New scintillators based on mixed oxide crystals

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Outline

- Motivation of study and scintillation characteristics of Ce-doped complex oxides;
- Growth methods;
- Behavior of light yield at variation of solid solution composition and possible mechanisms;
- Summary.

Motivation

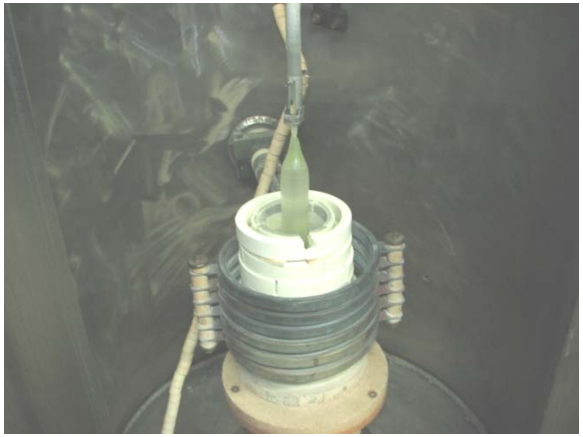
- ✓ Need for dense, fast (<50 ns) and bright scintillators for PET/CT, security scanning systems, well logging, etc.;
- ✓ Slow decay (>300 ns) in halide scintillators (CsI(Na), NaI(Tl)…) and oxides with intrinsic luminescence ($Bi_4Ge_3O_{12}$, $CdWO_4$…);
- ✓ The required properties can be combined in Ce^{3+} or Pr^{3+} doped complex oxides with fast 5d-4f luminescence.

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	9 – 11	50	0.02
Lu_2SiO_5 (LSO)	7.4	25000	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

Growth facilities

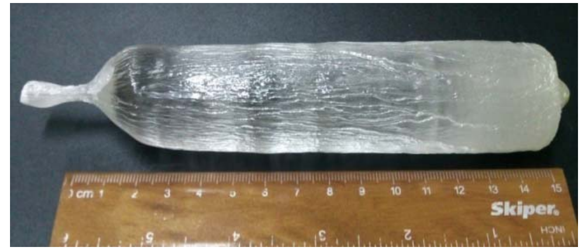
- Induction heating setups of “Oksid” and “Kristall” series for growth of crystals by the Czochralski method



- Induction heating;
- Ir crucibles
- Controlled vaccum chamber
- Diameter control by weight sensor
- Crystallization temperatures – up to ~2200°C;

Oxide scintillation crystals produced by ISMA

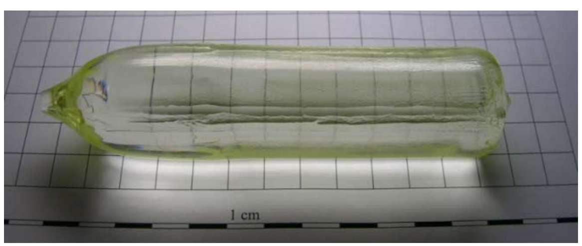
BGO up to 3” in dia.



LGSO:Ce

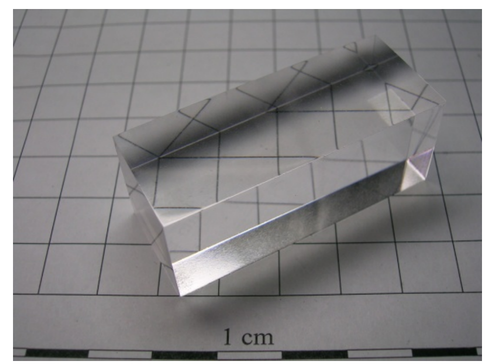
GSO:Ce up to 2” in dia.

LYSO:Ce



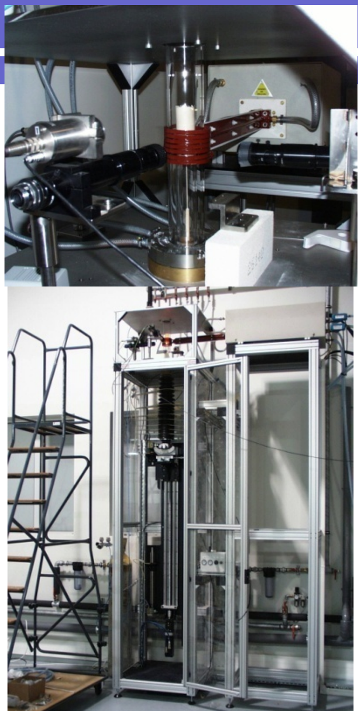
YAG

LuAG:Ce



LGSO:Ce element

Crystals Growth facilities in LPCML laboratory



μ-PD (Induction)

μ-PD (Résistive)

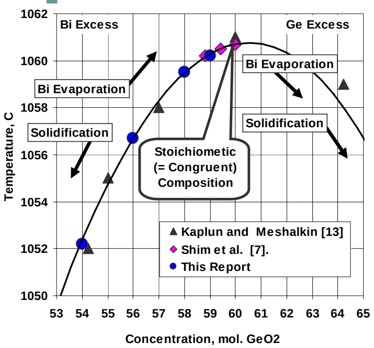
μ-PD (Résistive)

LHPG (Laser CO_2)

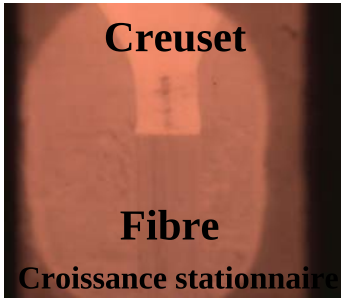
Creusets (Pt,Ir)

Machine Czochralski

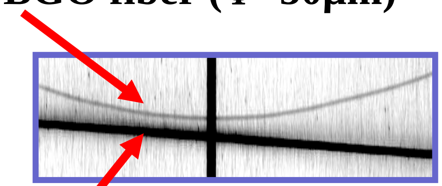
Fast scintillator fibers



Bi_2O_3-GeO_2



BGO fiber (Φ=50µm)



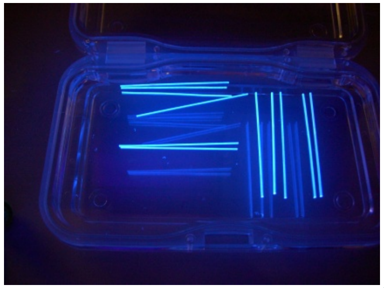
Human hair Φ(100-150µm)

Fiber bendability (over 100mm)

V.I.Chani, K.Lebbou, Crys. Res. Tech 41 (10)(2006)

Barreau LYSO

Coupe transversale

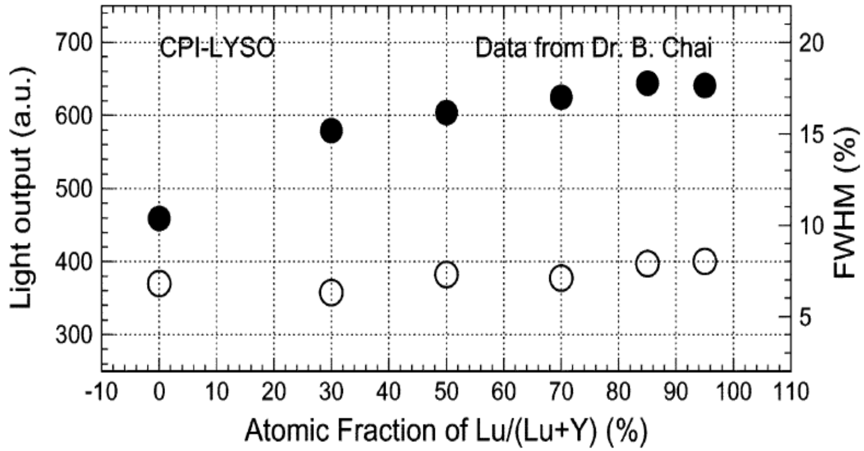


LYSO sous UV

Types of mixed oxide crystals

1. Systems with clear relationships between energy structure and scintillation parameters

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



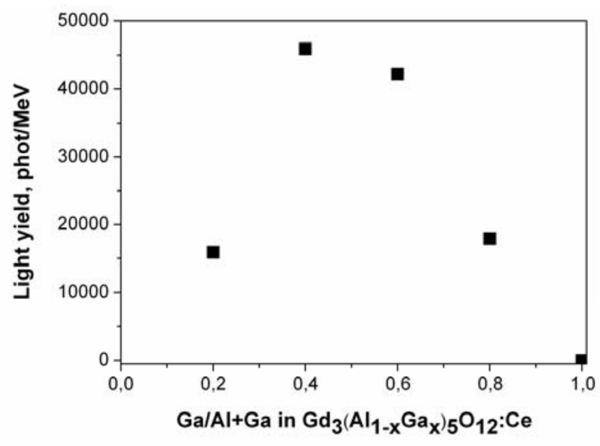
The light output (solid dots, left scale) and the energy resolution (open dots, right scale) as a function of the lutetium fraction in LYSO

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

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

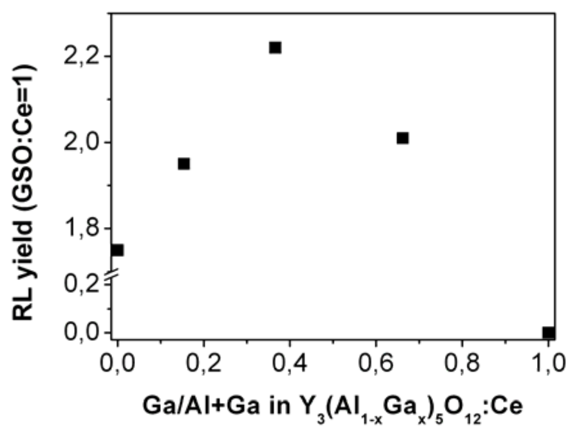
$Gd_{2x}Y_{2-2x}SiO_5$:Ce – improvement of mechanical properties compared to GSO:Ce at 0.8<x<1
[V. Bondar et al. Proc. of SCINT2005]

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



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

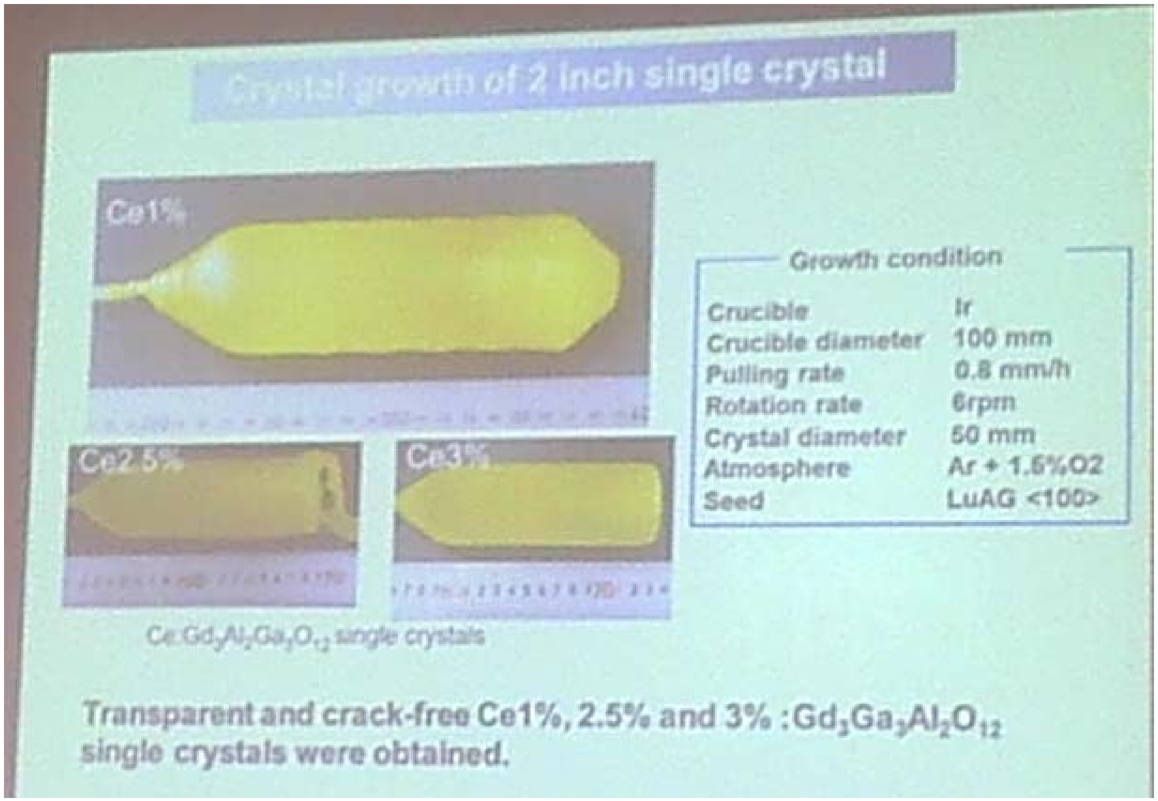
Kei Kamada, et al / Cryst. Growth Des. 11 (2011), 4484–4490.



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

O. Sidletskiy, V. Kononets, K. Lebbou, S. Neicheva, O. Voloshina, V. Bondar, V. Baumer, K. Belikov, A. Gektin, B. Grinyov, M.-F. Joubert, Mater. Res. Bull. Materials Research Bulletin 47 (2012) 3249–3252

Case of $Gd_3Al_2Ga_3O_{12}$:Ce



Lumdetr 2012
(A. Yoshikawa)

LY=65000 phot/MeV
R (662 KeV) = 4.6 %

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

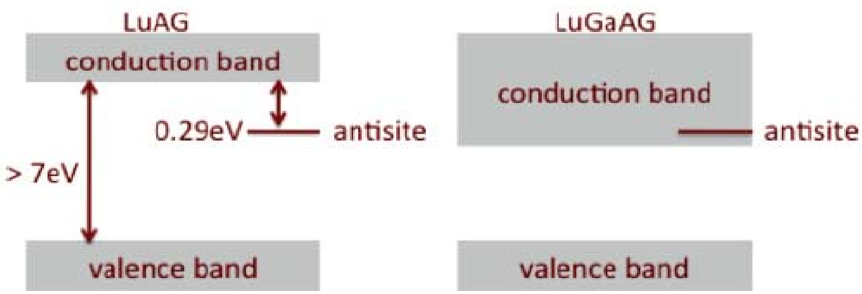
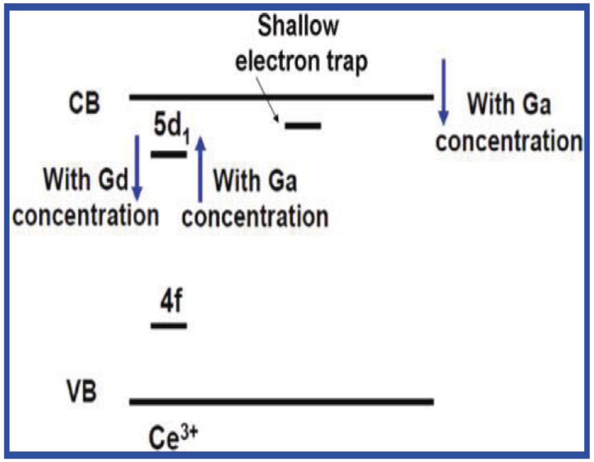


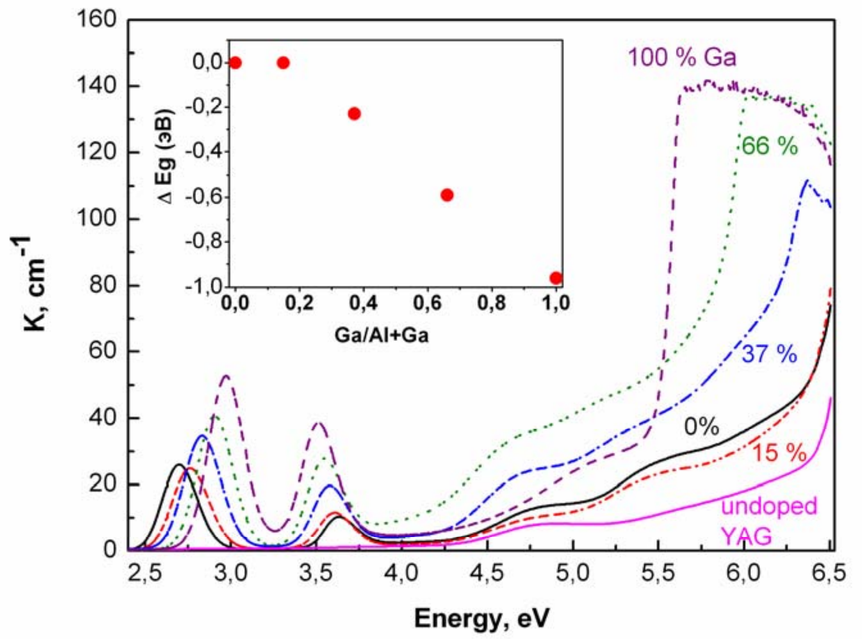
FIG. 1. (Color online) Schematic of the band structure of undoped LuAG (left-hand side), with a band gap of >7 eV and an antisite trap depth of 0.29 eV, compared to the proposed band shift due to Ga doping (right-hand side), where the antisite defect is no longer in the forbidden gap, but rather is enveloped by the CB.

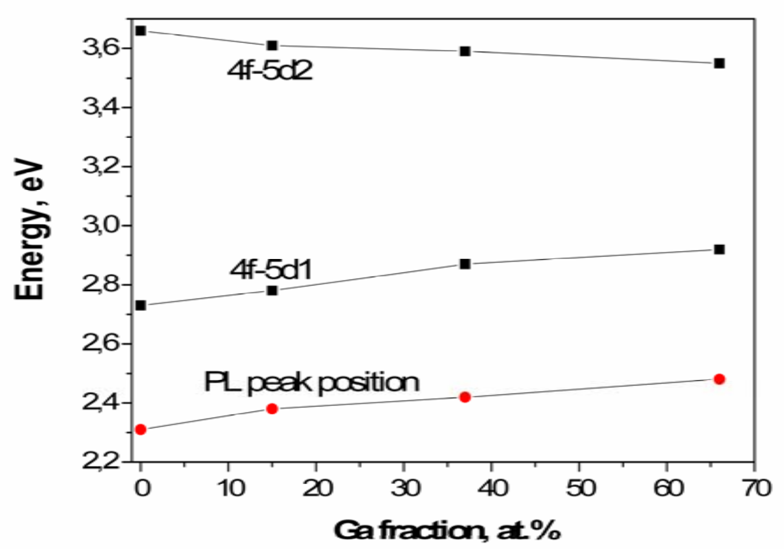


Energy level scheme related to the material design

M. Fasoli et al. Phys. Rev. B 84, 081102(R) (2011)
K. Kamada et al, Cryst. Growth Des. 2011, 11, 4484–4490.

Energy structure of $Y_3(Al_{1-x}Ga_x)_5O_{12}$:Ce



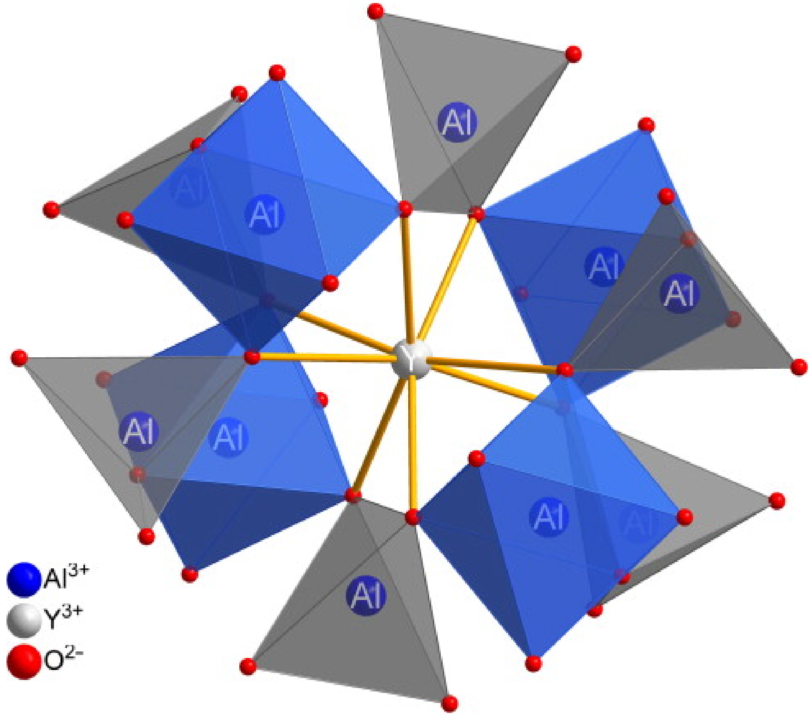


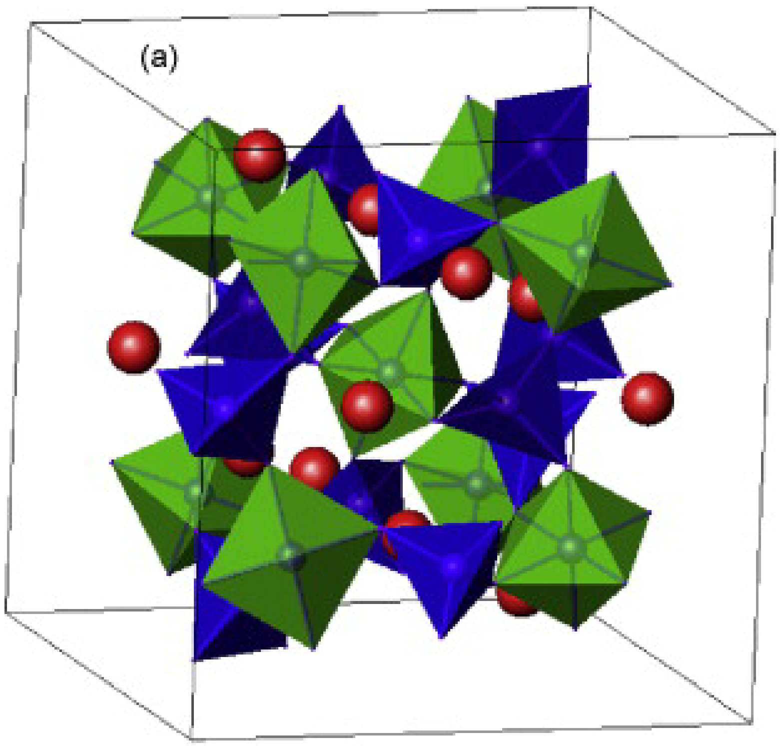
The shift of fundamental absorption edge indicates the bandgap decrease by ~ 1 eV, from YAG to YGG.

The splitting of Ce^{3+} 5d levels decreases due to the weakening of crystal field.

O. Sidletskiy, et al / Materials Research Bulletin 47, (2012) 3249–3252

Crystal structure of YAG:Ce

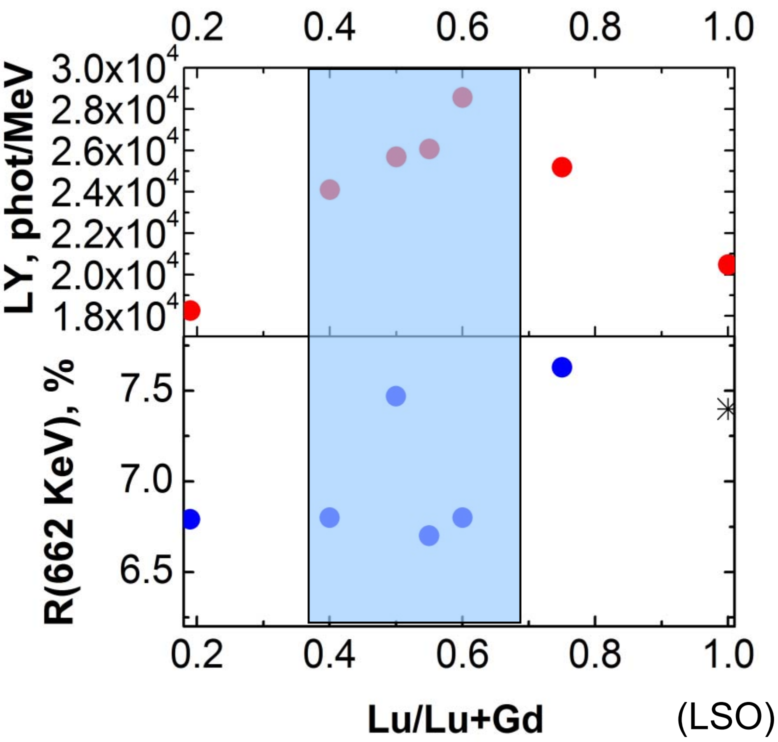


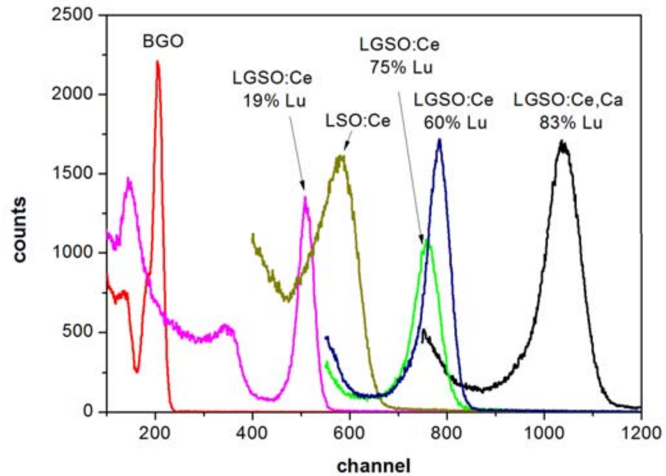


Types of mixed oxide crystals

2. Systems with deviations of scintillation yield from additivity rule without changes in energy structure of crystal

Scintillation characteristics of LGSO:Ce crystals



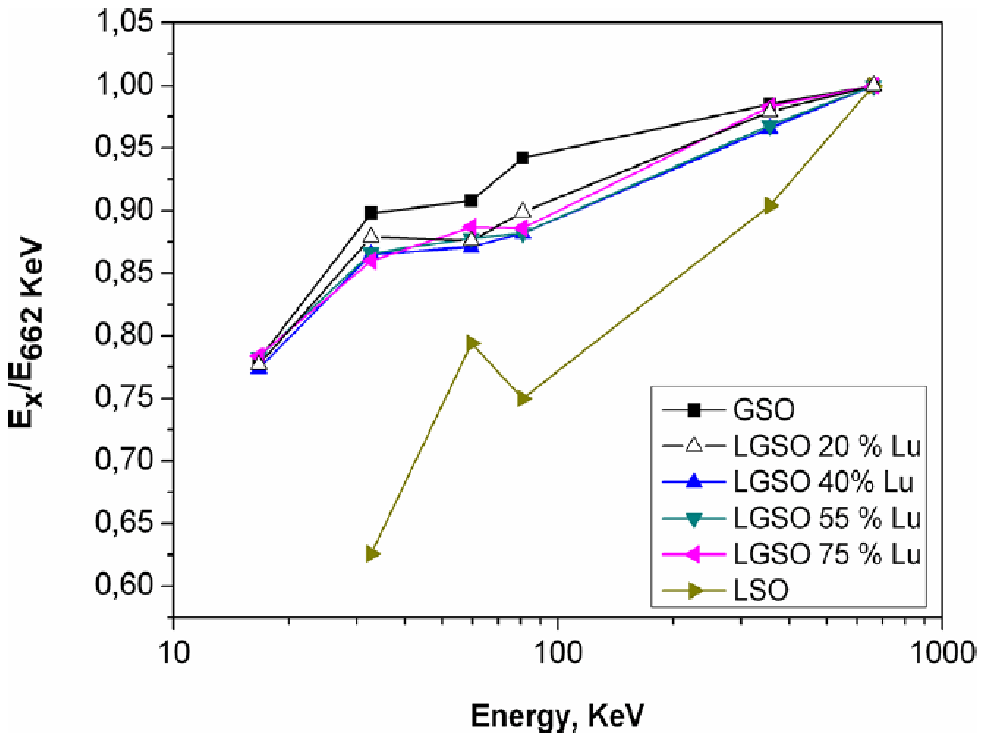


In the optimal host composition range
(30-70 % Lu)

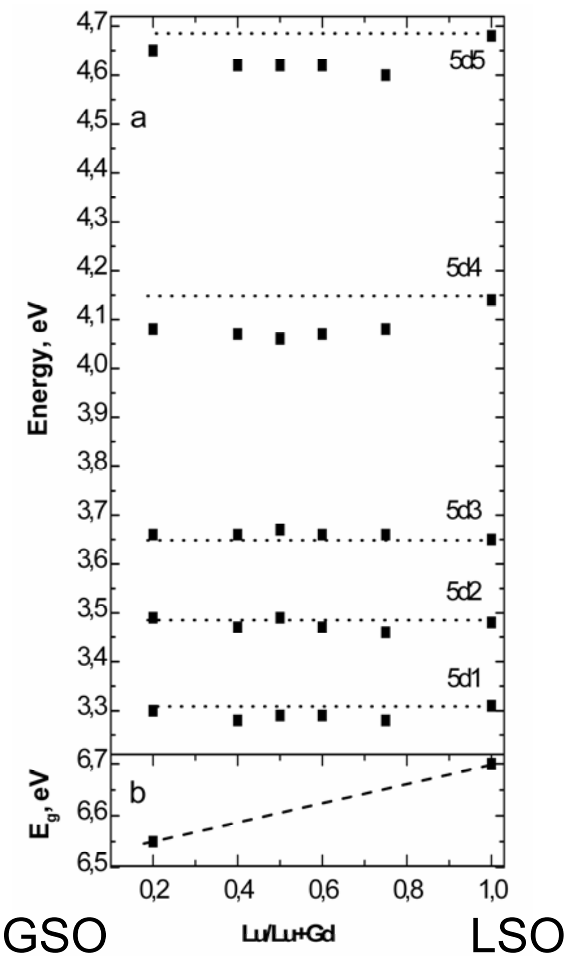
- Light yield 24000 – 29000 phot/MeV; (33700 phot/MeV in Ca codoped crystal);
- Energy resolution (662 KeV) - 6.7 – 7.3 %

O. Sidletskiy, V. Bondar, B. Grinyov, et al. *J. Cryst Growth*, 312 (2010) 601
O.Sidletskiy, A. Belsky, A. Gektin, S. Neicheva, D. Kurtsev, V.Kononets,Ch. Dujardin, K.Lebbou, O. Zelenskaya, V. Tarasov, K. Belikov, and Boris Grinyov. *Crystal Growth & Design*, 2012, 12, 441

Nonproportionality of LGSO:Ce



Energy structure of LGSO:Ce



- *Eg* = 6.1 - 6.6 eV in GSO и 6 - 6.8 eV in LSO;

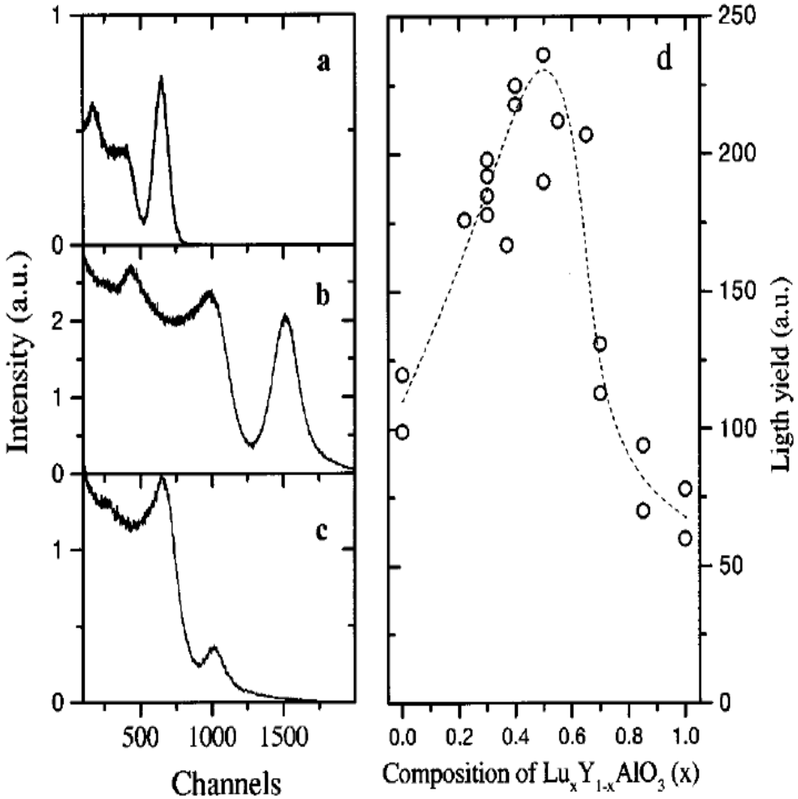
- In LGSO the bandgap changes by ≤0.15 eV, and Ce 5d levels shift by ≤ 0.1 eV relatively to the ground state.

O.Sidletskiy, A. Belsky, A. Gektin, S. Neicheva, D. Kurtsev, V.Kononets,Ch. Dujardin, K.Lebbou, O. Zelenskaya, V. Tarasov, K. Belikov, and Boris Grinyov. *Crystal Growth & Design*, 2012, 12, 441

$Lu_xY_{1-x}AlO_3$:Ce (LuYAP)

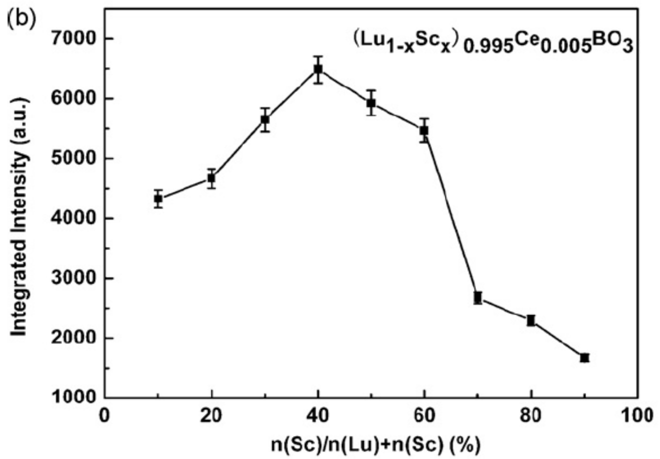
Amplitude distribution of scintillation pulses under Cs X-ray excitation:

(a) LuAP:Ce,
(b) (b) LuYAP(70%Lu):Ce,
(c) YAP:Ce.
(d) Light yield measured in Ce-doped Lu Y AlO crystals of various composition.

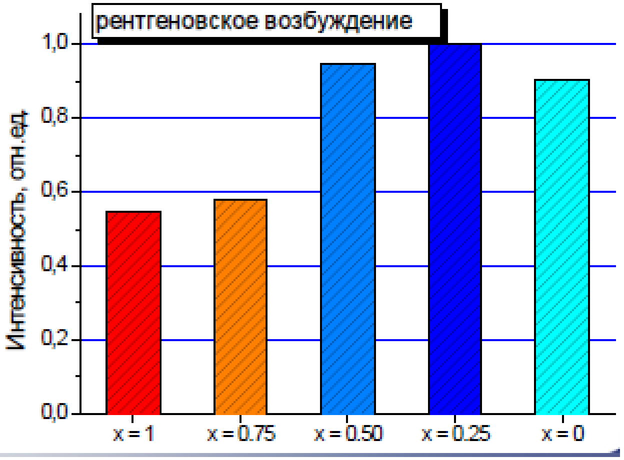


A.N. Belsky E. Auffray, P. Lecoq, C. Dujardin, N. Garnier, H. Canibano, C. Pedrini, and A. G. Petrosyan. IEEE Trans. Nucl. Sci. 48 (2001) 1095

Luminescence yield under X-rays in complex borates



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



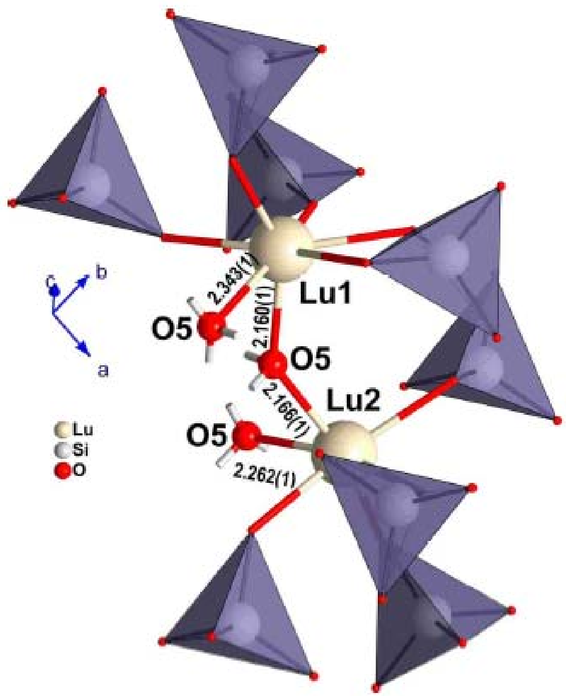
$Lu_xY_{1-x}BO_3:Eu^{3+}$

D. Spassky et al. ISMART-2012

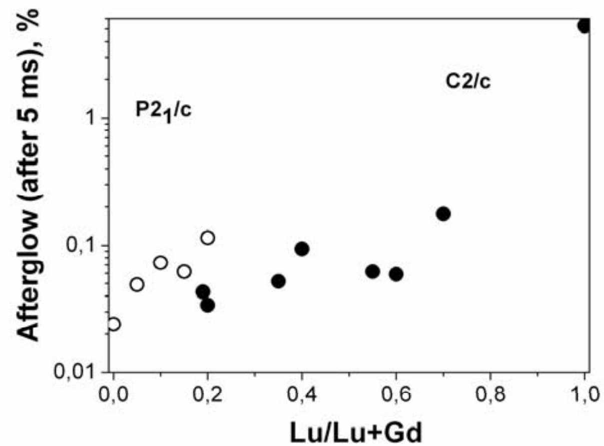
$Lu_xY_{1-x}BO_3:Ce^{3+}$

Increase of PL intensity in $Zn_{1-x}Mg_xWO_4$ solid solutions

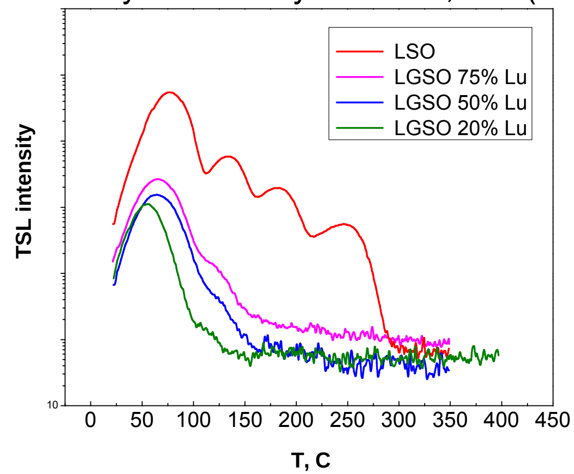
Version 1.
Elimination of electron traps in LGSO:Ce ?



A. Vedda et al, Phys. Rev. B 78 (2008) 195123.



O. Sidletskiy et al. J. Cryst Growth, 312 (2010) 601



Anna Vedda and Svetlana Neicheva (Milano, 2012)

Version 2.
Clusterization in mixed crystals?

Crystal field changes at the cluster boundaries may lead to decrease of separation length of secondary electrons and holes and advantage the localization of electronic excitations

↓

Light yield increase

Dimensions: 1 nm < r < 100 nm

Clusterization. History

1977

Fluctuations of composition in metal alloys led to modulation of crystal potential and decrease of electron diffusion length, providing the increase of electric resistance.

Iveronova, V. I.; Katsnelson, A. A. Short-range Order in Solid Solutions; Nauka: Moscow, 1977; p 256.

1995

Increase of the light yield and energy transfer efficiency for intermediate compositions in solid solutions has been related to the dependence of the short-order structure of solid solution on component concentration.

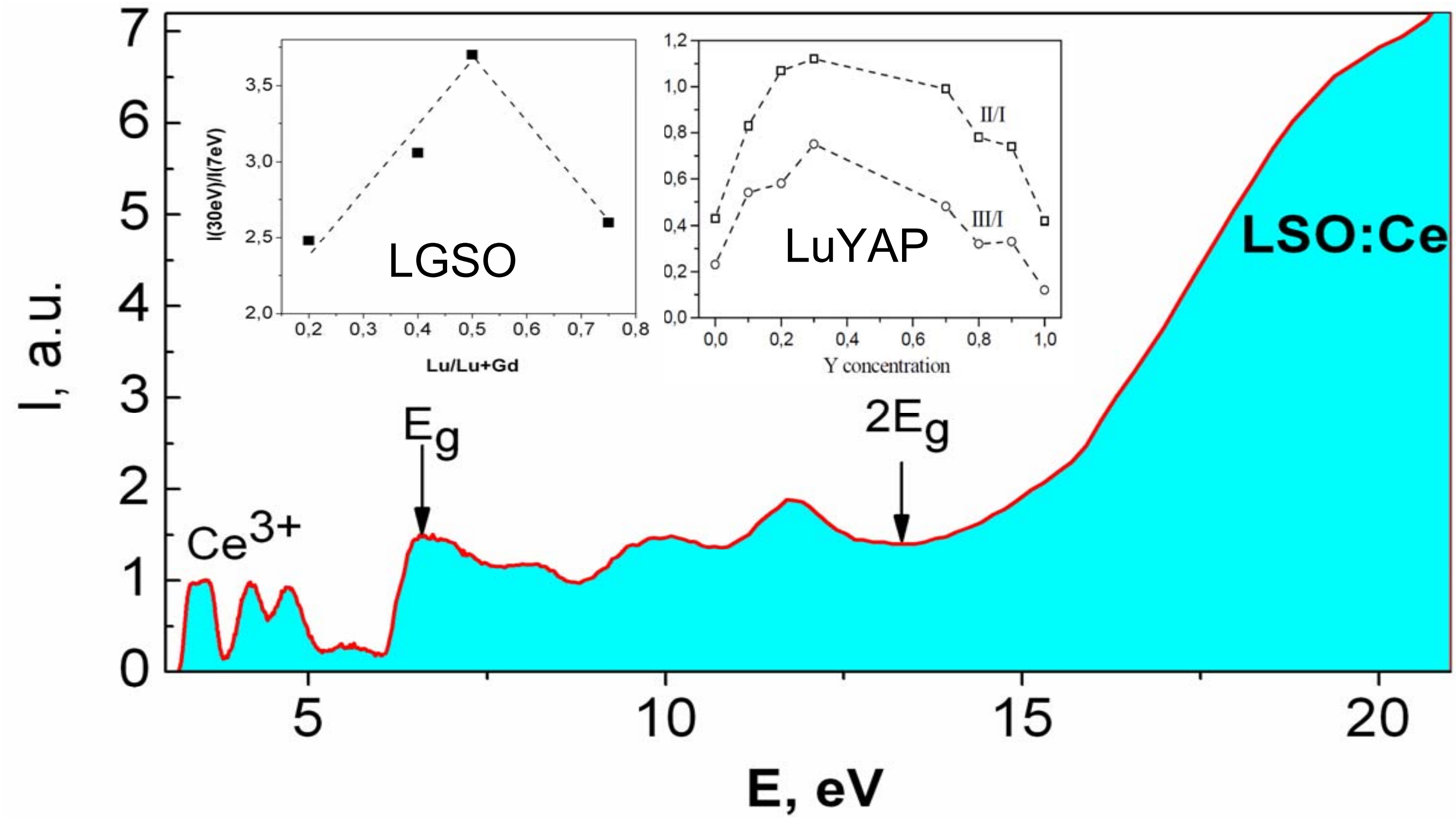
A. N. Belsky, A. V. Gektin, S. N. Klimov, J. C. Krupa, P. Martin, A. Mayolet, V. Mikhailin, C. Pedrini, A. N. Vasil'ev, and E. I. Zinin, "Solid solutions of scintillators: A way of improving properties," *Proc. of SCINT'95*, pp. 384–387.

1999

Modulation of crystal potential by the boundaries of such clusters may decrease the diffusion length of secondary electrons and holes and promote the localization of electronic excitations… and lead to an increase of the light yield.

A.N.Belsky, C.Dujardin, C.Pedrini, A.Petrosyan, W.Blanc, J.C.Gacon, E.Auffray, P.Lecoq. Status of development of YAP-LuAP mixed scintillators.Optical, luminescence and light yield studies, p.363

Influence of host composition on energy transfer

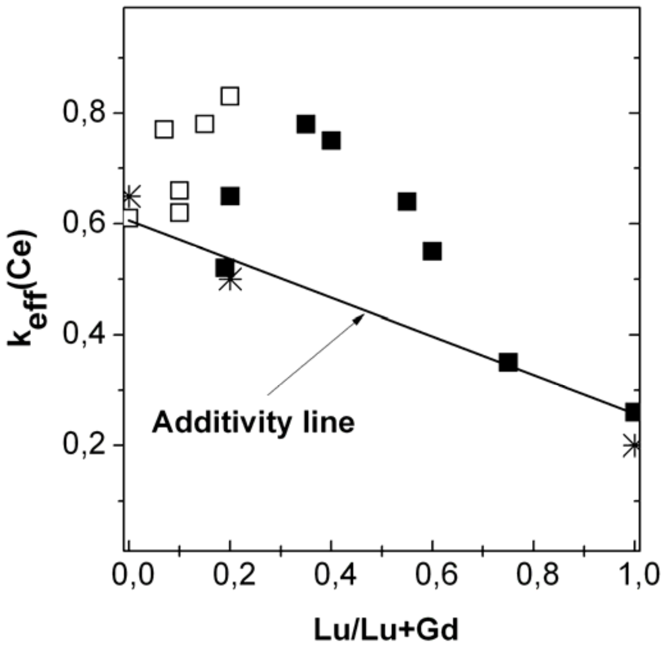


Efficiency of e-h pair transfer to Ce (which can can be evaluated as the ratio Ce emission intensities at $E>2E_g$ to $E=E_g$) is larger in the medium concentration range

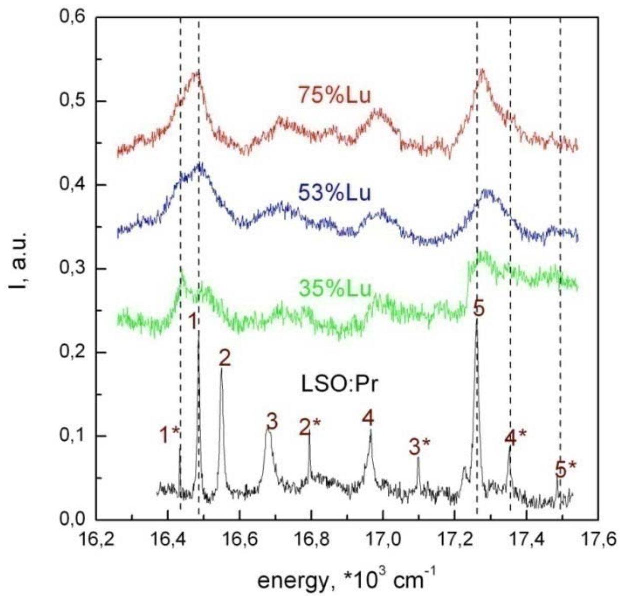
A. Belsky et al. Proc of SCINT'99, p.363

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

Other indirect evidences of crystal inhomogeneity



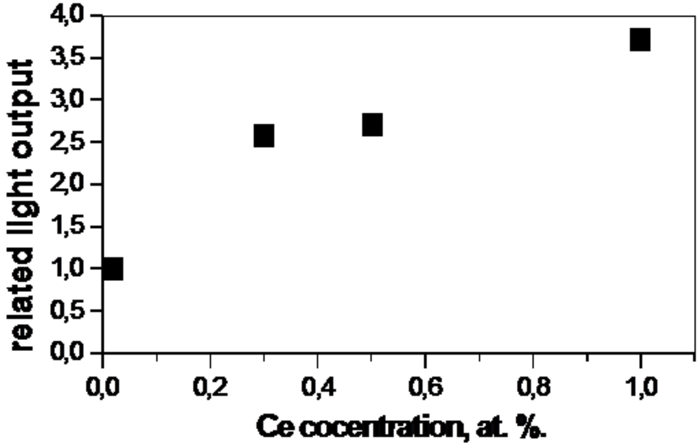
Non-additive increase
of k_{eff} (Ce) in LGSO:Ce



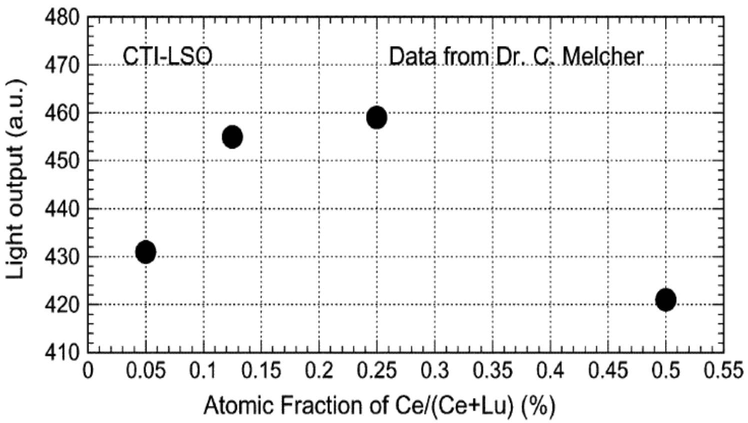
Absorption spectra of LGSO:Pr^{3+}

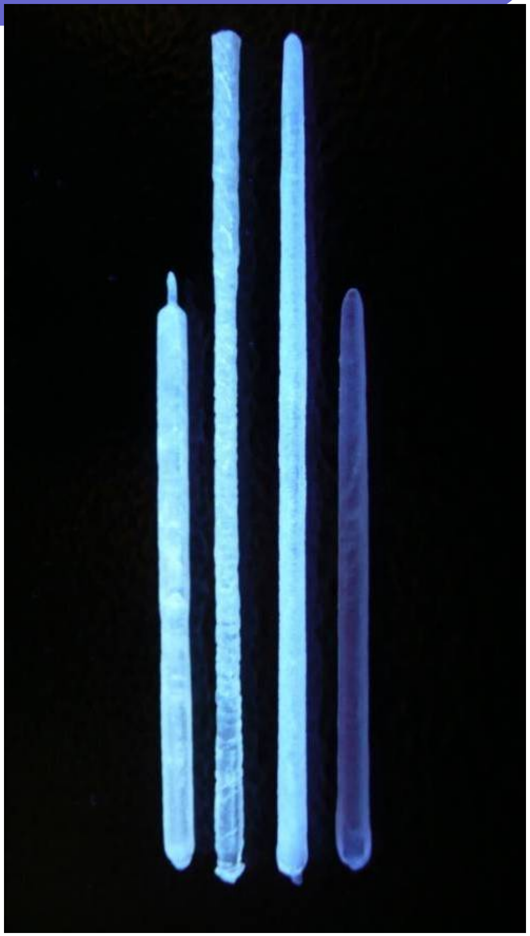
LGSO light yield vs. Ce content

V.Kononets,
K. Lebbou, 2012



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





LGSO fibers with different Ce content under UV-rays

How to predict the behavior of solid solution?

1) 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.

2) Goldschmidt's Rules. The ions of one element can extensively replace those of another in ionic crystals if their radii differ by less than approximately 10-15%.

- Zn/Mg – 2.8 % (however, large difference in electronegativities)
- Gd/Y – 4.2 %
- Y/Lu – 4.5 %
- Lu/Gd – 9%

-- 10 %

- Lu/Sc – 15.6 %
- Lu/Ce – 18.5 %

Summary

❑ A series of new efficient scintillation crystals based on solid solution has been developed:
- LGSO:Ce – with light yield up to 34000 phot/MeV and R(662 KeV) = 6.7 %;
- YAGG:Ce – with light yield up to 25000 phot/MeV;
- GAGG:Ce – with light yield up to 65000 phot/MeV, R(662 KeV) = 4.6 %;
- GPS:Ce – with light yield up to 40000 phot/MeV, R(662 KeV) = 8 %;

❑ Scintillation mechanisms in some of them are not well-studied so far. Light yield increase in Ce-doped LGSO, LuYAP, LSBO can be attributed to limitation of separation of electron-hole pairs due to in inhomogeneities in crystals.

❑ How to obtain direct evidences of these inhomogeneities?
- EXAFS (extended X-ray absorption fine structure);
- low-angle X-ray scattering;
- some other methods (microluminescent analysis) ?

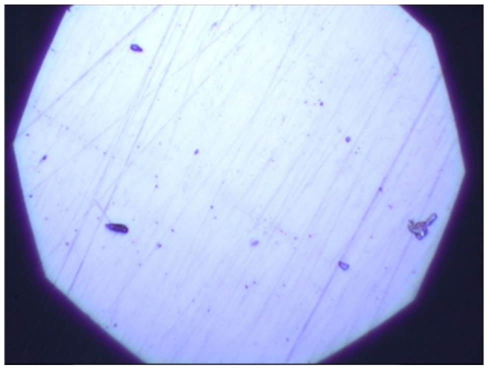
Confocal microscopy measurements: LGSO(25%Lu with Ce)

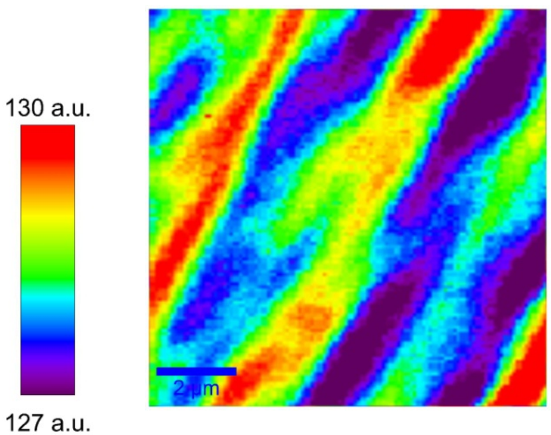
Excitation: 405nm CW laser diode ~490µW (~0.36 MW/cm^2) x50 (NA = 0.55) objective

Filter: BLP01 (cut-off at 418 nm)

D. Dobrovolskas, G. Tamulaitis (Vilnius University, Lithuania)

X-Y plane

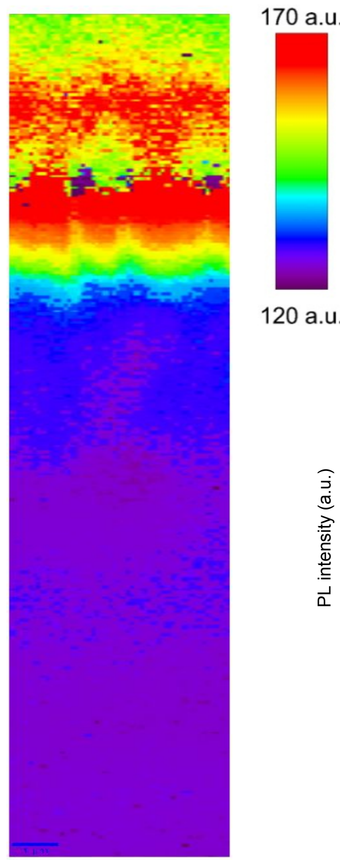




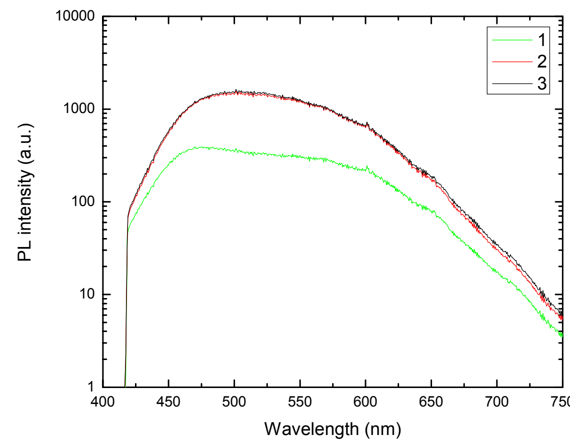
PL spectra FWHM

Depth scan (X-Z)

5x30 µm



PL spectra FWHM



Spatially averaged PL spectra from various depths