Ce1 and Ce2 emission centers in $Lu_{2-2x}Gg_{2x}SiO_5$ solid solutions

S. Neicheva[a], A. Gektin[a], O. Sidletskiy[a], A. Belsky[d]

[a] Institute for Scintillation Materials, 60 Lenin Avenue, 61001 Kharkov, Ukraine
[d] Laboratoire de Physico-Chimie des Materiaux Luminescents, UMR 5620 CNRS, Universite Claude Bernard Lyon 1, 69622 Villeurbanne Cedex, France

3rd IWASOM Gdansk, 2011

ERA–WIDE

SUCCESS

Introduction

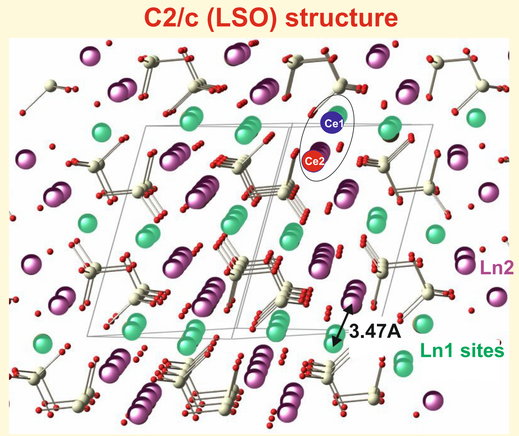
LSO and GSO crystals are well studied and used as scintillators. This study is focused on $Lu_{2x}Gd_{2-2x}SiO_5$ (LGSO) crystals in the range from Gd_2SiO_5 (GSO) to Lu_2SiO_5 (LSO).

On the one hand $Lu_{2x}Gd_{2-2x}SiO_5$ solid solutions have been investigated for the purpose to improve characteristics and eliminate disadvantages of initial hosts.

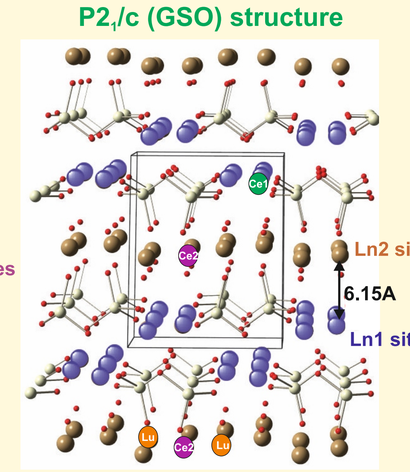
On the other hand $Lu_{2x}Gd_{2-2x}SiO_5$ has the continuous solid solution series with different type of structures depending on Lu/Gd ratio. Inclusion of large Gd ions into LSO lattice leads to growth of elementary cell volume and then the polymorph transition between $P2_1/c$ and C2/c symmetry group occurs at 80% Gd.

In both cases Ce^{3+} ions occupy Ln1 and Ln2 (Ln= Lu or Gd) non-equivalent positions with different oxygen coordination. Ce^{3+} as well as Gd^{3+} ions preferably occupy sites with larger volume: 7-fold sites in LSO type crystals and 9-fold sites in GSO type crystals. In LSO the number of Ce1 centers is~ 95% , the number of Ce2 centers is~ 5%. In GSO the number of Ce2 centers reaches ~ 44%.

C2/c (LSO) structure



$P2_1/c$ (GSO) structure



The aim of present work is the study of the influence of solid solution structure on Ce luminescence.

Evolution of excitation and emission spectra depending on Gd/Lu ratio

C2/c (LSO)- structure

Ce1

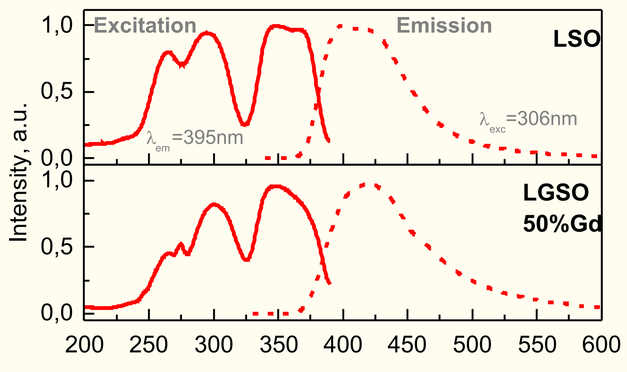


Fig. 1

Ce2

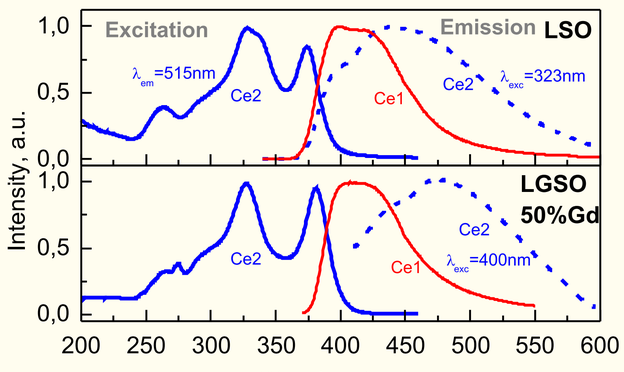


Fig. 2

$P2_1/c$ (GSO) - structure

Ce1

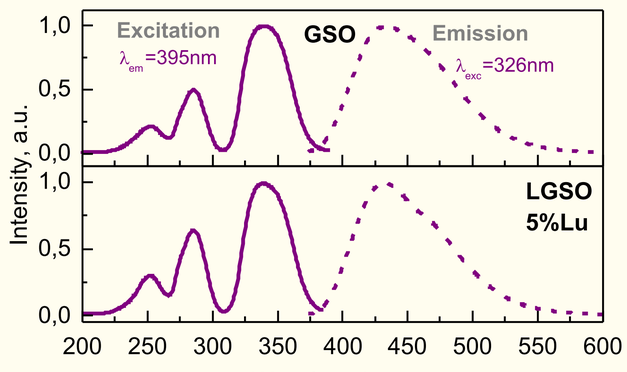


Fig. 3

Ce2

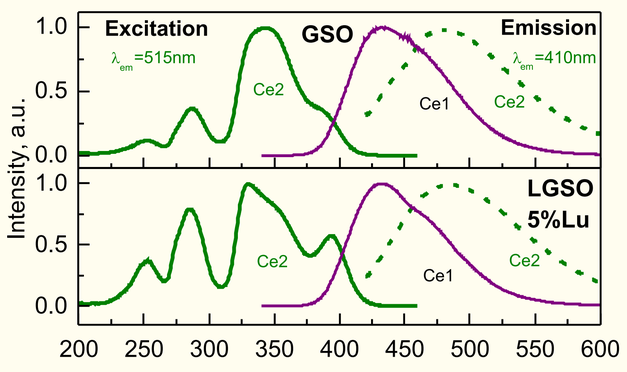


Fig. 4

Difference of Ce1 centers decay times in LSO and GSO at T=295K

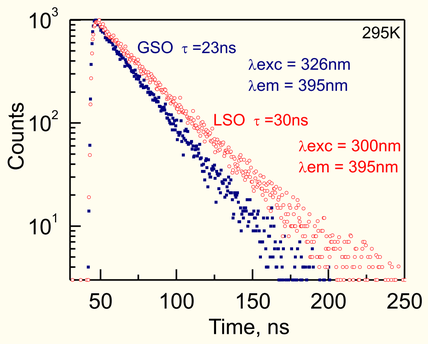


Fig. 5

- Decay time of GSO is 23ns whereas in LSO decay is delayed to 30ns at intracenter excitation. (these values are close to data in [2] t=22ns for GSO and [3] t=32ns for LSO)
- Excitation spectra of LSO and GSO are similar. Zero phonon line position in both cases coincides (~380nm). It points to similar 5d levels splitting of Ce1 in LSO and GSO, so the lowest 5d states of Ce1 are the same. It is logical to suppose that life times have to be approximately equal in the both cases.
- One of the possible causes of delayed decay time in LSO is reabsorption of Ce1 luminescence.
- In LSO excitation and emission spectra substantially overlap in contrast to GSO (Fig. 1 and 3). Therefore one can assume that reabsorption of Ce luminescence is negligible in GSO but significant in LSO.

Non-exponential kinetics of Ce1 luminescence in solid solutions with C2/c structure

Ce1 (C2/c structure)

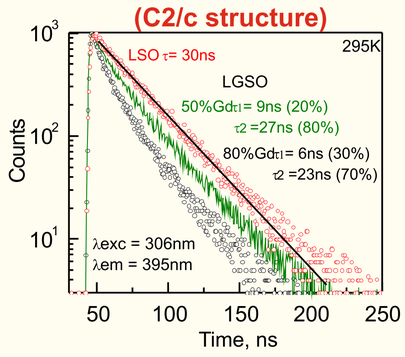


Fig. 6

- It has been found that kinetics of Ce1 emission in solid solutions with C2/c structure is non-exponential. Time profiles are characteristic for radiationless excitation' transfer (dipole-dipole) from emission centers to defects.

ratio of Ce1 and Ce2 in X-luminescence spectra

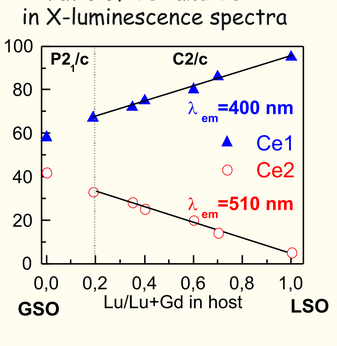
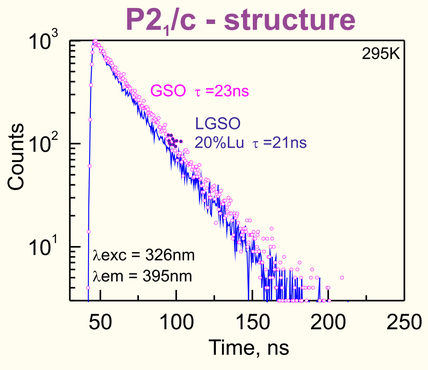


Fig. 7

- Increasing of Gd concentration results in Ce2 band intensity increasing in luminescence spectra.

Ce1 $P2_1/c$ - structure



- Significant overlapping of Ce2 excitation and Ce1 luminescence bands is observed. One can suppose that reabsorption of Ce1 luminescence by Ce2 centers occurs.

However, in crystals with high Gd concentration (P21/c structure) the number of Ce2 centers is high, but Ce1 emission kinetics is exponential.

It should be noted that relative position of Ce1 and Ce2 centers are different in P21/c and C2/c structures. In the case of P21/c structure Ln1 and Ln2 sites are situated in different layers with the lowest distance 6.15Å between them.

In C2/c structure the lowest distance between Ln1 and Ln2 positions is 3.47Å, so Ce1 and Ce2 centers are close and dipole-dipole excitation' transfer is possible.

Temperature dependence of Ce2 emission decay in crystals with $P2_1/c$ structure

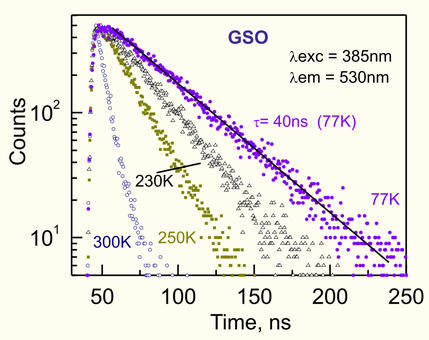


Fig. 9

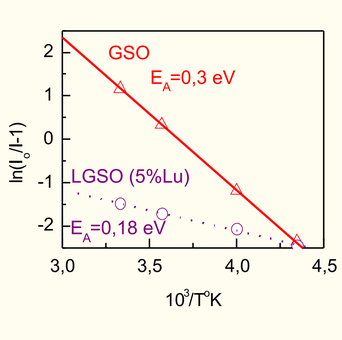
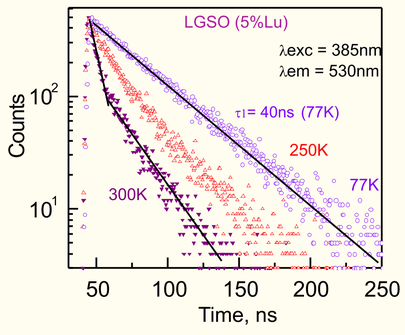


Fig. 10

In GSO Ce2 luminescence kinetics is monoexponential with t=6ns at 300K. Temperature decreasing results in decay time increase. Time profiles remain monoexponential. It points to temperature quenching of luminescence. Our results confirmed data in [2].



In solid solutions with P21/c structure kinetics of Ce2 luminescence has two components at 300K. At 77K time profile is monoexponential as well as in GSO.

In solid solutions with P21/c structure Lu3+ ions preferably occupies 7-fold (Ln2) sites . Therefore Lu ions influence on Ce2 centers only. It is confirmed by excitation and emission spectra Fig 4. Spectral and kinetic characteristics of Ce1 centers don't depend on Lu occurrence in contrast to Ce2 centers.

Shift of excitation bands' positions of Ce2 centers relative to GSO points to changes in surroundings of Ce2 centers at Lu inclusion in lattice.

T,K	τ, ns (GSO)	τ, ns (LGSO 5%Lu)
300	4ns	4ns + 21ns (67%)
280	9ns	6ns + 26ns (66%)
250	19ns	9ns + 30ns (77%)
230	30ns	10ns + 32ns (92%)
210	43	34ns
77	43ns	40ns

Whereas two component in kinetics are observed one can suppose that in LGSO ($P2_1/c$) a part of Ce2 centers is in surroungings of Gd ions but another part is situated near the Lu ions.

Summary

The influence of solid solutions structure on Ce luminescence is studied.

One of the possible causes of delayed decay time of Ce1 centers in LSO in contrast to GSO is reabsorption of Ce1 luminescence

In LGSO with C2/c structure dipole-dipole excitation' transfer from Ce1 to Ce2 centers is possible.

In GSO the temperature quenching of Ce2 luminescence is observed. Lu ions influence on Ce2 centers spectral and kinetic characteristics of LGSO with P21/c structure.

References

1. O. Sidletskiy et al., J. Cryst Growth, 312 (2010) 601
2. H. Suzuki et al., NIM A 320 (1992) 263
3. C. Melcher et al. IEEE (2011) in press

This work is supported by 7th FP INCO.2010-6.1 grant agreement No 266531 (project acronym SUCCESS).