried out by a two-step thermal treatment in air: first at 500 ^{o}C for 1 h, and then at 800-1000 ^{o}C for one more hour.

Luminescence spectra were registered and intensity measurements were performed under excitation with the 365 nm Hg-line (Fig. 1). For higher resolution spectra and decay studies, excitation with the third harmonic pulses of a Nd- YAG laser was applied (Figs. 2, 3, 4). Excitation spectra were obtained using a deuterium lamp and lumogen red for spectra correction.

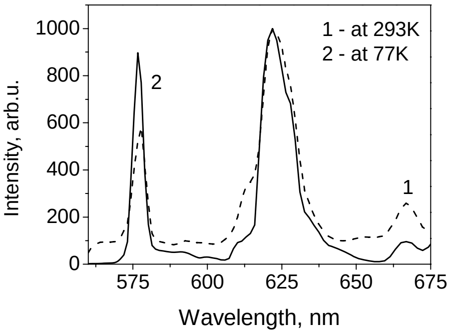

Fig. 1. Luminescence spectra of CeO_2:Sm,Li (excited with the 365 nm Hg line).

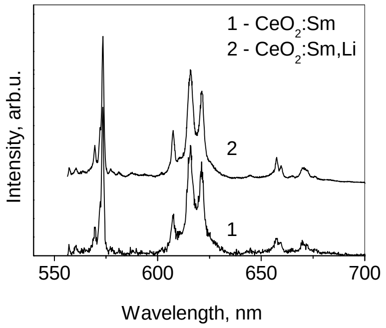

Fig. 2. Luminescence spectra of CeO_2:Sm and CeO_2:Sm,Li, at a higher resolution

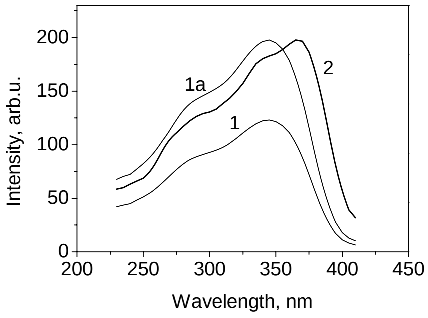

Fig. 3. Excitation spectra: 1 - CeO_2:Sm, 2 - CeO_2:Sm/Li, 1a - CeO_2:Sm normalized

3. Discussion

The experimental data presented in Tables 1, 2 and 3 shows the influence of the precursor type, of the introduced amounts of Sm and Li, and of the preparation temperature on luminescence efficiency. It is seen (Table 1) that preference should be given to cerium (III) oxalate or carbonate as precursors. The best results were achieved when 1 mol % Sm and 3 mol % Li were added (Table 2) and their incorporation was carried out during the decomposition and oxidation to CeO_2 by heating for 1 h in air at 850-900 °C (Table 3).

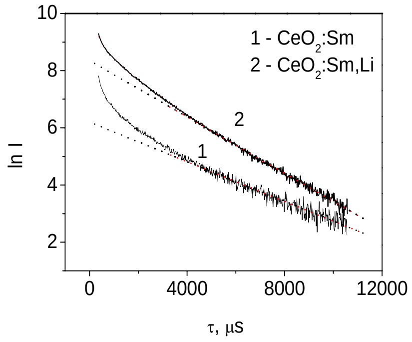

Fig. 4. Luminescence decay of the emission at 615.7 nm (excitation with the third harmonic pulses of a Nd:YAG laser).

Table 1. Influence of the precursor kind (I - intensity of f-f emission,manifold 600-630 nm ($^4G_{5/2} \rightarrow {}^6H_{7/2}$))

Cerium(III) compound	I, arb. units	
	1 mol % Sm	1 mol % Sm, 3 mol % Li
oxalate	2050	7500
carbonate	1750	5600
hydroxide	850	
nitrate	590	
formate	550	

Table 2. Dependence of the intensity on the concentration of Sm, Li and Na

Sm, mol%	I, a.u.	Li (or Na), mol % (1 mol % Sm)	I, a.u.
0,1	1100	1 (Li)	4600
0,3	1150	3 (Li)	7500
1,0	1460	6 (Li)	7000
3,0	950	3 (Na)	2900

Table 3. Dependence of the intensity on the preparation temperature (1 mol % Sm, 3 mol % Li)

Temperature, °C	I, a. u.
800	5700
850	7500
900	6900
1000	6250
1100	5500

It can be seen in Table 2 that the intensity of the emission after introducing Li^+ into CeO_2:Sm increases substantially. The samples doped with bigger amounts of Li (6%) have spectra and intensities close to these of CeO_2:Sm with 3% Li. This fact, together with the absence of differences in the X-rayograms of these luminophores, shows that no luminophore based on lithium cerate was obtained, neither has a phase different from CeO_2 been formed.

According to the results shown in Table 2, co-activation by the addition of $NaNO_3$ instead of $LiNO_3$ leads to a much lower enhancement of the Sm^{3+} emission. Probably Li^+ whose radius is substantially smaller that that of Na^+, populates interstitial positions, compensating in this way the effective negative charge of the samarium ions in the cation centers of CeO_2. Thus, the favourable influence of Li^+ could be connected with suppression of the formation of oxygen vacancies, which should be generated when Sm^{3+} incorporates in CeO_2 in the absence of Li^+. Therefore the assumption is made that the lithium salt does not play the role of a flux only, but is also a source of Li^+ ions which participate in the formation of the activator surrounding in CeO_2:Sm,Li. Assuming that oxygen vacancies V_o act as quenching centres for Sm^{3+} luminescence and that Li^+ ions may be located in interstitial lattice sites, the efficiency increase due to lithium could be explained by Li_2O dissolution in the CeO_2 matrix: thus, a decrease in the V_o concentration may be expected according to the equation:

$$Li_2O + V_o^x \rightarrow 2Li_i + O_o^x$$

where Li_i are interstitial Li^+ ions.

Moreover, the enhanced solubility of Sm_2O_3 in CeO_2 in the presence of $LiNO_3$ (i.e. Li_2O) could contribute to the stronger Sm emission of CeO_2:Sm,Li, as compared to that of CeO_2:Sm and CeO_2:Sm,Na. In the latter case, the interstitial sites should be occupied to a lower extent by Na^+ ions than by Li^+ ions, due to the considerably greater size of the former.

The luminescence spectrum of CeO_2:Sm, Li obtained under excitation at 293 K is the same as that of CeO_2:Sm, and this holds also at 77 K (Fig. 1). A coincidence is found even in the details, when comparing the intensities and spectral positions of the respective lines at higher resolution (Nd-YAG laser excitation (Fig. 2)). Therefore, it seems reasonable to conclude that V_o and Li_i are not the nearest neighbours of Sm^{3+} in the luminescence centres. Otherwise, they would affect the spectral distribution of the Sm f-f luminescence. It should be mentioned that the luminescence spectra registered at high resolution show a multiband structure. Taking into account that the crystal lattice of CeO_2 has a high degree of symmetry (fluorite type, space group O_h^5), these complicated spectra give reason to assume that more than one kind of emitting lanthanoide center was formed, including ones with decreased symmetry.

The excitation spectra of CeO_2:Sm and CeO_2:Sm,Li provide evidence of a relatively strong emission in a wide range of wavelengths of the exciting light, between 230 and 390 nm (Fig. 3). In addition to the two excitation bands at 280 and 350 nm in CeO_2:Sm, another band appears at about 380 nm in CeO_2:Sm,Li.

The decay of the Sm^{3+} luminescence excited with 355 nm pulses and measured at 573,3 nm ($^4G_{5/2}\rightarrow{}^6H_{5/2}$ transition) is also influenced to some extent by the introduction of Li, as seen in Fig. 4. The deviation from the exponential law is greater in the absence of Li, and the slope differences give lifetime values of 2.9 ms for CeO_2:Sm and of 2.0 ms for CeO_2:Sm,Li.

The results concerning the excitation spectra and decay, compared to those for the emission spectra, suggest that Li^+ ions which are not situated next to the Sm^{3+} ions are involved in the luminescence process in CeO_2:Sm,Li, since they influence to some extent the excitation spectra, the emission decay and the dependence of the f-f luminescence on temperature, but do not affect the spectral distribution of the emission at all.

According to the results of preliminary investigations, luminescence due to f-f transitions may also be observed in CeO_2 doped with europium and erbium, under conditions similar to those described above.

4. Conclusions

Lithium salt, used as co-activator, introduces Li^+ ions in CeO_2:Sm which affect the activator's surroundings and increases the Sm emission. Thus, a considerably higher efficiency of the Sm luminescence is observed for DeO_2:Sm,Li in comparison to CeO_2:Sm.

Li^+ ions affect the decay of the Sm luminescence, but do not affect the structure of the luminescence spectrum itself. Co-doping causes a new spectral band in the CeO_2:Sm,Li excitation spectrum.

A possible mechanism for the increase of the Sm f-f luminescence is a decrease in the concentration of oxygen vacancies, since Li^+ ions might be located in interstitial lattice sites. Oxygen vacancies probably act as quenching centres.

Some preliminary results show that CeO_2 specimens activated with Er or Eu under similar conditions also exhibit considerable f-f luminescence.

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References

[1] M. Toshiyki, Y. Hiroshi, J. Am. Ceram. Soc. **79**, 3309 (1996).
[2] M. Teuvo, J. Ahola, Appl. Catal. B **12**, 287 (1997).
[3] W. Huang, M. Greenblatt, Solid State Ionics **100**, 29 (1977).
[4] S. Bel'tyukova, G. Balamtsarashvili, Ukr. Khim. Zh. **62**, 45 (1996).
[5] N. Poluectov, Ural. Conf. Spectrosk. **7h**, 19 (1971).

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