Mechanisms of light yield improvement in Ce-doped LGSO mixed oxide scintillator

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Outline

- ❑ Motivation of study. Light yield behaviour vs. host composition in Ce-doped mixed scintillators;

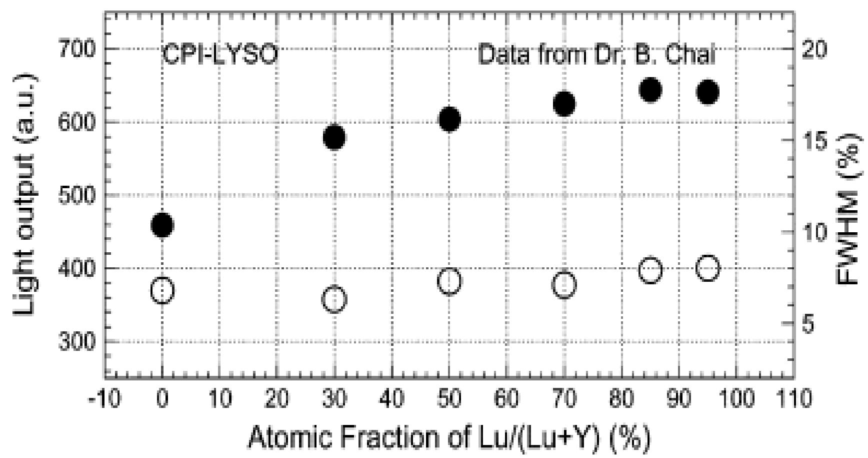
- ❑ Possible mechanisms of light yield improvement:
  -Energy structure engineering
  -Short-range separation in mixed crystal

- ❑ Summary. How to predict light yield behavior in mixed scintillators.

Scintillation characteristics of some Ce-doped oxides

Crystal	Density, g/cm3	Light yield, phot/MeV	Energy resolution, % (^{137}Cs, 662 KeV)	Decay time, ns (γ -exc.)	Afterglow, % (after 5 ms),
Gd_2SiO_5 (GSO)	6.7	8000-11000	9 – 11	50	0.02
Lu_2SiO_5 (LSO)	7.4	25000-30000	7.3 – 9.7	40	> 1
$Lu_2Si_2O_7$ (LPS)	6.2	26000	9.5	38	~0.02
$Y_3Al_5O_{12}$ (YAG)	4.55	24000	7.3	85 + slow	ND
$Lu_3Al_5O_{12}$ (LuAG)	6.7	12500	ND	44	ND
$YAlO_3$ (YAP)	5.35	21000	6.7	27	ND
$LuAlO_3$ (LuAP)	8.34	11000	14	16 + slow	ND

$Lu_{2x}Y_{2-2x}SiO_5:Ce$ (LYSO)



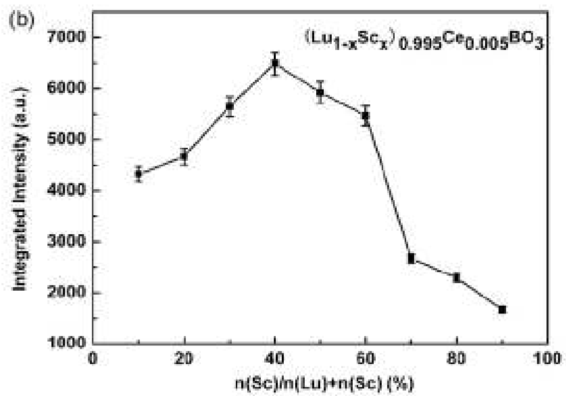
The light output (solid dots, left scale) and the energy resolution (open dots, right scale) as a function of the lutetium fraction in LYSO

[J. Chen et al.IEEE Trans. Nucl. Sci., 52, 2005) 3133]

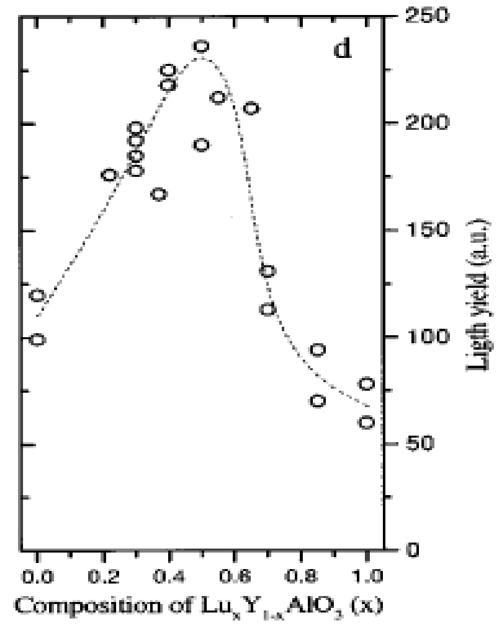
Tm (LSO) = 2150 °C
Tm (LYSO) = ~2000 °C

$Gd_{2x}Y_{2-2x}SiO_5:Ce$ – improvement of mechanical properties compared to GSO:Ce at $0.8<x<1$
[V. Bondar et al. Proc. of SCINT2005]

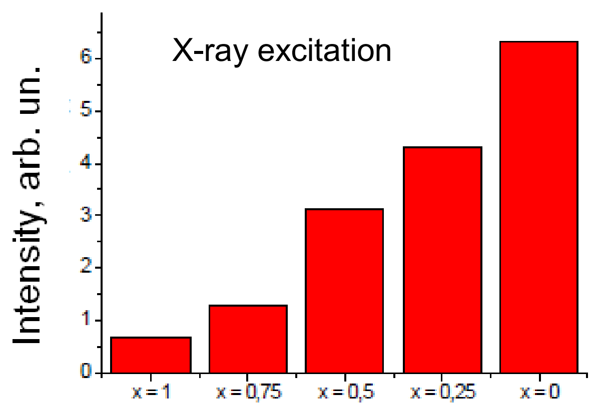
Some other examples of LY vs. component ratio



Y. Wu et al. / Journ Alloys Comp *509 (2011) 366–371*



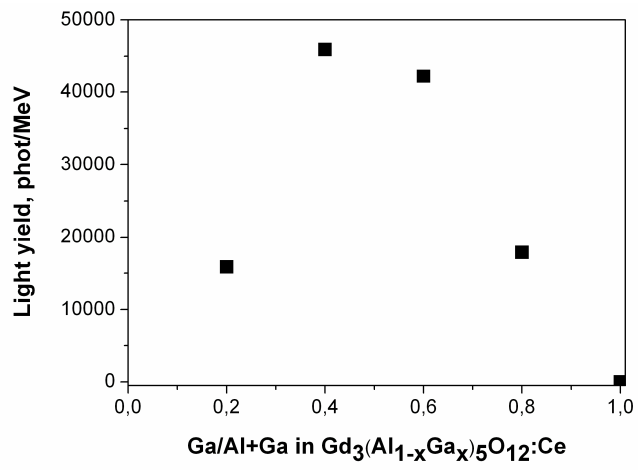
A.N. Belsky.
IEEE TNS 48 (2001) 1095



$Lu_xY_{1-x}BO_3$:Ce^{3+}(D. Spassky et al. ISMART-2012)

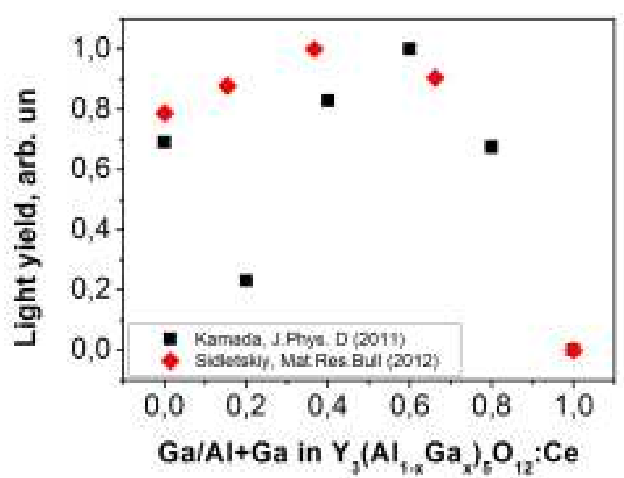
Besides these, increase of luminosity in:
$BaBr_{2-x}I_x$:Eu (G. Gundiah et al. / NIM A 652 (2011) 234)

Light yield vs. Ga fraction in Al-Ga substituted garnets



$Gd_3(Al_xGa_{1-x})_5O_{12}$:Ce (GAGG)

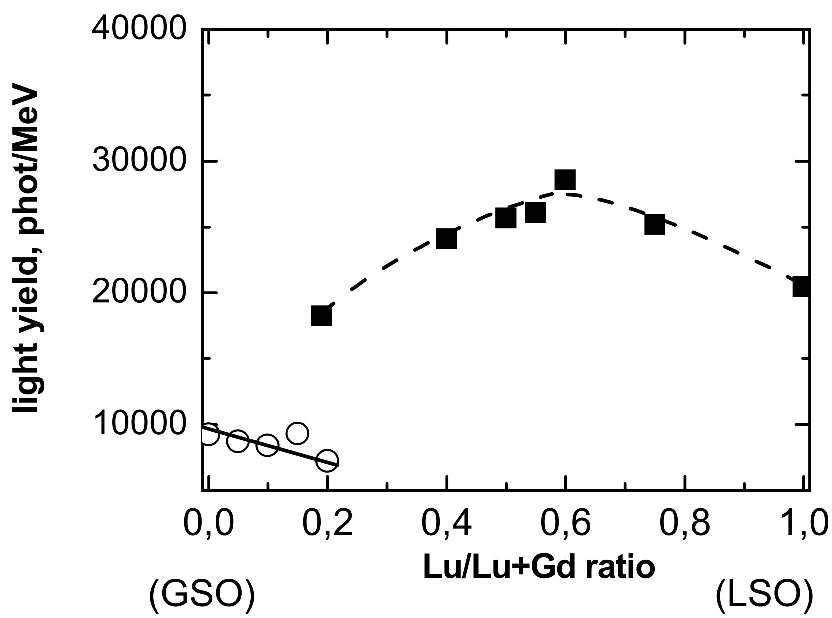
Kei Kamada, et al / Cryst. Growth Des. 11 (2011), 4484–4490.

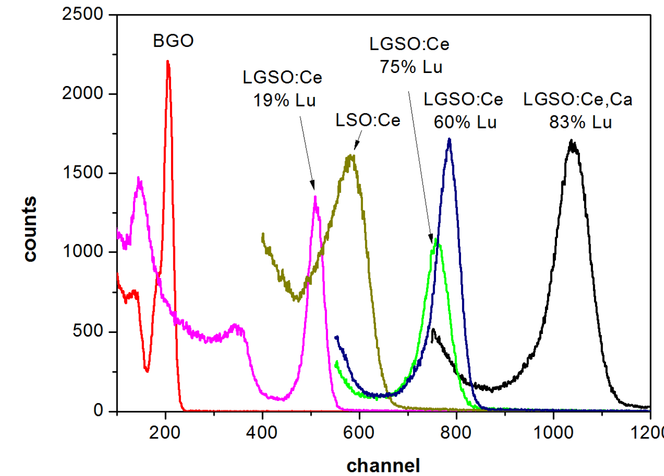


$Y_3(Al_xGa_{1-x})_5O_{12}$:Ce (YAGG)

'o-PD (K. Kamada et al. / J.Phys.D: Appl.Phys. **44** (2011) 104)
O. Sidletskiy et al. / Mater.Res.Bull. **47** (2012) 3249)

Scintillation characteristics of LGSO:Ce crystals





<u>In the optimal host composition range (30-70 % Lu)</u>

- ❑ Light yield 24000 – 29000 phot/MeV (33700 phot/MeV in Ca codoped crystal);
- ❑ Energy resolution (662 KeV) - 6.7 – 7.3 %

O. Sidletskiy, V. Bondar, B. Grinyov, et al. *J. Cryst Growth*, 312 (2010) 601
O.Sidletskiy, A. Belsky, A. Gektin, et al. *Crys Growth & Des*, 2012, 12, 441

Low light yield in LSO:Ce

1) Melcher, C. L.; Sweitzer, J. S. IEEE TNS, 1992, 39 (4), 502.
2) Dorenbos, P.; van Eijk, C. W. E.; Bos, A. J. J.; Melcher, C. L. J.Phys.: Condens. Matter 1994, 6, 41674180.
3) V. Jary, M. Nikl, E. Mihokova, et al IEEE TNS, 2012, 59(5) 2079

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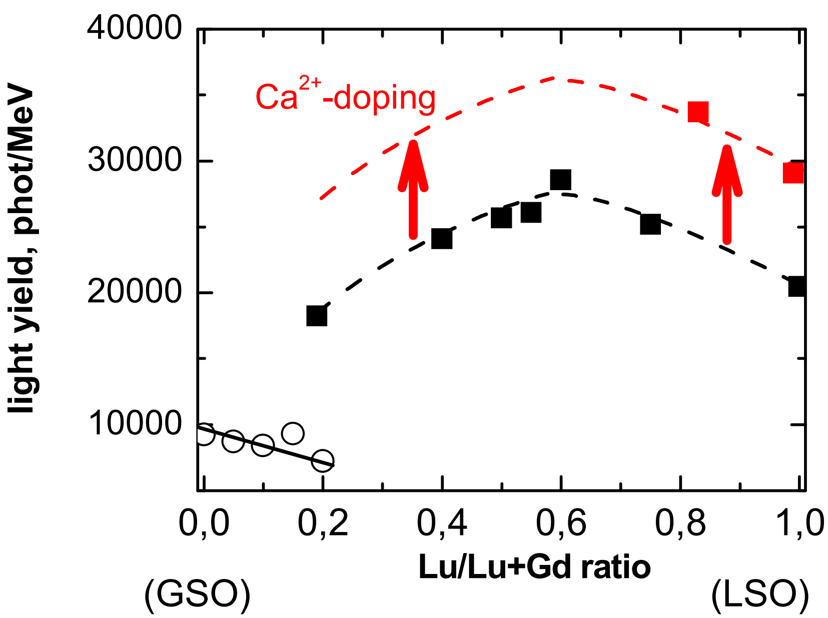

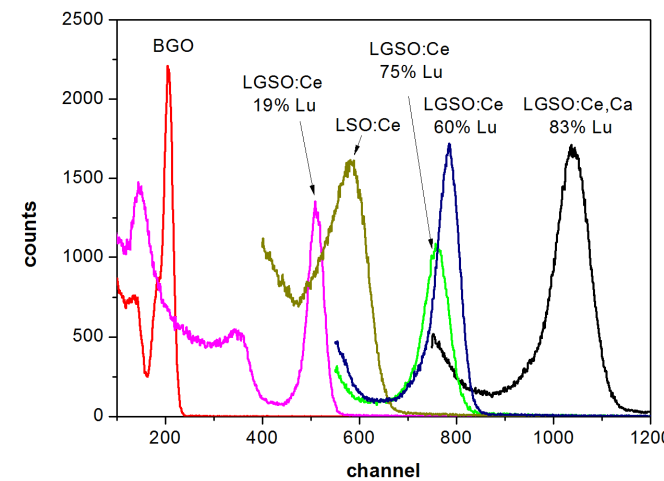

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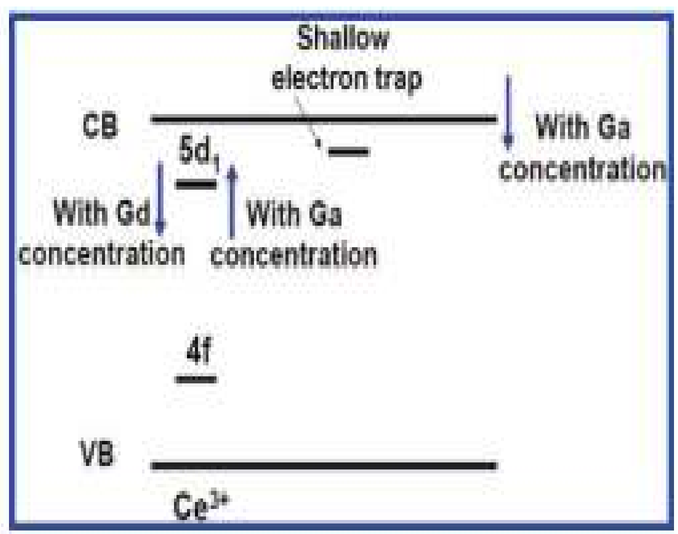
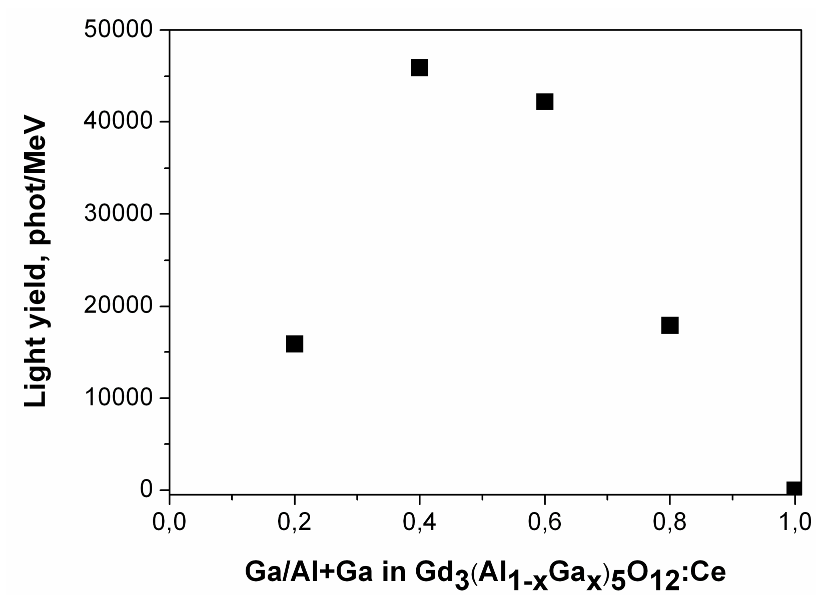
Energy structure engineering in rare-earth garnets $Lu_yGd_{1-y}RE_3(Al_xGa_{1-x})_5O_{12}$:Ce



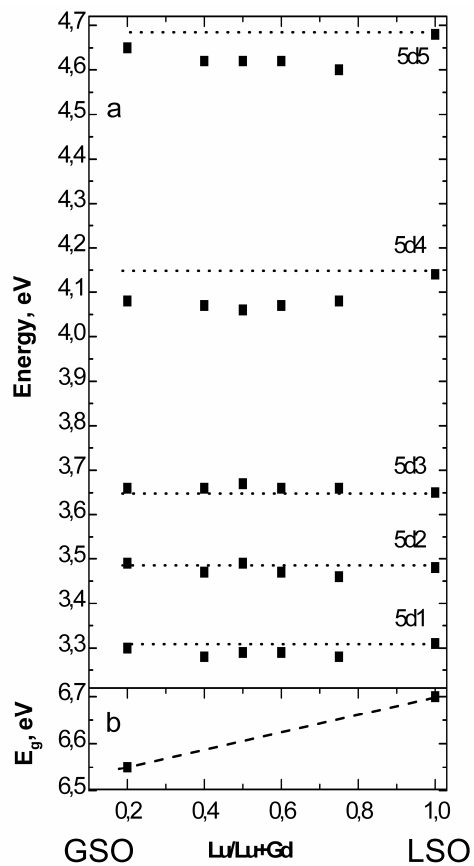
M. Fasoli et al. Phys. Rev. B 84, 081102(R) (2011)



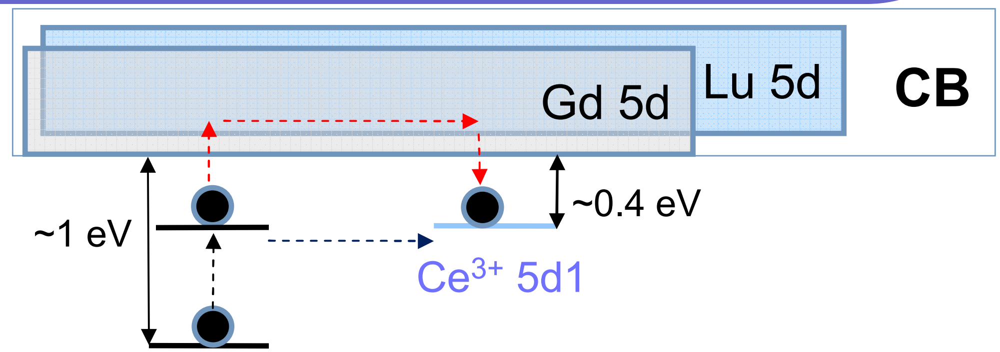
However,

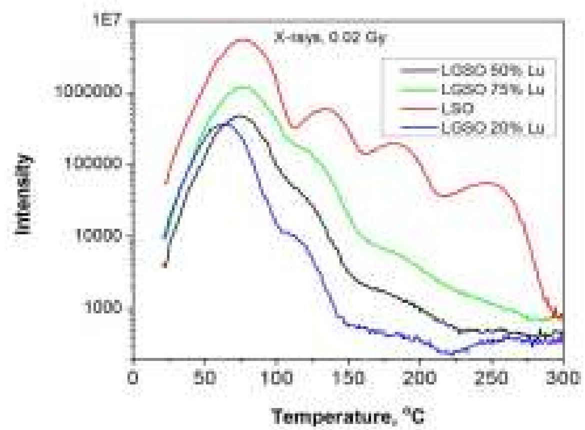
- Bangap change is not so large to call light yield increase by 2-3 times
- Not describes light yield improvement in some other mixed crystals

Energy structure of LGSO:Ce

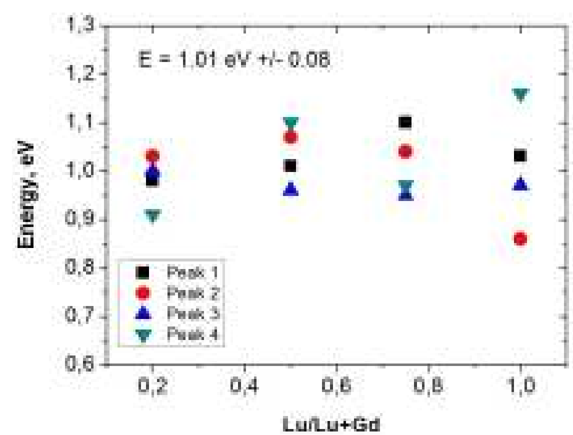


O.Sidletskiy, A. Belsky, A. Gektin, *Cryst Growth & Des*, 2012, 12, 441



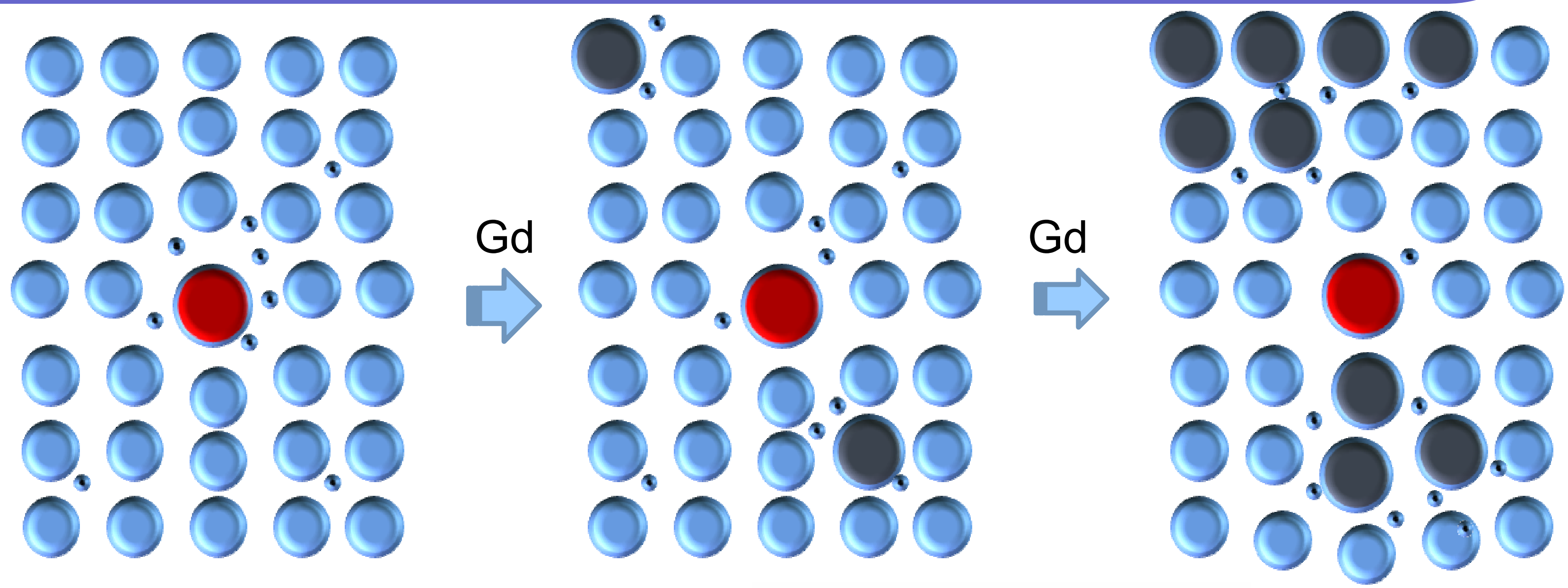


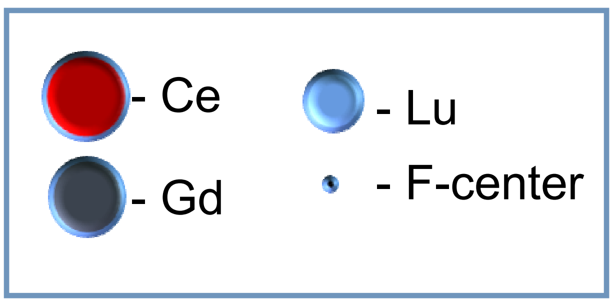
Trap depth in LGSO:Ce

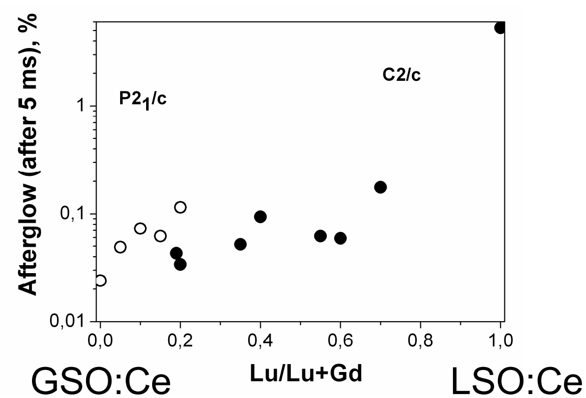


The bandgap changes by ≤ 0.15 eV, and Ce 5d levels shift by ≤ 0.1 eV relatively to the ground state.

Redistribution of oxygen vacancies at Gd addition







Issues of short-range separation in mixed crystal

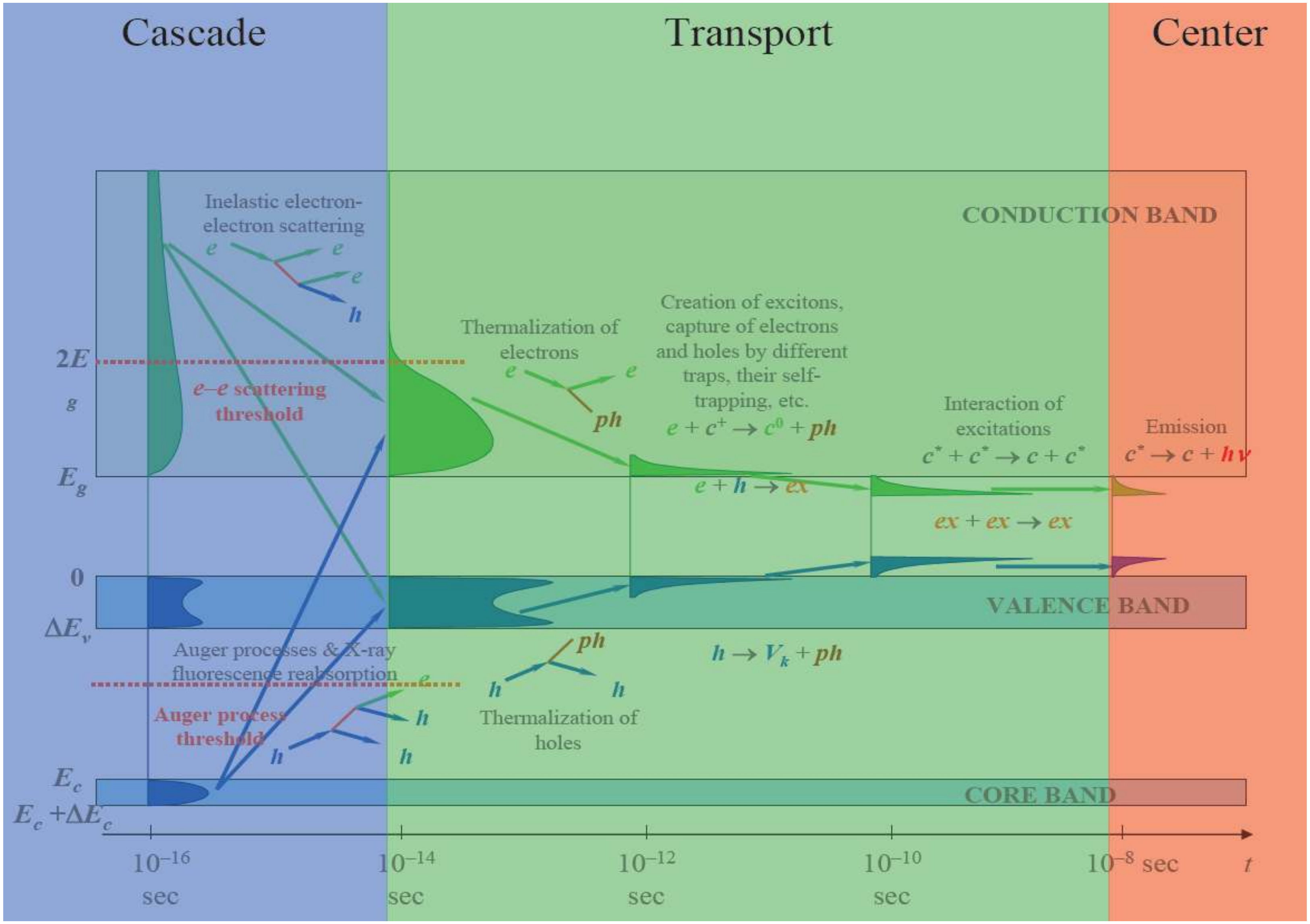
I. Modulation of electronic structure.
Modulation of band gap by variation of cations or anions ratio in mixed crystals

II. Formation of potential barriers limiting the e&h diffusion length

III. Modification of phonon spectrum of the crystal and distribution of electronic states may slow down hot carriers

<u>Details and history on the topic</u>:
A.Gektin, Friday, O6.1

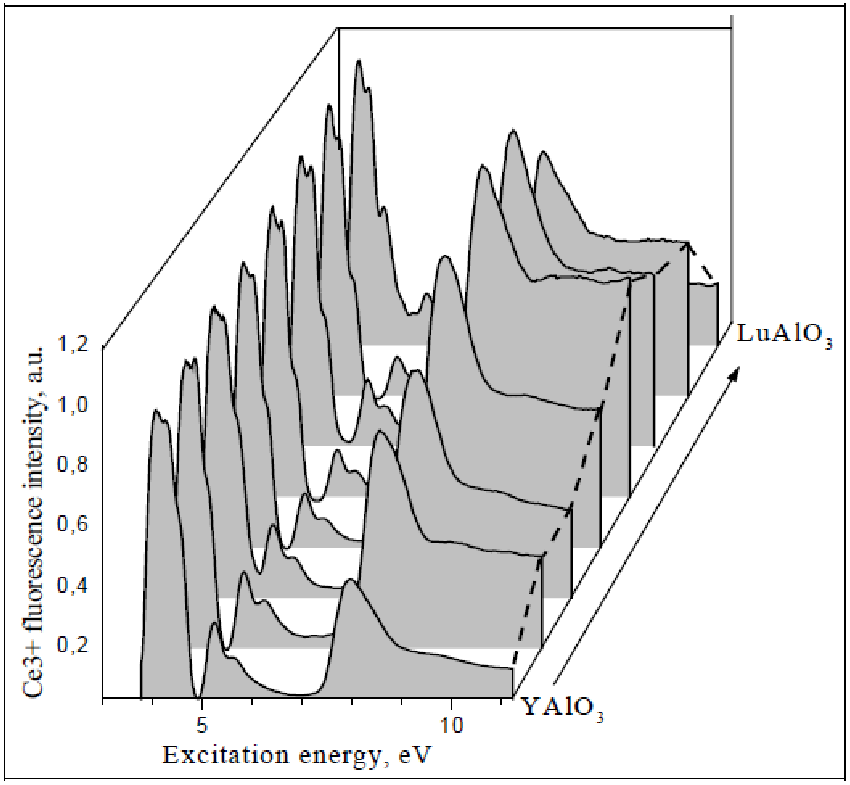
A.N.Vasil'ev, SCINT99



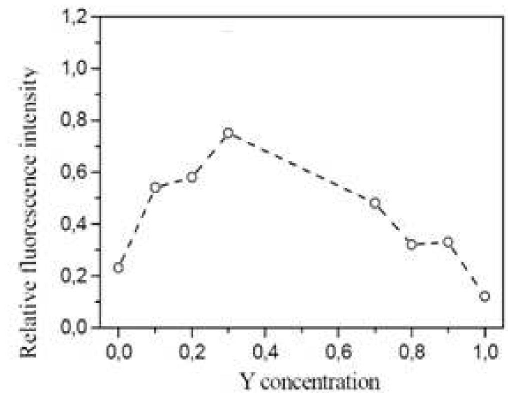
Short-range separation

'Energy structure engin '

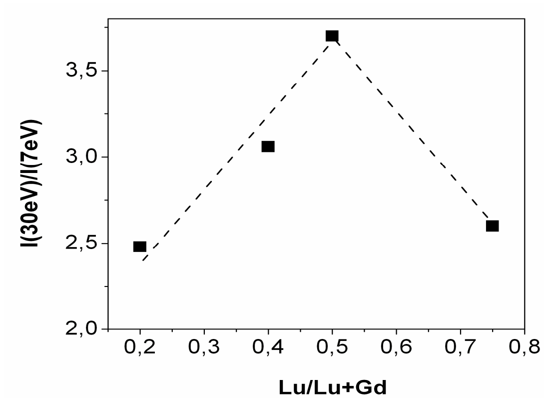
Influence of host composition on energy transfer



LuYAP



LGSO

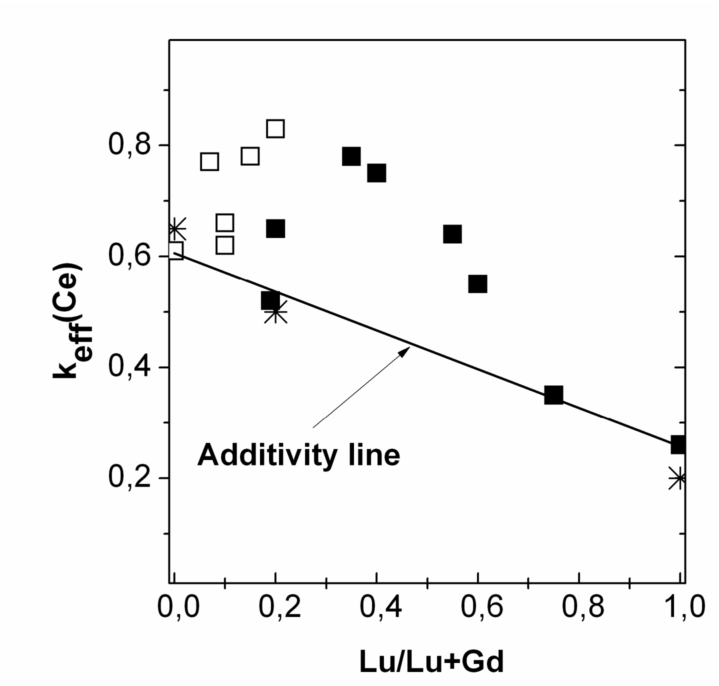


Efficiency of e-h pair transfer to Ce (which can be evaluated as the ratio Ce emission intensities at $E>2E_g$ to $E=E_g$) is larger in the medium concentration range

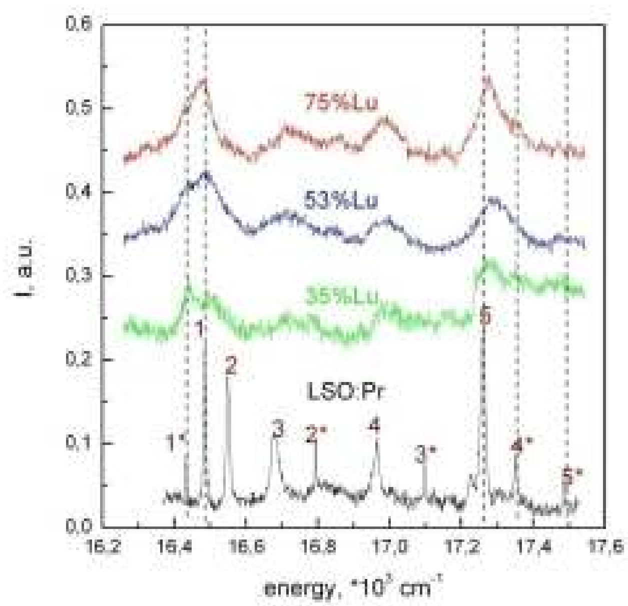
A. Belsky et al. Proc of SCINT'99, p.363

O.Sidletskiy et al. Crystal Growth & Design, 2012, 12, 441

Other indirect evidences of crystal inhomogeneity



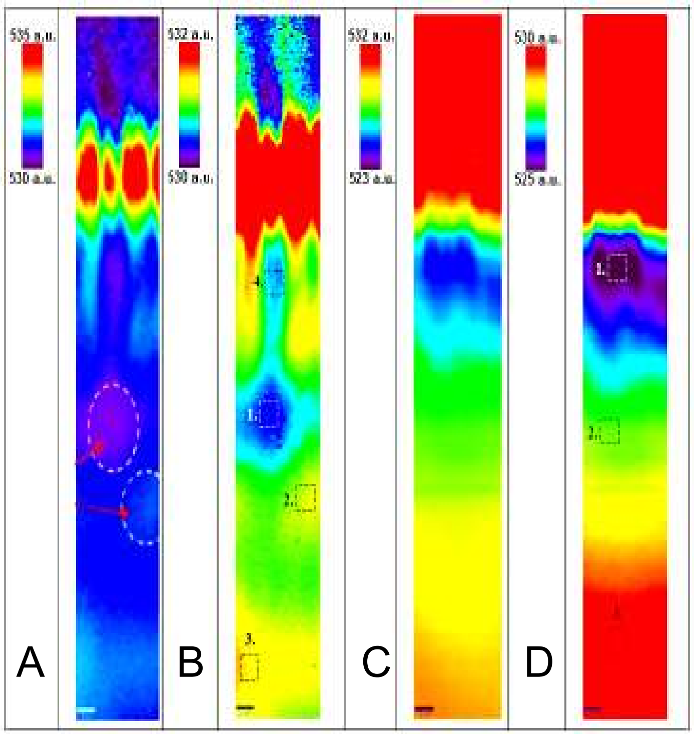
Non-additive increase
of k_{eff} (Ce) in LGSO:Ce



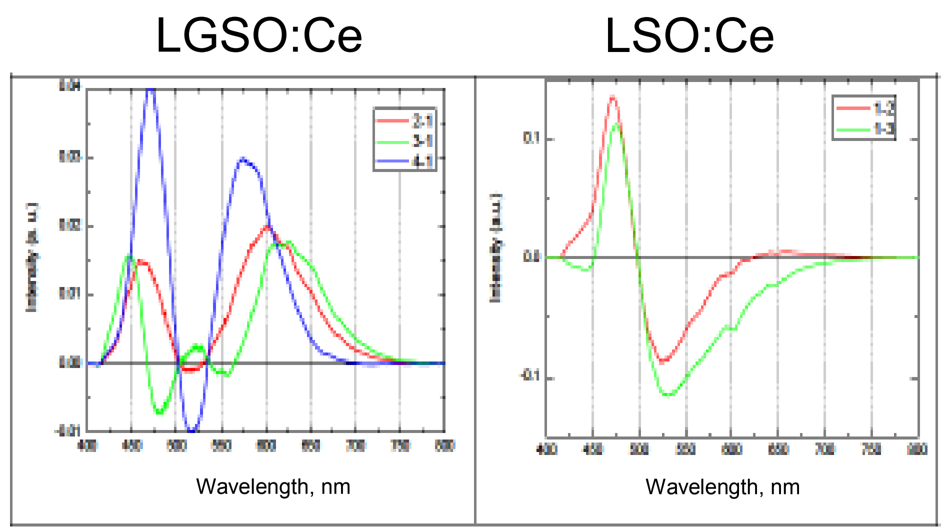
Absorption spectra of LGSO:Pr^{3+}

Confocal microscopy measurements

(Thursday, V. Kononets et al, P4.10)



Spatial distribution of PL band center of mass in LGSO:Ce (A, B), LSO:Ce (C, D) samples.



Difference between the PL normalized by their maxima before subtraction.

Spatial inhomogeneity of the spectral component observed in the red region (>550 nm) of LGSO:Ce reflects fluctuations in Lu/Gd ratio across the crystal.

How to predict the behavior of solid solution?

1) **The stronger the differnece between substituting atoms, the better.**

- Zn/Mg – 2.8 % (however, large difference in electronegativities)
- Gd/Y – 4.2 %
- Y/Lu – 4.5 %
- Lu/Gd – 9%
- Al/Ga – 13.7 %
- Lu/Sc – 15.6 %
- Lu/Ce – 18.5 %

2) The larger difference in Eg between the components, the better.

3) Strong crystal field of a host

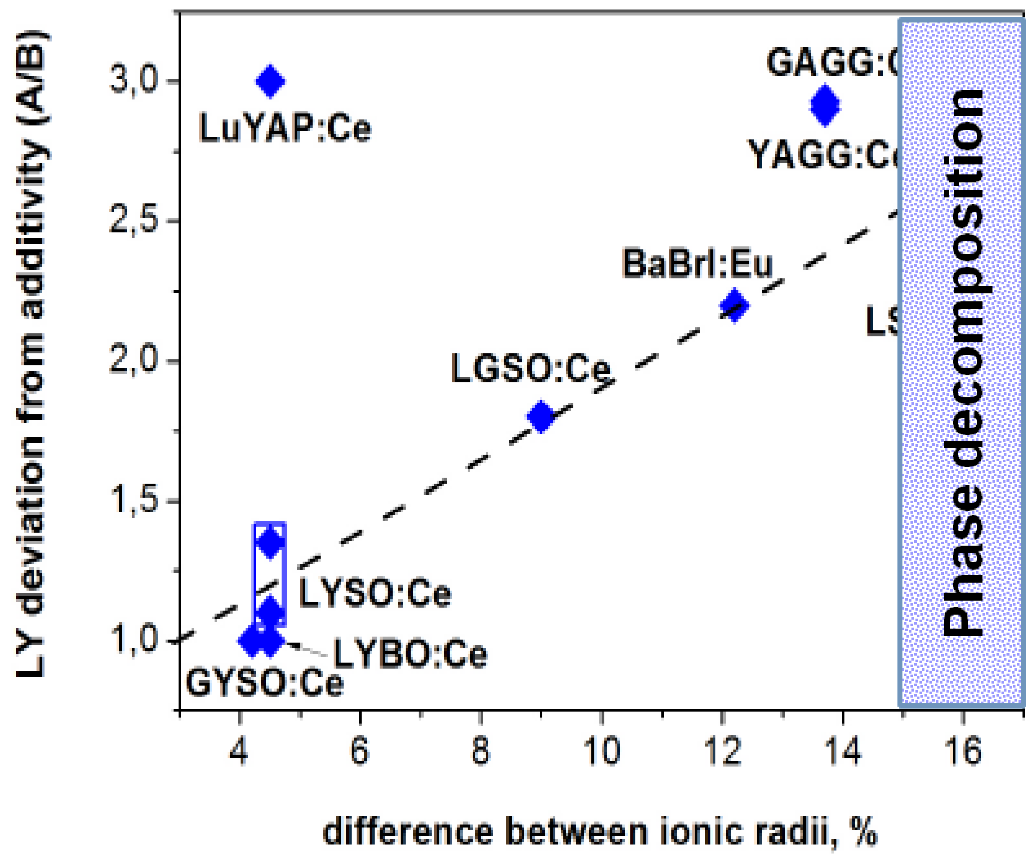
Energy of 5d level splitting of activator
$Y_3Al_5O_{12}$:Ce - 27000 см$^{-1}$
Lu_2SiO_5:Ce – 20700 см$^{-1}$
$LuBO_3$:Ce (valerite) - >18500 см$^{-1}$
$YAlO_3$:Ce – 12700 см$^{-1}$

P. Dorenbos, J. Lumin. 99 (2002) 283-299
P. Dorenbos, Phys. Rev. B64, 125117.

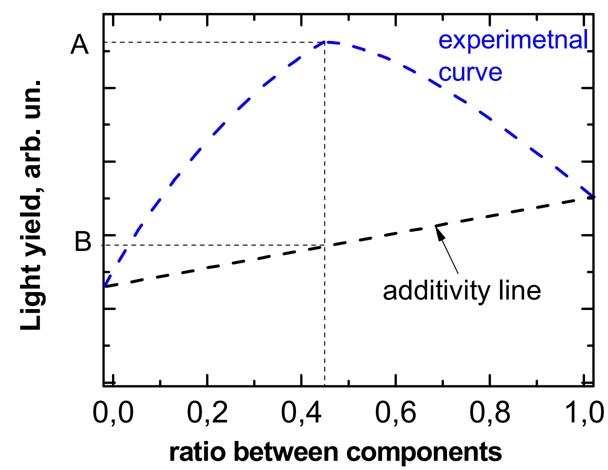
Material	Evidences of inhomogeneity	Energy structure modification	Rate of LY deviation
GYSO*	-	-	1
LYBO	-	weak	~ 1
LYSO	-	weak	1.1-1.35
LGSO	+	weak	1.8
LSBO	+	?	~ 2
YAGG	+	+	2.9
GAGG	+	+	2.9
LuYAP	+	-	~ 3

* for GSO-type structure

Summary



LY deviation from additivity (A/B)
3,0
2,5
2,0
1,5
1,0
LuYAP:Ce
GAGG:C
YAGG:Ce
BaBrI:Eu
LGSO:Ce
LYSO:Ce
LYBO:Ce
GYSO:Ce
LS
Phase decomposition
4
6
8
10
12
14
16
difference between ionic radii, %



Light yield, arb. un.
A
B
experimetnal
curve
additivity line
0,0
0,2
0,4
0,6
0,8
1,0
ratio between components

Conclusions & Acknowledgements

❑ Both changes in energy structure and issues of short-range separation seem to influence the light yield amplitude in mixed crystal. **There is a correlation between magnitude of light yield improvement and the difference in ionic radii of substituted atoms.**

❑ Feasibility of the proposed mechanism is supported by systematization of the data obtained with different mixed scintillators. However, no direct evidences of nanosized domains existence enriched with one of components have been obtained yet.

❑ Engineering of Ce-doped mixed oxide scintillation crystals provides improvement of light yield by up to ~3 times in respect to that in accordance with the Vegard's law. The proposed approach can be a tool for prediction of light yield values at development of new mixed crystal scintillators.

The work is supported by the Project FP7-INCO-2011-6 ("SUCCESS") and Project No. 28317ZC in the framework of France-Ukrainian Science and Technical Collaboratrion "DNIPRO".

Thank you for your attention!
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