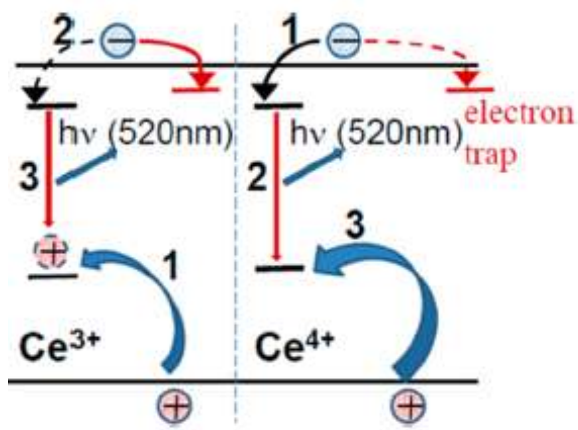
Growth of garnet and perovskite scintillators with non-isovalent minor components and related effects

A. Petrosyan[1], K. Hovhannesyan[1], M. Derdzyan[1], A. Yeganyan[1], R. Sargsyan[1], F. Moretti[2], C. Dujardin[2]

[1]*Institute for Physical Research, National Academy of Sciences, 0203 Ashtarak, Armenia*
[2]*Institut Lumière Matière, UMR 5306 Université Lyon 1-CNRS, Villeurbanne, France*

Co-doping Ce-materials with divalent impurities to stabilize Ce4+

S. Blahuta, et al, IEEE Trans. Nucl. Sci., 2013; **LYSO:Ce,Ca(Mg)** - **Czochralski**
M. Nikl, et al, Cryst. Growth & Design, 2014; **LuAG:Ce,Mg** - **micro-pulling**



Due to addition of divalent impurities, a partial oxidation of Ce3+ into Ce4+ takes place.

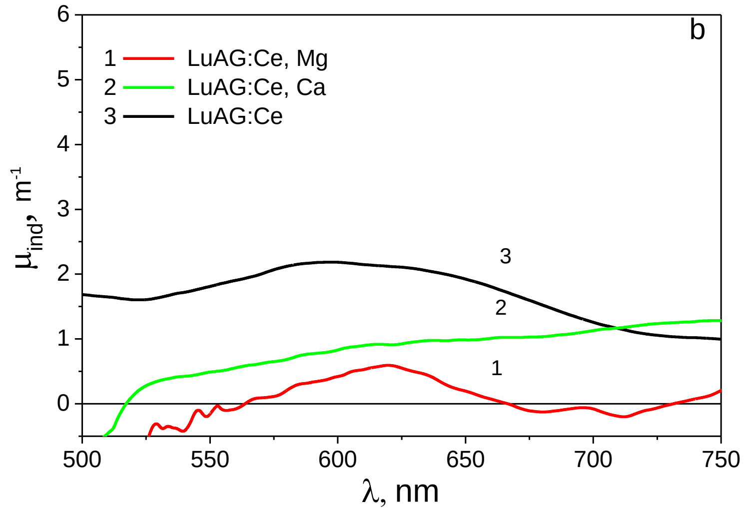
What are advantages of Ce4+?

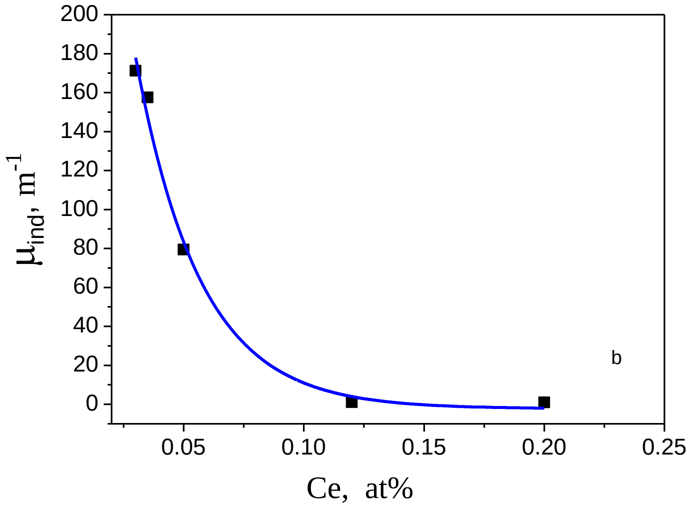
- Ce4+ can be considered as a pre-prepared Ce3+ which has already trapped a hole. This avoids the delays in hole trapping prior to electron trapping in the case of Ce3+.

- The result is acceleration of the decay and suppression of long decay components.

Can the divalent co-doping approach be useful for materials other than silicates and garnets?
Can co-doping with monovalent impurities be applied to stabilize Ce4+?

Radiation hardness





Induced absorption for Ca and Mg co-doped crystals (1 kGy).

Variation of induced absorption at 620 nm with Ce concentration (Ca=100 ppm)

In addition, the fact that Ce^{4+} competes with other traps for electrons, Ca(Mg) co-doping improves the radiation hardness, if a proper balance between Ce and co-dopant concentrations is optimized

A.G. Petrosyan, et al, J. Cryst. Growth, 2015; **LuAG:Ce,Ca**

F. Moretti, et al, SCINT 2015; **LuAG:Ce,Ca(Mg)**

Contents: materials and characterization

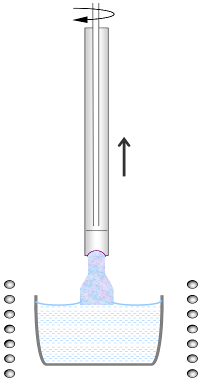
- Can the divalent co-doping approach be useful for materials other than silicates and garnets?
- Can co-doping with monovalent impurities be applied to stabilize Ce^{4+}?

- **YAP : Ce, Ca**
- **YAG : Ce with Li^+ and Na^+**
- **Crystal chemistry and substitution**
- **Defects (examples for LuAG:Ce,Ca(Mg)**
- **Absorption**
- **Annealing effects**
- **Compositions which can be readily grown as quality single crystals**

Perovskite single crystals with Ca co-doping

- **Czochralski $YAlO_3$: Ce,Ca**

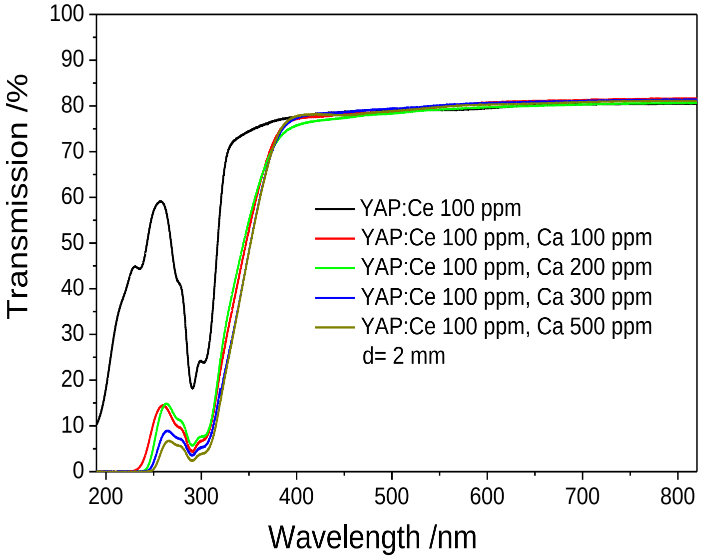
- (1) [Ce]= 1 at% (in the melt), [Ca]= 0, 100, 300, 500 ppm
- (2) [Ce]= 100 ppm (in the melt), [Ca]= 0, 100, 300, 500 ppm



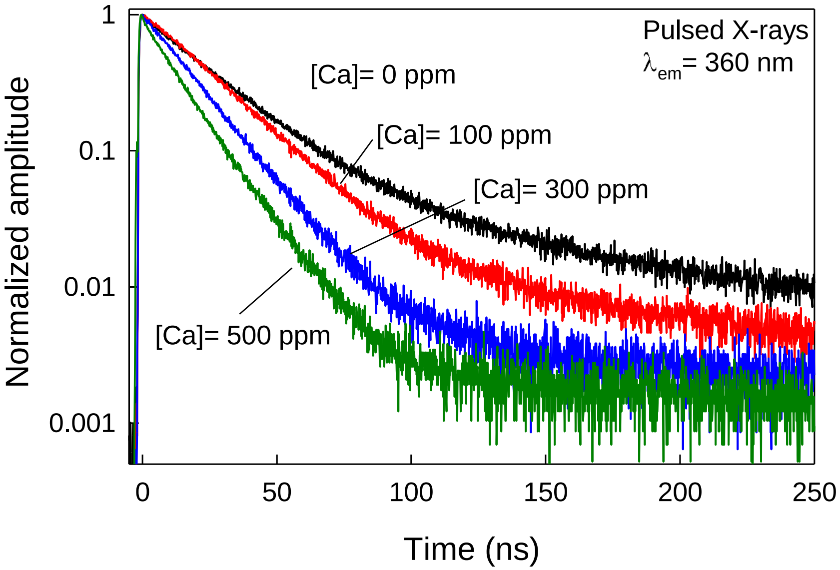
No degradation of crystalline quality is observed for introduced concentrations of Ca, so that single crystals can be grown under conditions usually applied to YAP:Ce

YAP : Ce,Ca

Transmission of YAP:Ce,Ca series



Decay



Decay is accelerated with increasing Ca concentration, which is a positive effect. The radioluminescence intensity is however decreased; among the reasons is the degrading transmission in the range of emission (300-450 nm).

Similar effects were recorded in LuAP:Ce,Ca

F. Moretti , et al, ICDIM 2016

Garnet single crystals

Vertical Bridgman method; tested compositions:

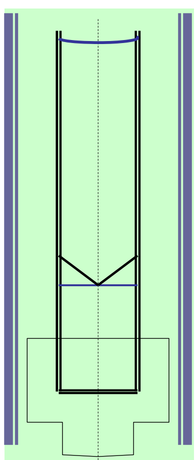
(1) LuAG:Ce,Ca (Ce = 0.5-1 at%; Ca = 50 - 300 ppm)*

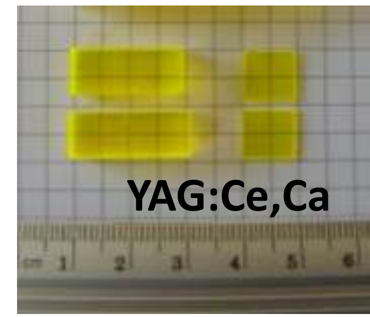
(2) LuAG:Ce,Mg (Ce = 0.5–1 at%; Mg = 50–150 ppm)

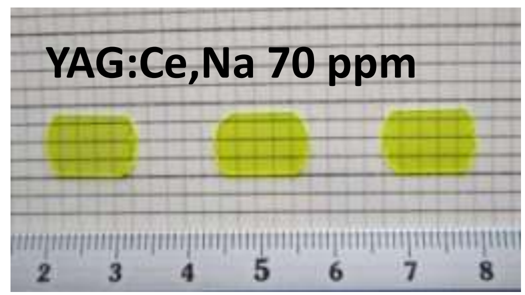
(3) YAG:Ce,Ca (Ce = 0.5 - 1 at% ; Ca = 200 ppm)

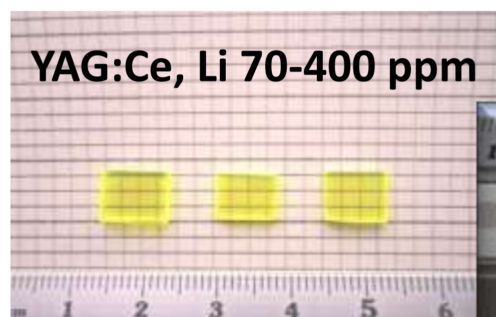
(4) YAG:Ce,Li (Ce = 0.7 at% ; Li = 30 – 420 ppm)

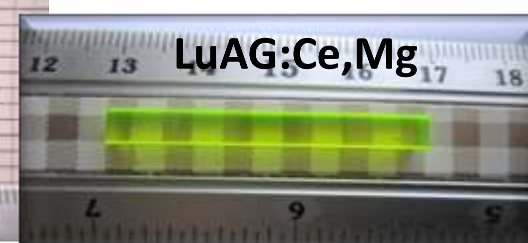
(5) YAG:Ce,Na (Ce = 0.7 at% ; Na = 70 ppm)











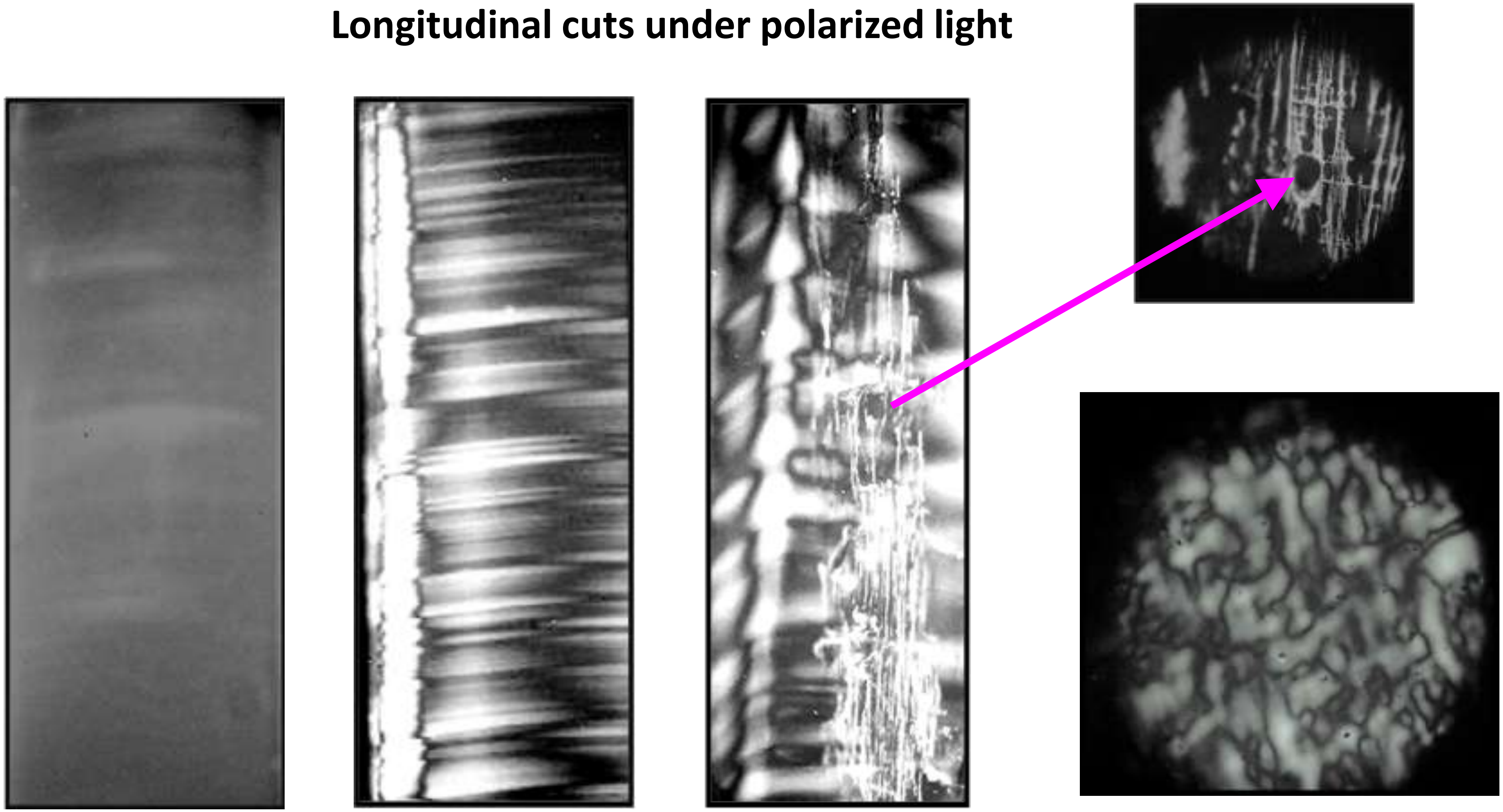
*)K. Hovhannesyan, et al, ICDIM 2016

Melt compositions for quality crystals

- **YAP: Ce, Ca** - Ce ≤ 1%, Ca ≤ 500 ppm
- **LuAP: Ce, Ca** - Ce ≤ 0.5%, Ca ≤ 100 ppm
- **LuAG: Ce, Ca** - Ce ≤ 0.8 %, Ca ≤ 150 ppm
- **LuAG: Ce, Mg** - Ce ≤ 0.8 %, Mg ≤ 150 ppm
- **YAG: Ce, Ca** - Ce ≤ 1 %, Ca ≤ 200 ppm
- **YAG:Ce, Li** - Ce ≤ 1 %, Li ≤ 420 ppm
- **YAG: Ce, Na** - Ce ≤ 0.7 %, Na ≤ 70 ppm

Defects in LuAG:Ce,Ca

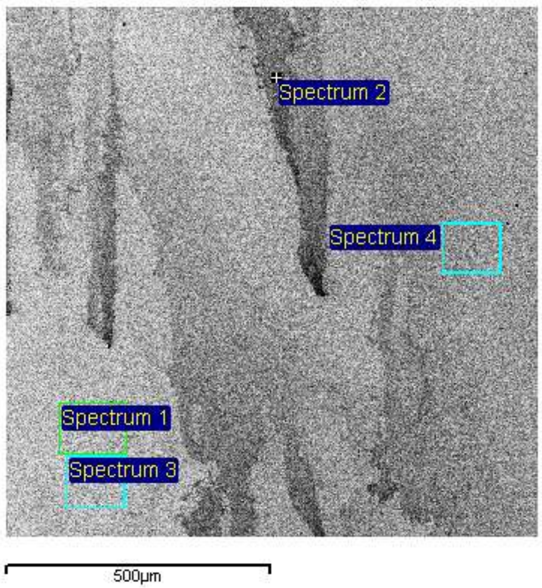
Longitudinal cuts under polarized light



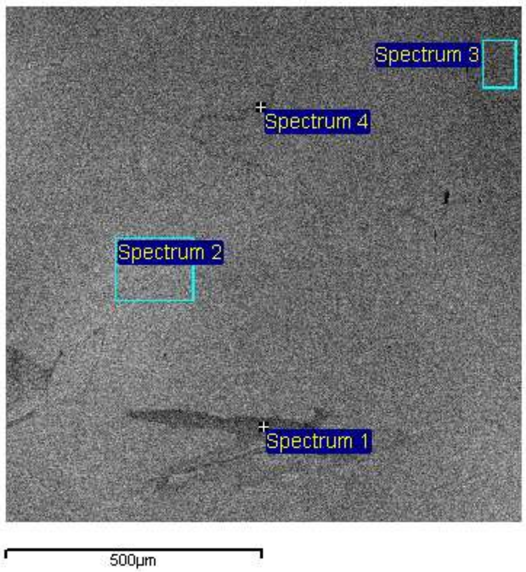
Ca = 0   **Ca = 100 ppm**   **Ca = 250 ppm**   **Ca = 300 ppm**

Defects

LuAG:Ce,Ca100 ppm, Mg 60 ppm



LuAG:Ce, Mg 150 ppm

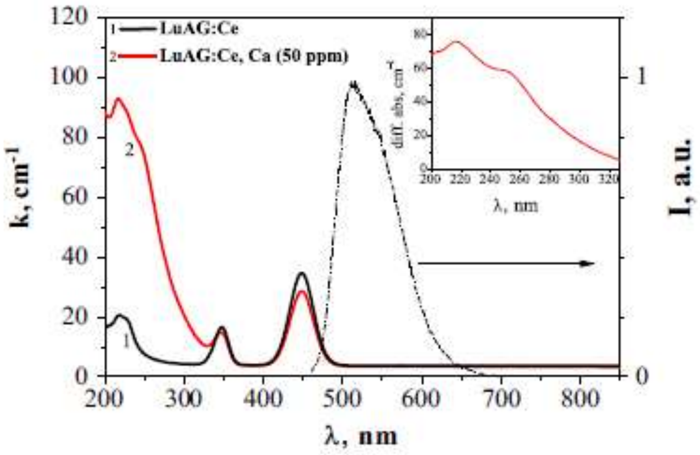


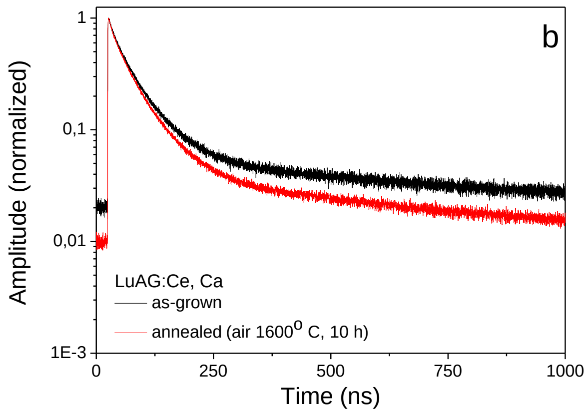
Microphotographs obtained by the detector back-scattered electrons. Microanalysis performed on the scanning electron microscope (SEM) VEGATS 5130MM with the system INCA Energy 300 of EDS microanalysis.

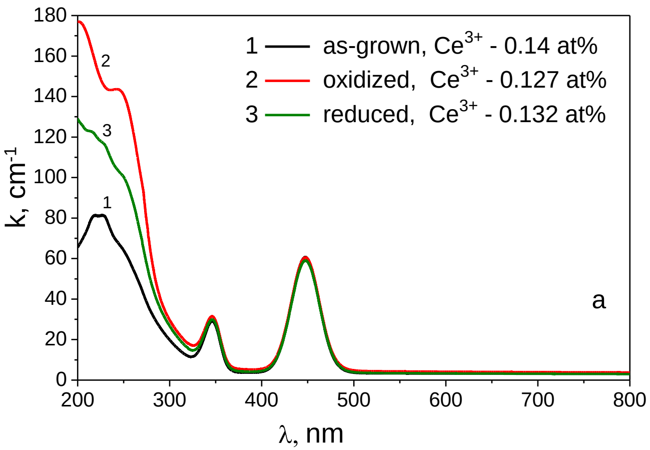
The concentration of Ce is non-homogeneous, increasing in dark spots

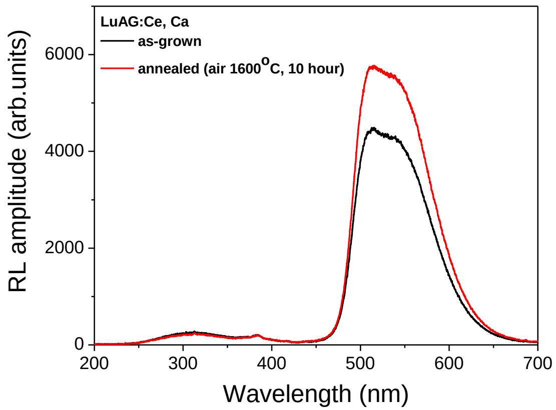
Annealing effects

LuAG: Ce, Ca









Oxidizing annealing is efficient to increase the concentration of Ce4+ , so that lower amounts of 2+ co-dopants can be introduced

Li and Na in garnets

Li^+ : a and d sites

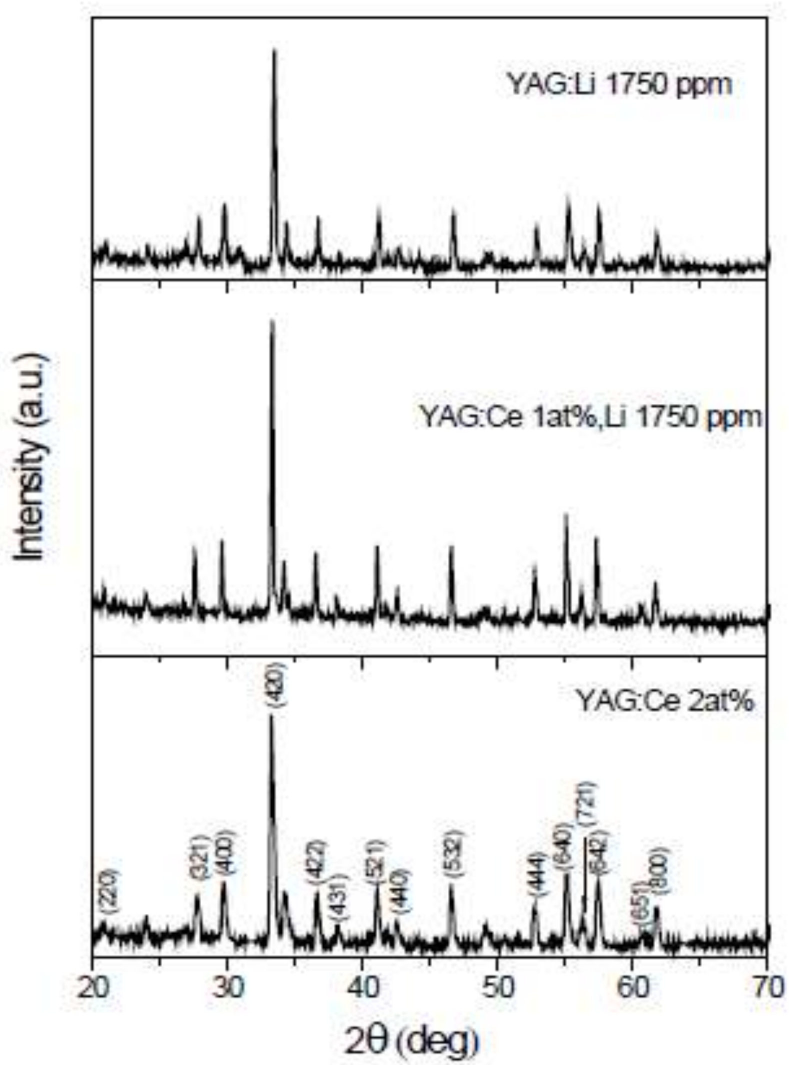
$\{Ca_3\}$ [Li M^{2+}] (V_3) O_{12} M=Mg, Co, Ni, Cu, Zn - Vanadates with garnet structure (G. Bayer, 1965)
$\{Na_3\}$ $[Al_2]$ (Li_3) F_{12} – cryolithionite (G. Menzer, 1930)

Na^+ : c sites

$\{NaCa_2\}$ $[Mn_2]$ (As_3) O_{12} - berzelit (F. Machatschki, 1930)
$\{Na_3\}$ $[Al_2]$ (P_3) O_{12} - (E. Thilo, 1941)

YAG:Nd,Li - P. Arsenev, et al, phys. stat. sol (a) 1973
LuAG:Ce,Li - K. Kamada, M. Nikl, et al, J, Crystal Growth 2016 (accepted paper)

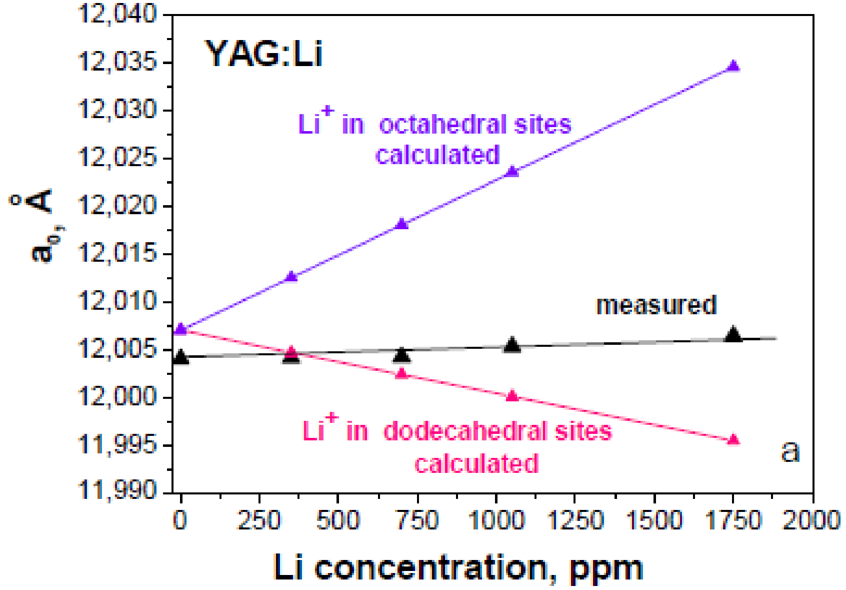
X-ray diffraction in YAG:Ce with Li co-doping

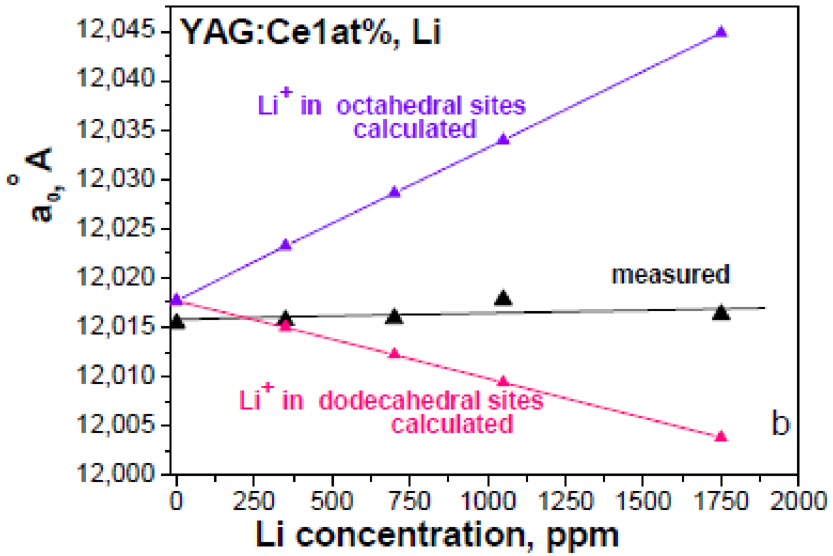


Ceramic samples
1600 C, air

Single phase garnet structure is conserved in YAG:Li and YAG:Ce,Li even at very high Li concentrations (1750 ppm).

Lattice parameters of YAG:Li and YAG:Ce,Li

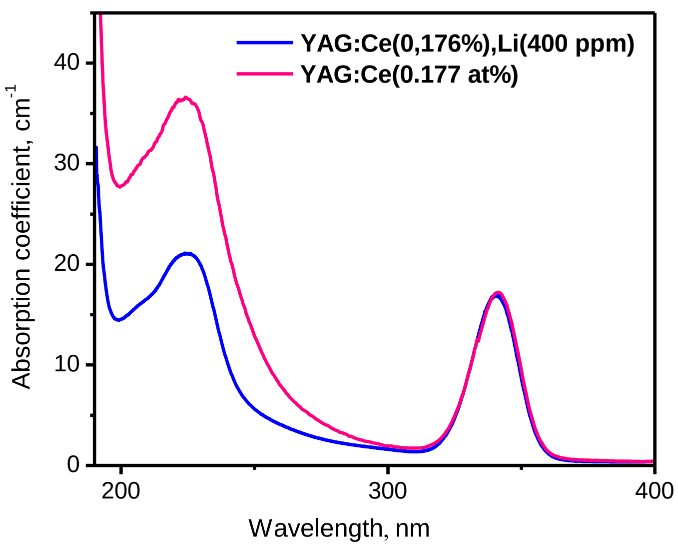


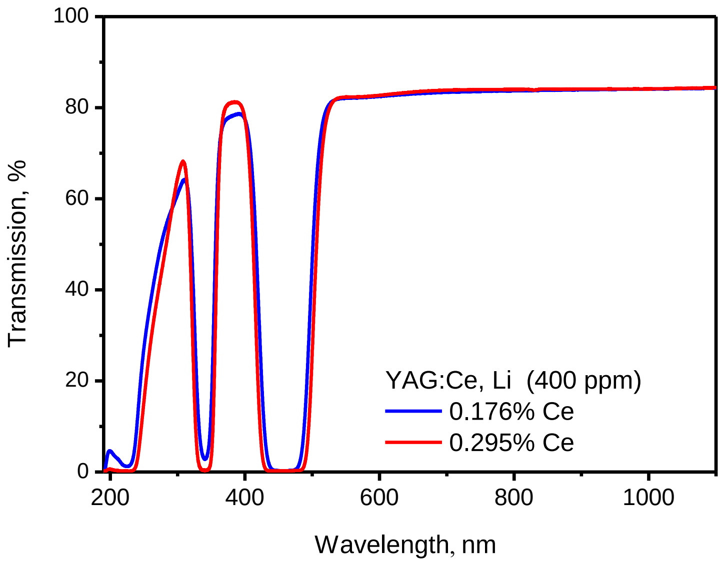


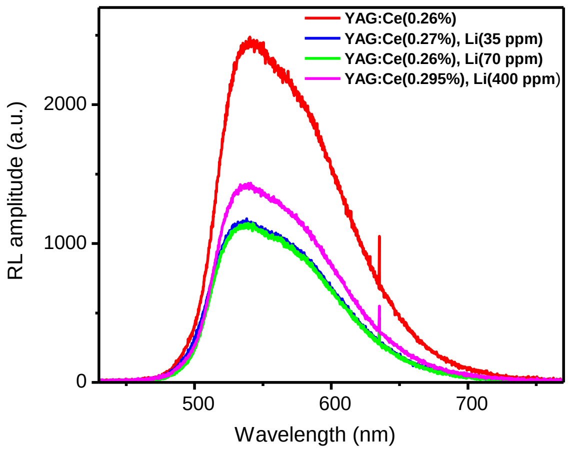
Li^{+} - 0.92 Å (8); 0.76 Å (6). Y3+ - 1.02 Å (8). Al3+ – 0.53 Å (6)

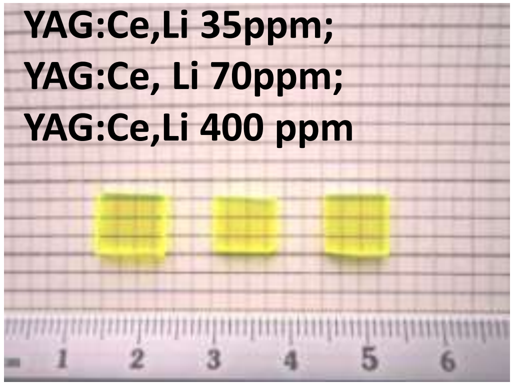
Most of Li+ probably goes to interstitial positions

YAG:Ce, Li single crystals

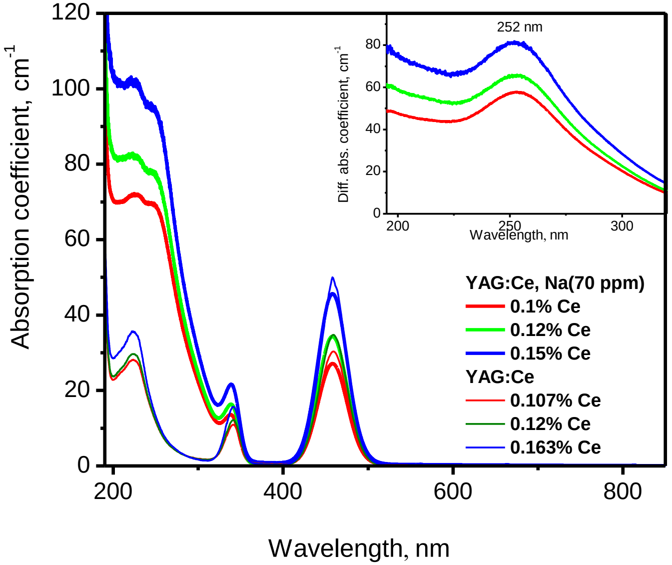


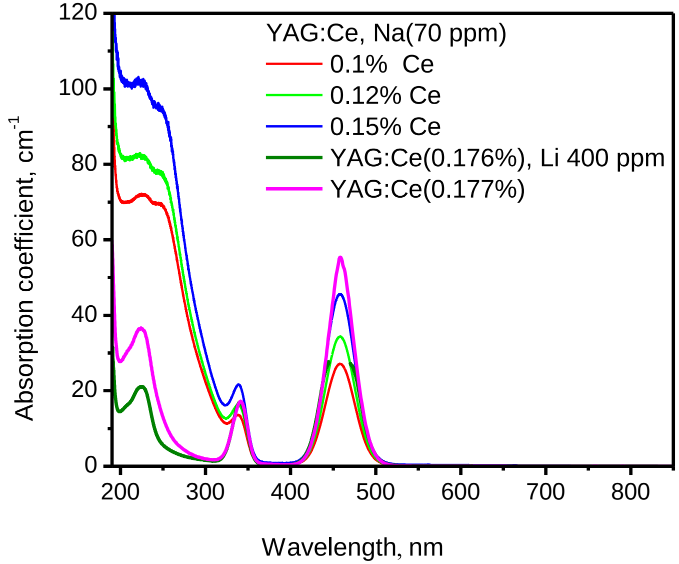






Co-doping of YAG:Ce with Na+





Absorption in UV in Na co-doped crystals is high, comparable to those in Ca or Mg co-doped.

Na+ is efficient to stabilize Ce4+ states

Summary

- **The maximum concentrations of additional divalent or monovalent impurities that can be introduced, while conserving high quality of single crystals, were determined in different hosts .**
- **Oxidizing annealing of garnets is efficient to additionally increase the concentration of Ce4+.**
- **Co-doping of YAP with Ca leads to acceleration of the decay, however the emission intensity is decreased.**
- **Introduction of Li+ into YAG:Ce does not lead to formation of Ce4+ states. Basing on lattice parameters, it is suggested that Li+ goes to interstitial positions.**
- **Na+ is efficient to stabilize Ce4+ states in YAG:Ce single crystals.**

Thank you for your attention

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and
EU H2020 programme grant n. 644260
(INTELUM)

Experimental (ILM – CNRS)

Radioluminescence spectra were recorded at RT under X-ray irradiation. The excitation source was X-ray tube (Philips 2274) operated at 30 kV, 20 mA, exposure time is 5 seconds. Monochromator working in the range 430-770 nm and 230-570 nm for YAG:Ce,Li(Ca) and LuAG:Pr,Ca respectively.

Scintillation decay measurements were performed at room temperature under X-ray excitation using a picosecond pulsed laser (C10196; Hamamatsu Inc.) with 100 kHz and 0.2 mA, using interference filters YG11 and 320BP10 for YAG:Ce,Li(Ca) and LuAG:Pr,Ca respectively. To analyze the temporal histogram for the counts TCSPC module (PicoHarp 300) is adopted.