Issues of carbon doping in YAG and YAG:Ce scintillators

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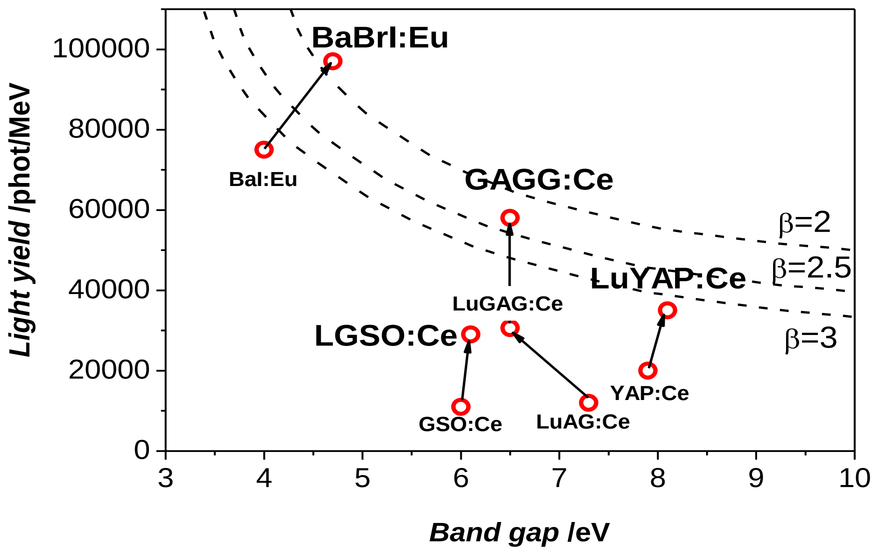
Motivation



$$N_{ph} = S\, Q\, E_{\gamma} / E_{e\text{-}h} = S\, Q\, E_{\gamma}\; / \beta E_g$$

- The theoretical light yield limit (60 kphot/MeV) was achieved in Ce-doped multicomponent garnets by the Lu/Gd/Y и Al/Ga substitution due to inactivation of electron traps

[M. Fasoli et al, *Phys. Rev. B* **2011**, *84*, 081102(R)
K. Kamada et al, *Opt. Mater*. **2014**, *36*, 1942]

- Ir purchase/refining cost is up to half of the crystal price

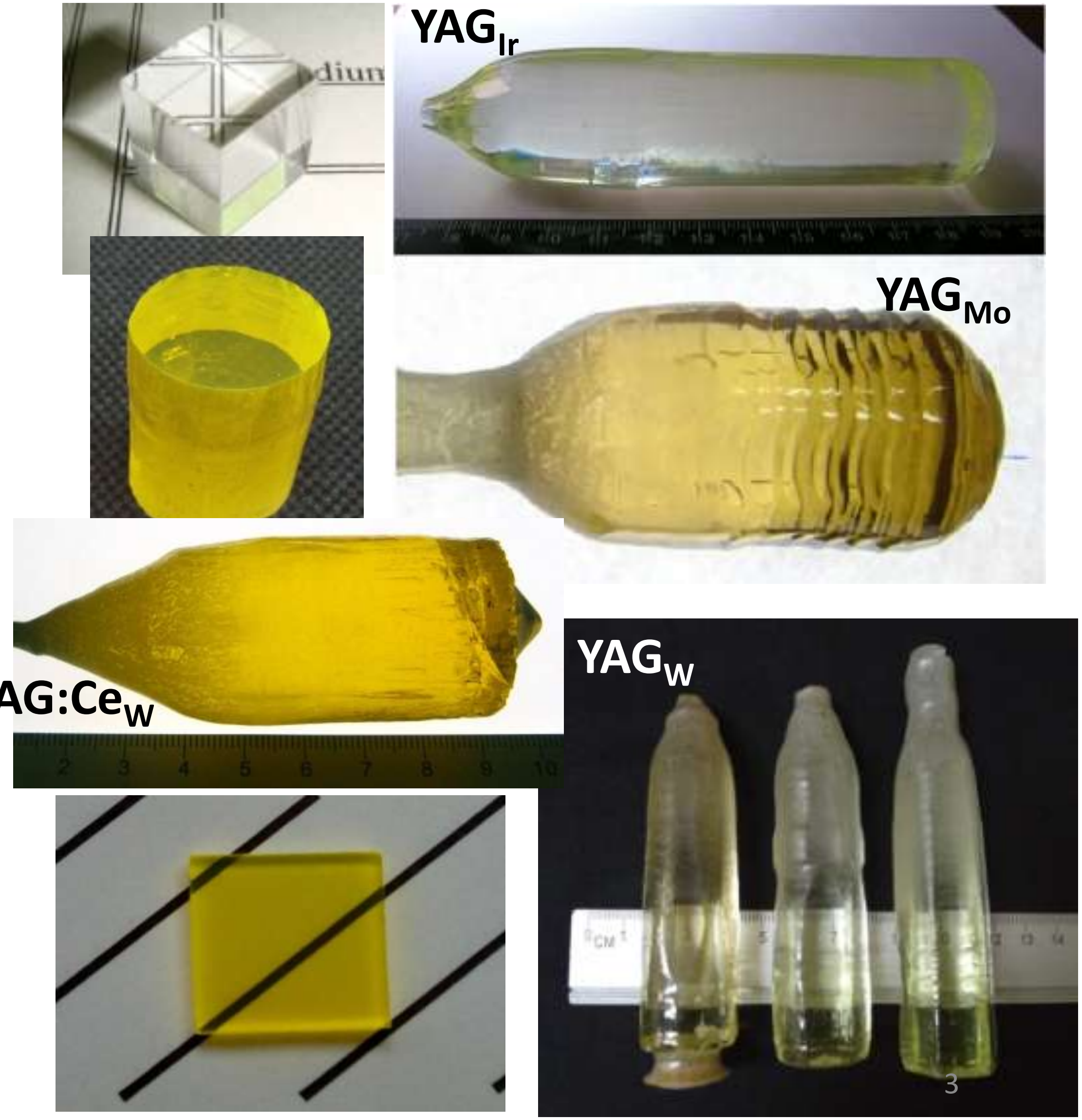
YAG:Ce crystals are cheap and can be grown rather easy compared to other complex oxide crystals

But light yield in “simple” garnets and perovskites (YAG, YAP, LuAG) is far from the theoretical limit (15-20 kphot/MeV)

Aim: search for new crystal fabrication methods of garnet-based scintillators with enhanced parameters

Features of growth under reducing conditions in CO-containing atmosphere

- Mo and W crucibles;
- Thermal range of crystallization – up to ~3400 °C (vs. ~2100 °C with using Ir crucibles)
- Graphite heat insulation creates the Ar+CO atmosphere;
- Introduction of Ce3+ in the form of $CeAlO_3$



P. Arhipov, Func. Mater, **2014**, 21, 472
P. Arhipov, J. Cryst Growth, **2015**, *430*, 116
P. Arhipov, J. Cryst Growth, **2016**, *449*, 104
Pat UA 123344 (**2018**)

Concentrations of some basic admixtures in crystals vs. their preparation conditions

No.	Crystal/admixture conc. (wt.ppm)	Mo	Fe	Si	C
1	YAG_{Ir}	< 1	< 5	< 10	-
2	YAG_{Mo}	100-150	< 3	<10	144
3	YAG_{Mo} (recrystallized #2)	<30	< 3	1	114
4	YAG_{Mo} (melt soaking)	ND	ND	ND	235 **(~1at.%) !!!**

(ND – not determined)

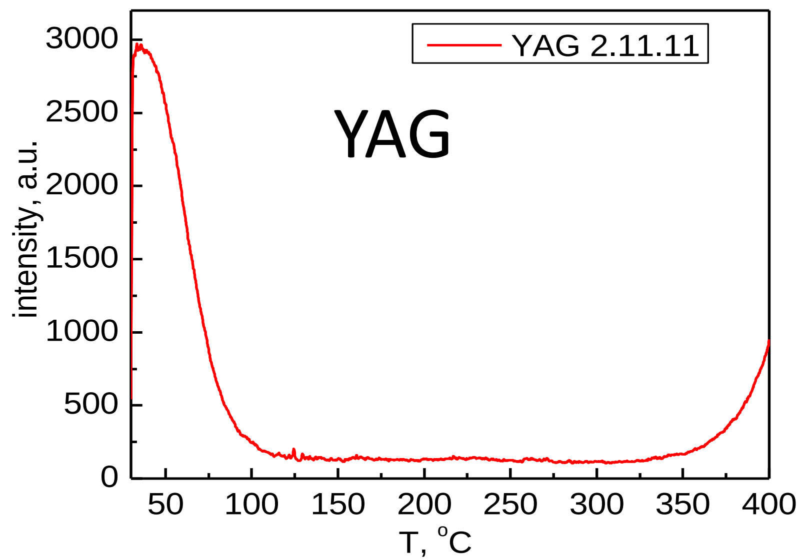
❑ At least 1 at.% of C can be introduced into crystals

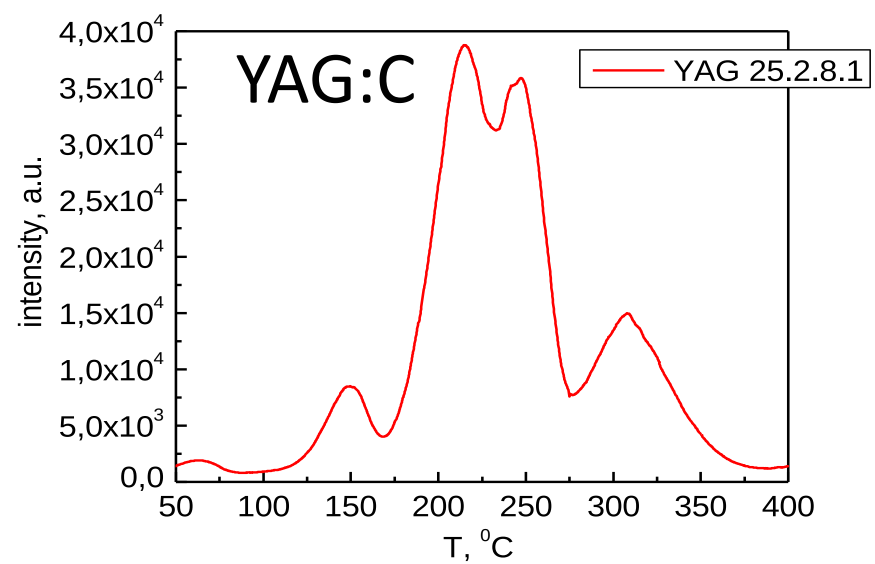
C-doped complex oxides for dosimetry

$Y_3Al_5O_{12}$ (Kulkarni, 2008)
Undoped and Ce^{3+}, Tb^{3+}, Er^{3+}, or Yb^{3+} doped $Y_3Al_5O_{12}$ (Xin-Bo Yang, 2009)
$Y_3Al_5O_{12}$, $YAlO_3$ and $Y_4Al_2O_9$ (Zhydachevskii, 2018)

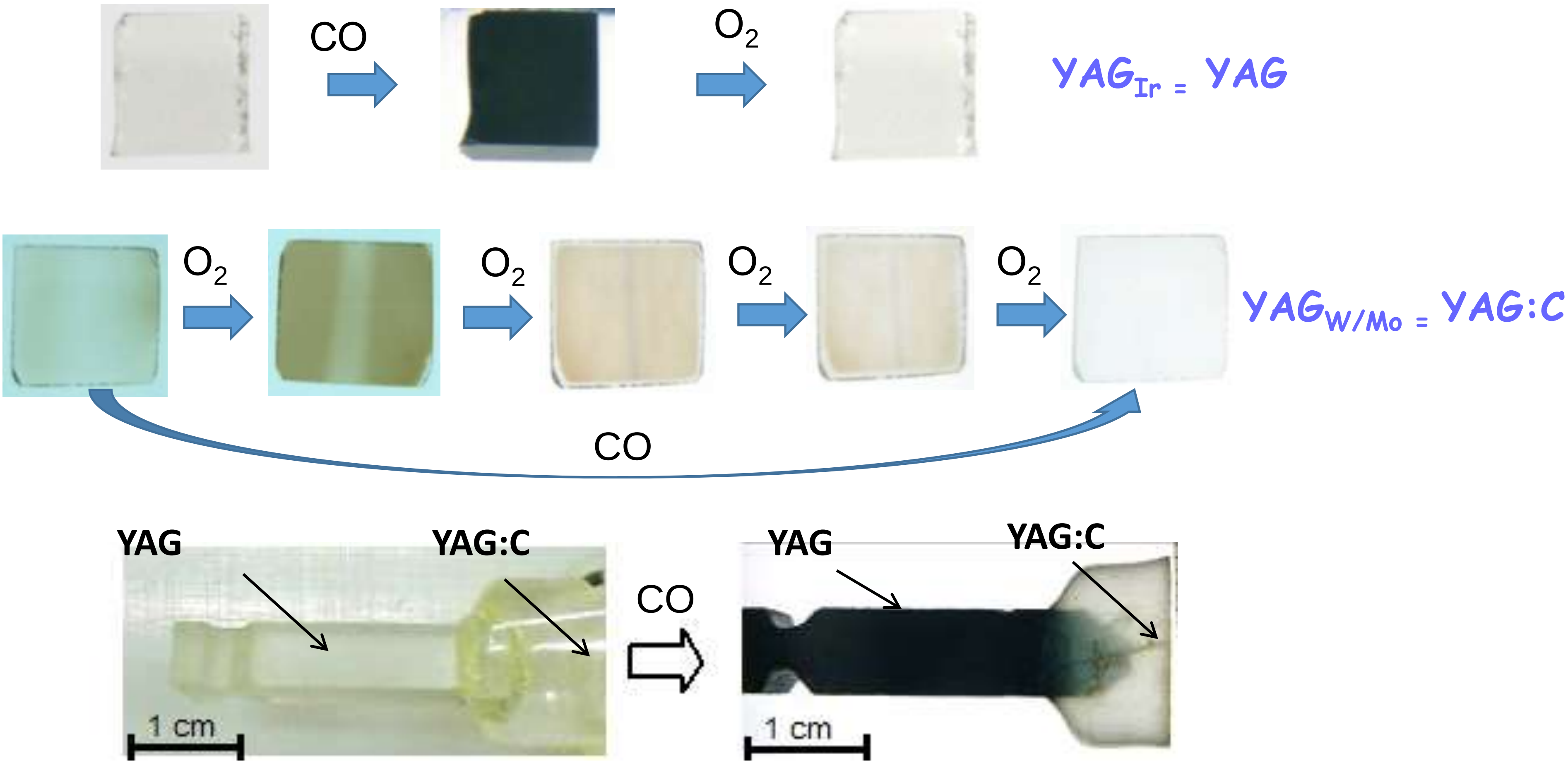
"….Two-valent carbon ions replace the three-valent cations of Al in the YAG crystal, and oxygen vacancies are formed as the charge compensators. This causes the high concentration of *F*+ centers in as-grown YAG:C crystal…."

In this work…..



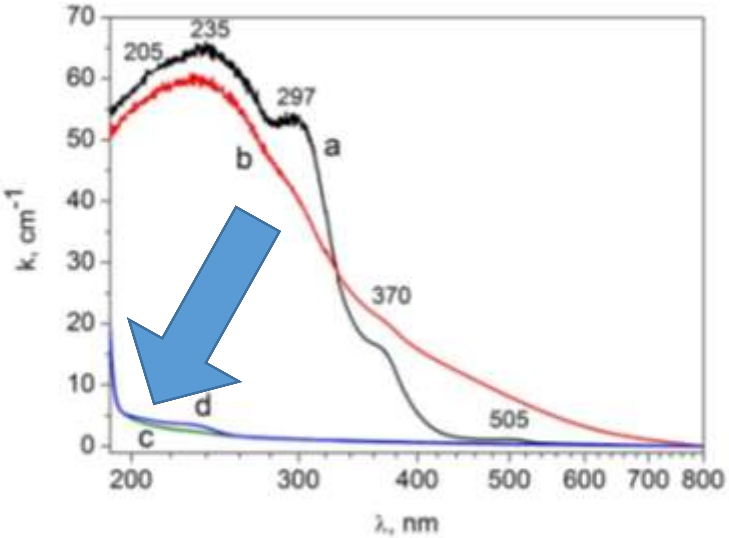


Post-growth annealing of YAG and YAG:C

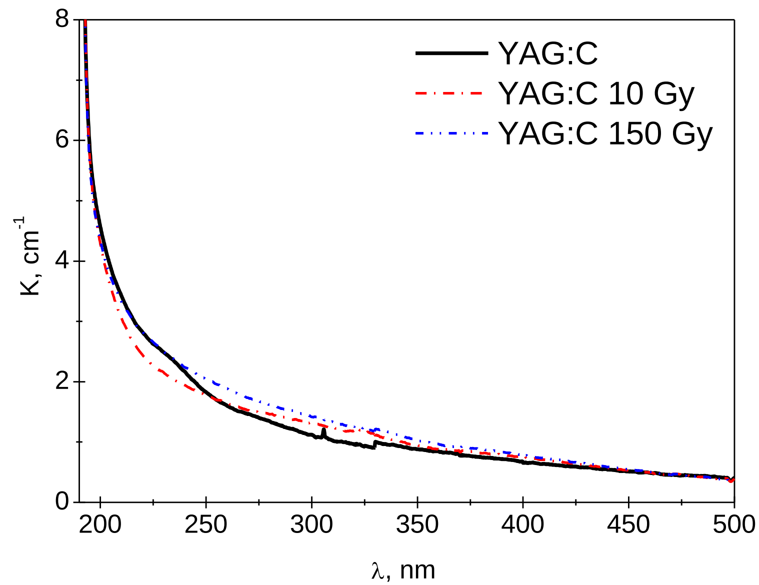


- ❑ $YAG_{W,Mo}$ bleaches after both oxidizing and reducing annealing!
- ❑ The bleaching of $YAG_{W,Mo}$ is not reversible by any further annealing

Effect of annealing on absorption in YAG:C



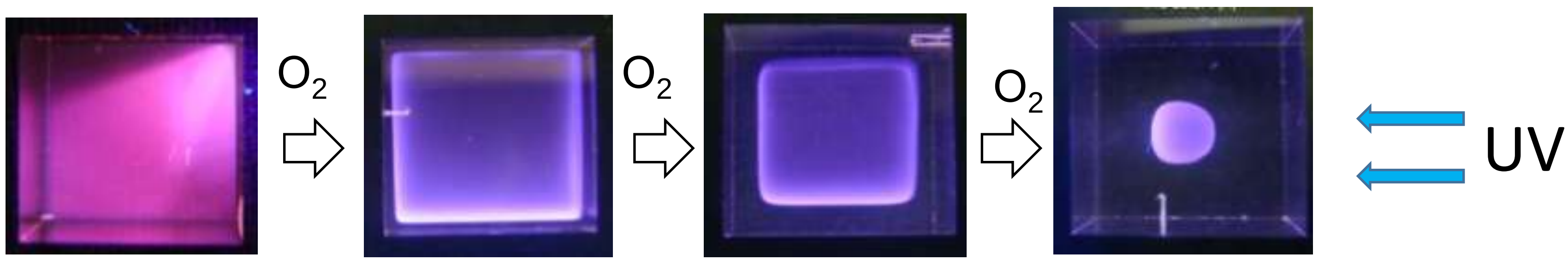
YAG_{Mo} absorption spectra:
a – as grown,
b – after oxidizing annealing during 3 hours,
c – after reducing annealing during 6 hours,
d – after oxidizing annealing during 25 hours.



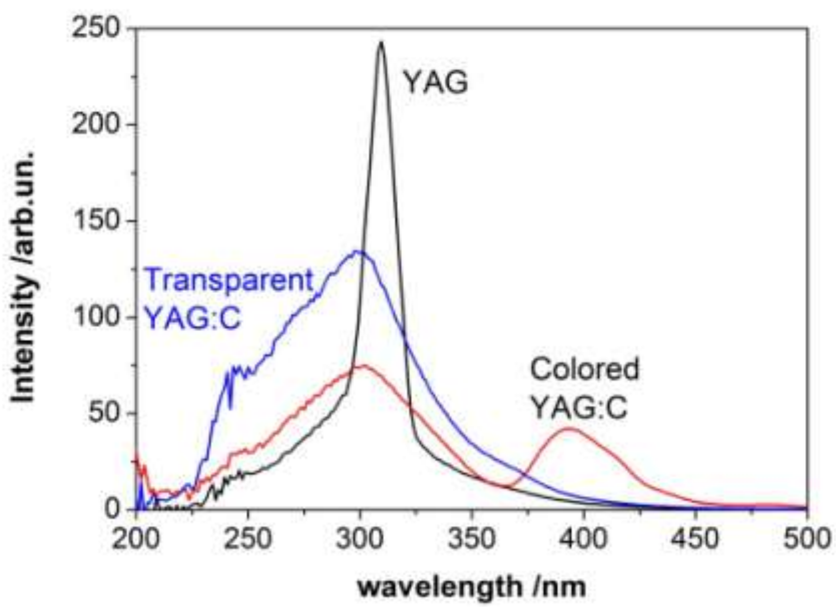
Good radiation hardness of annealed YAG:C

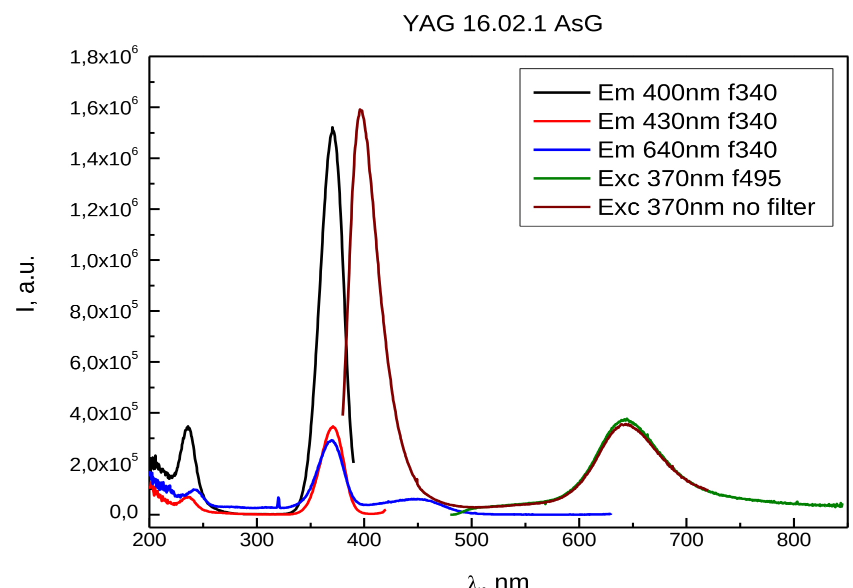
- The similar behavior of optical transmission in annealed YAG:C grown in Mo, W, Ir crucibles points that the high transmission is linked just to the carbon presence;
- Likely, after annealing, carbon-related defects compete with garnet intrinsic defects for electron capture thus blocking F^{+}- center formation

Blue F^+-center luminescence in YAG:C



YAG:C

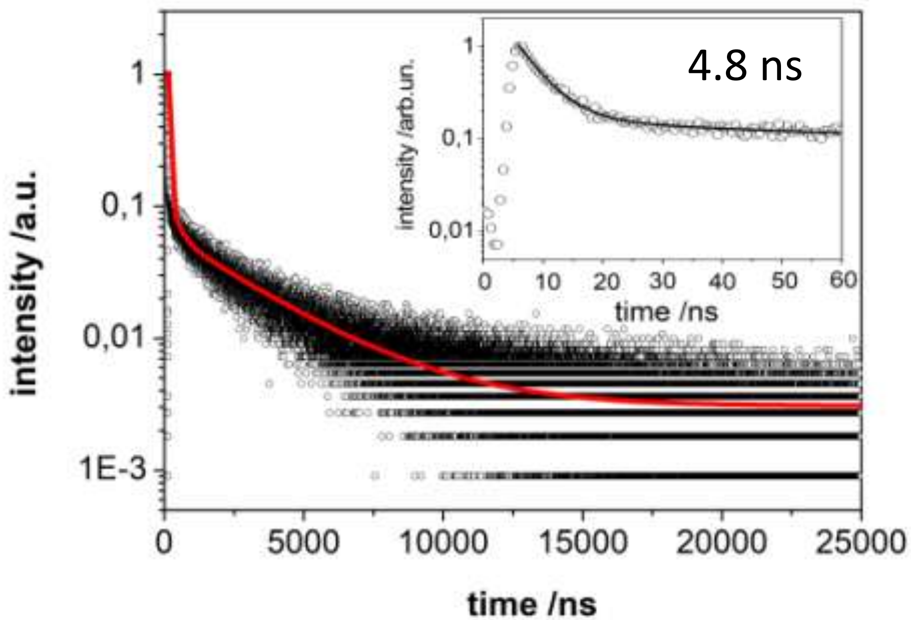


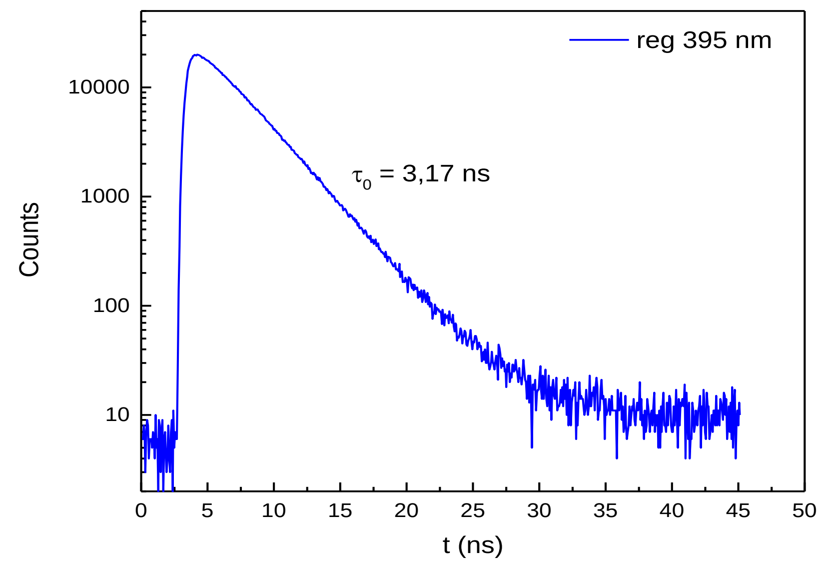


400 nm luminescence in **YAG** is attributed to F^+ -centers localized near Y_{Al} antisite*

*Y. Zorenko, IOP Conf. Series: Materials Science and Engineering **15** (2010) 012060

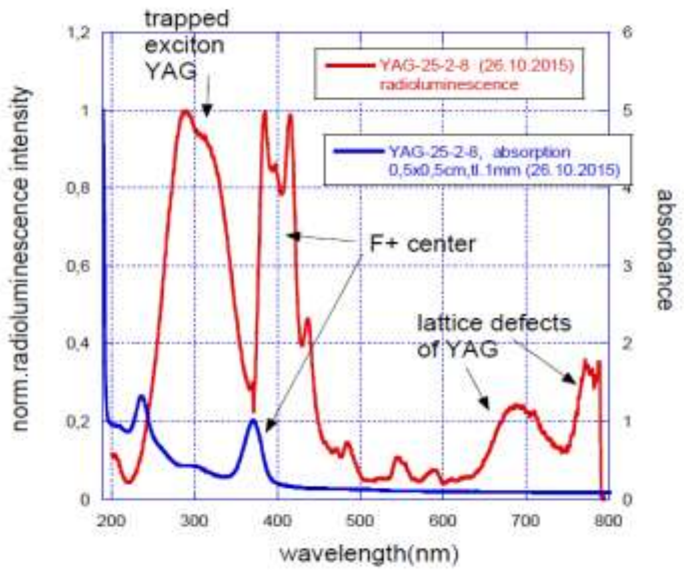
Fast luminescence decay in YAG:C

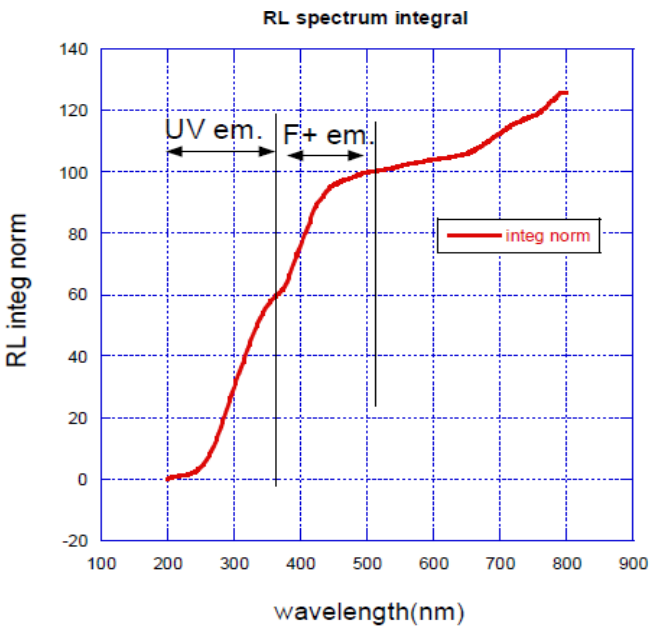




- The fast F+-center luminescence with 4-6 ns decay time under X-rays and 3 ns under UV-exc.
- Light yield up to 22700 phot/MeV under 137Cs

Spectral composition of YAG:C luminescence





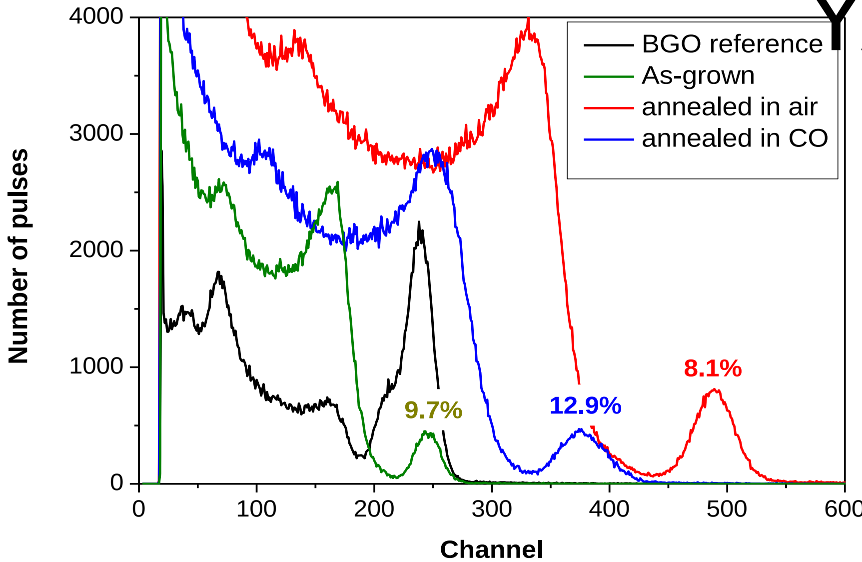
- ~60% comes from UV host emission and ~40% from F^+ center.
- In the scintillation decay, however, only 4% comes directly from F^+ centers. Therefore, the major part of F^+ emission comes from energy transfer from UV band

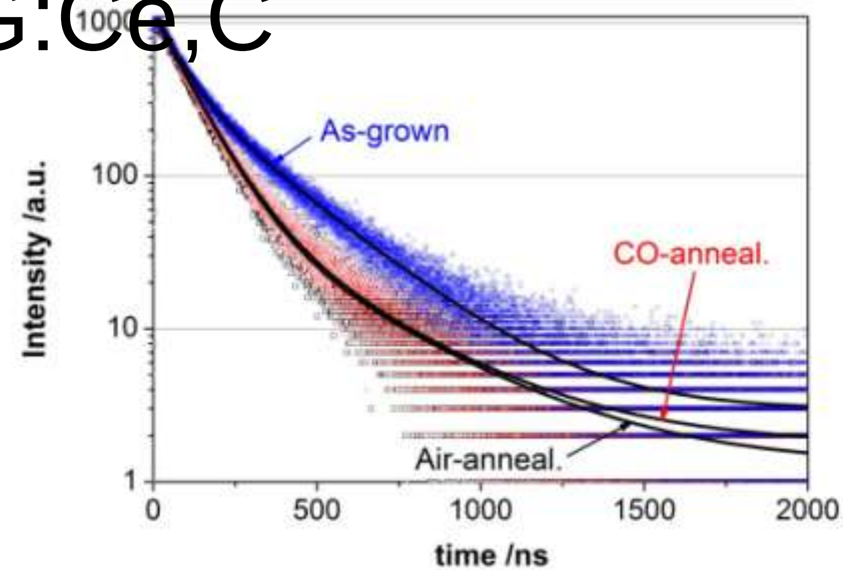
Fast scintillation component contribution can be increased by diminishing the UV-host emission

Scintillation properties of YAG and YAG:C

	Colored YAG:C (this work)	Colored YAG	Transparent YAG:C (this work)	Transparent YAG
Light yield, phot/MeV	up to 22700	50000/5.5 MeV [Seki, 2012]	up to 20000	14300 [Fujimoto, 2014] 60000/5.5MeV [Seki, 2012]
Luminescence decay times, ns	~5 + slow	3-4 + slow [Varney, 2012] 35, 179, 974 [Seki, 2012]	~ 400 + slow	460 [Fujimoto, 2014] 3-4, 750-1000 [Varney, 2012] 51, 373 [Seki, 2012]
Radiation hardness	Bad	No data	Good	Good
Energy resolution at 662 keV, %	~19	16-18 [Varney, 2012]	17	11-14 [Varney, 2012]

Scintillation parameters of YAG:Ce,C

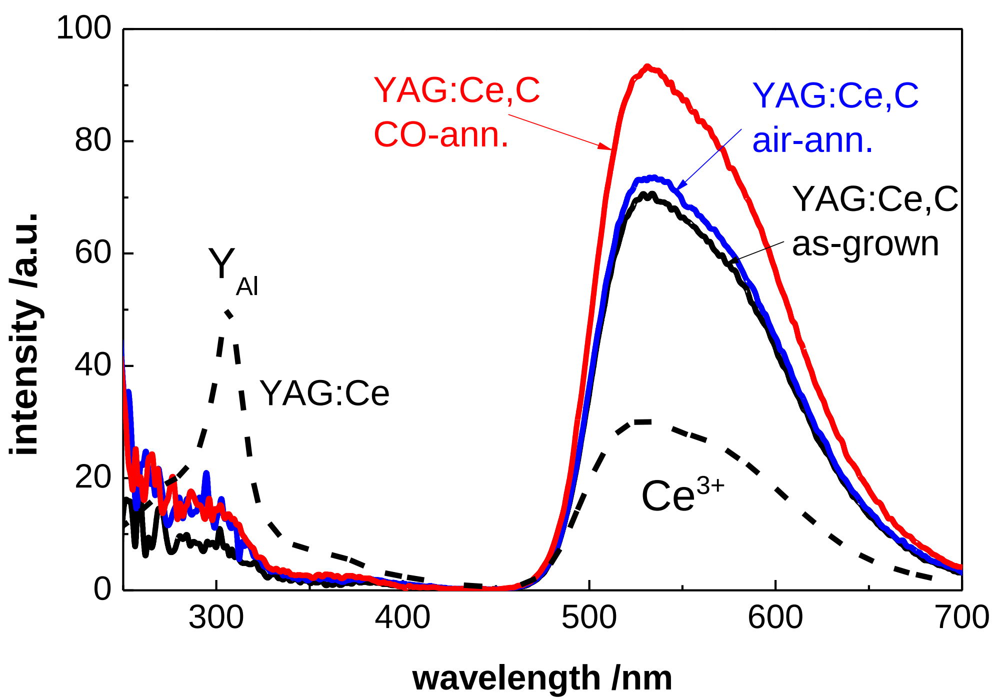


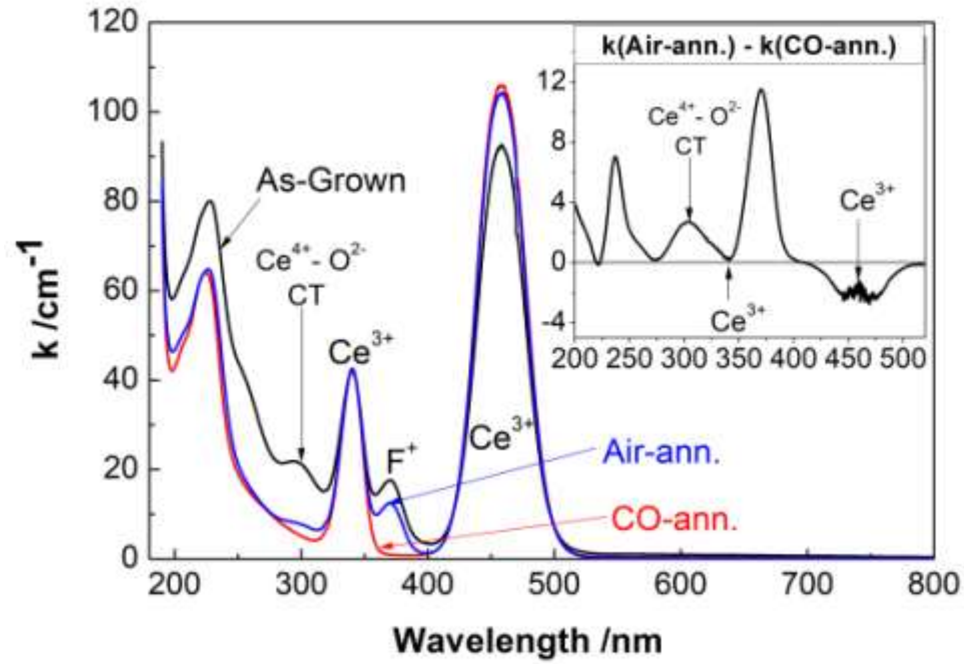


Crystal	Growth method	Crucible material	Light yield [phot MeV^{-1}]	Energy resolution [%]	Decay times [ns]	Background level [%] after 3 µs
YAG:C,Ce	Cz, as-grown	Mo/W	14200	9.7	73 (30%), 254 (70%)	2.94
YAG:C,Ce	Cz, CO-anneal.	Mo/W	21700	12.9	100 (77%), 331 (23%)	1.77
YAG:C,Ce	**Cz, Air-anneal.**	**Mo/W**	**28200**	**7.8 -8.5**	**98 (79%), 349 (21%)**	**1.30**
YAG:Ce [1]	HDC	Mo	15000-18000	8-10	-	-
YAG:Ce [2]	Cz	No data	16700	-	-	-
YAG:Ce [3]	Cz	No data	-	-	119+slow	-
YAG:Ce [4]	Cz	Mo	30000	-	-	-

[1] S. Nizhankovsky, *Funct. Mater*. **2008**, *15*, 546; [2] M. Moszynski, *IEEE Trans. Nucl. Sci.* **1997**, *44*, 1052;
[3] E. Mihokova, *J. Lumin*. **2007**, *126*, 77; [4] M. Nikl , *J. Lumin*. 169 (2016) 539

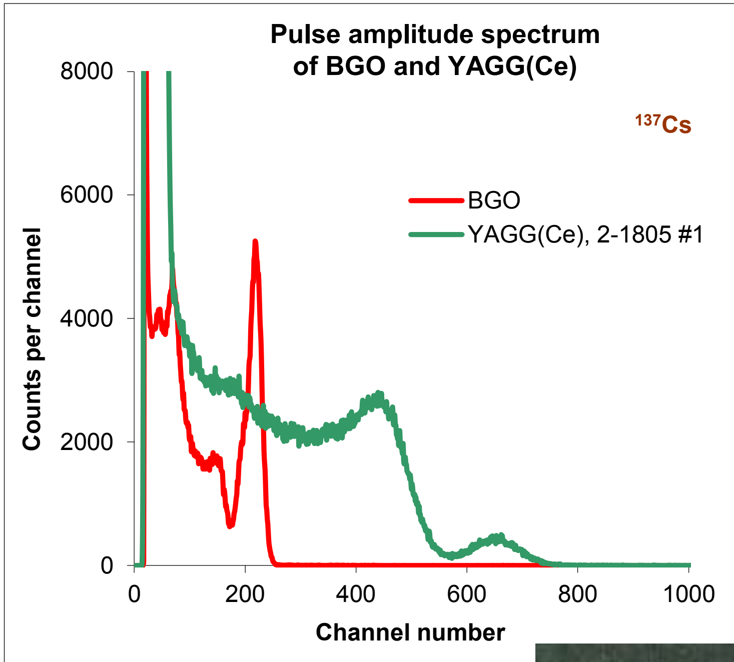
Ce3+ ↔ Ce4+ transformations in YAG:Ce,C

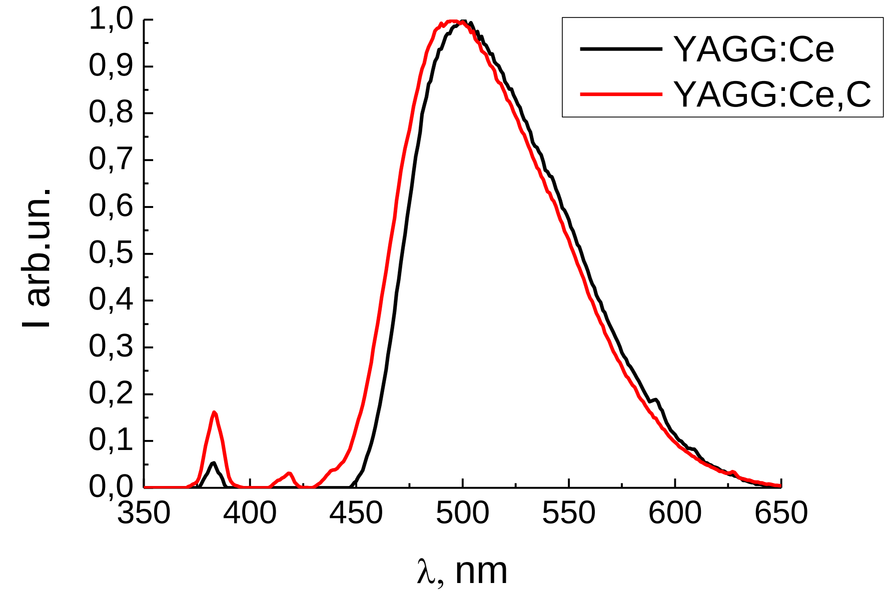




- ❑ The highest RL intensity is achieved in CO-annealed samples
- ❑ UV-absorption irreversibly decreases after annealing

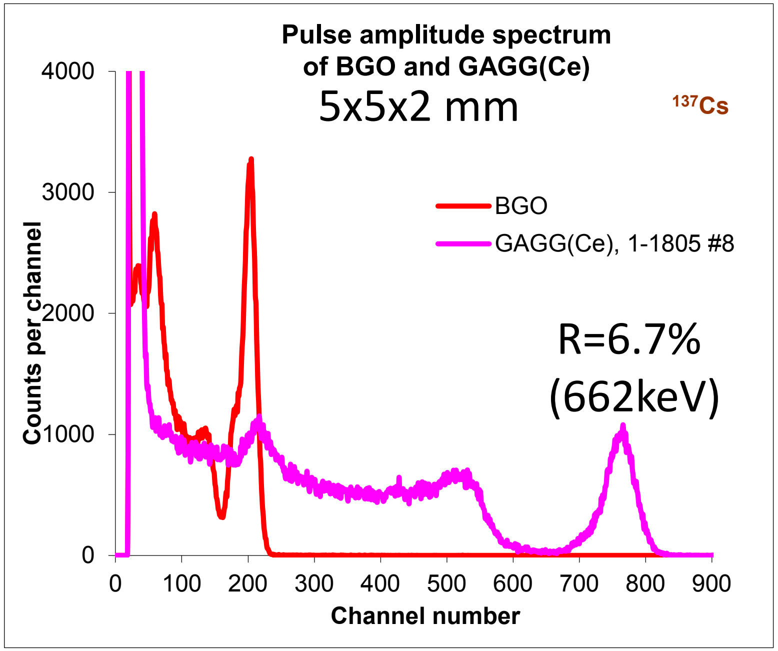
YAGG:Ce,C

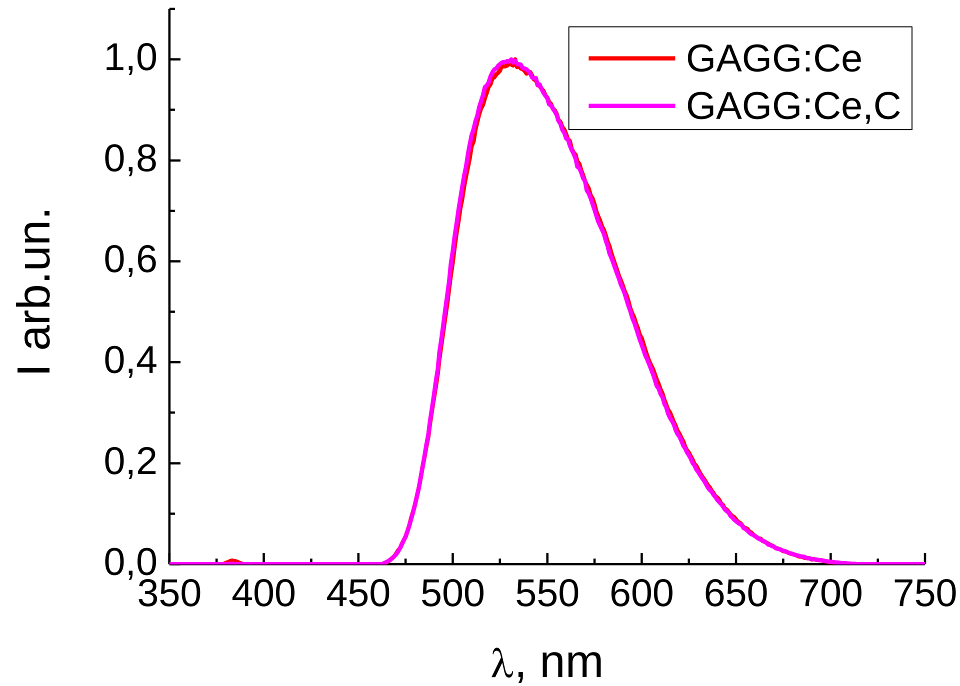




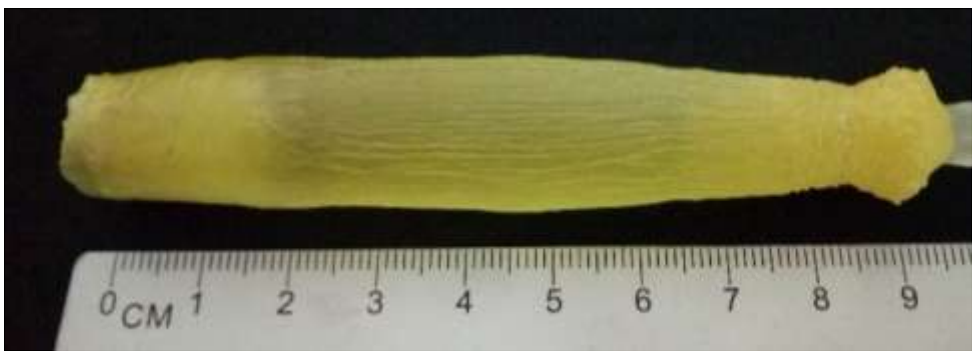
Light output of YAGG:Ce,C = 300 % BGO = 125% YAGG:Ce (~40000 phot/MeV)

GAGG:Ce,C



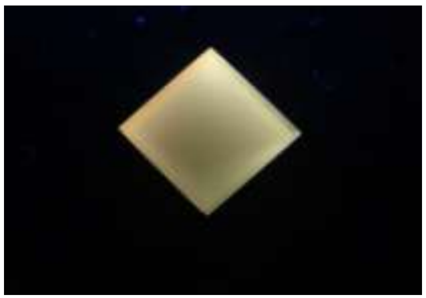


Light output of GAGG:Ce,C = 370 % BGO = 110% GAGG:Ce (52000 phot/MeV)



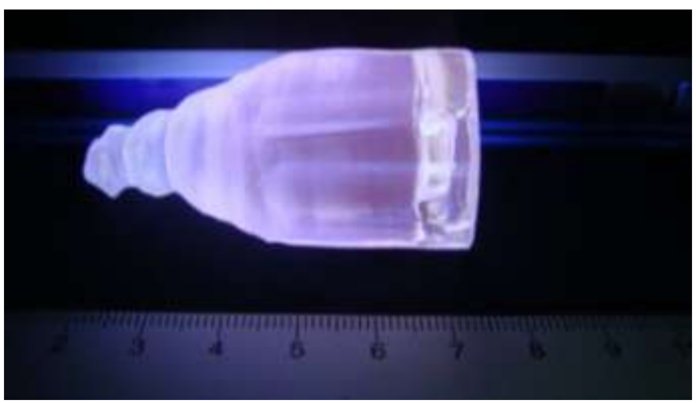
Other crystals grown by this technology in ISM

YAP:C



LuAG:Sc,C

LuAG:Pr,C



Summary

- C-doped YAG demonstrates the highest ever published light yield of up to 22700 phot/MeV and the fast F^{+}-center luminescence decay component of 4-7 ns;

- YAG:Ce,C crystals possess a very high light yield >28000 phot MeV^{-1} and a good energy resolution of ~8 % at 662 keV. The contribution of fast ~100 ns luminescence decay component in air-annealed YAG:Ce,C reaches 79 %;

- Enhancement of the light yield by 10-25% is registered in YAGG:Ce and GAGG:Ce at C-codoping;

- C-doping calls the formation of F^{+}-centers in YAG (but, somehow, blocks F^{+}-center formation in annealed crystals), and promotes the $Ce^{3+} \rightarrow Ce^{4+}$ transformation in Ce-doped garnets.

Intelum
H2020-MSCA-RISE-2014, no.644260

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