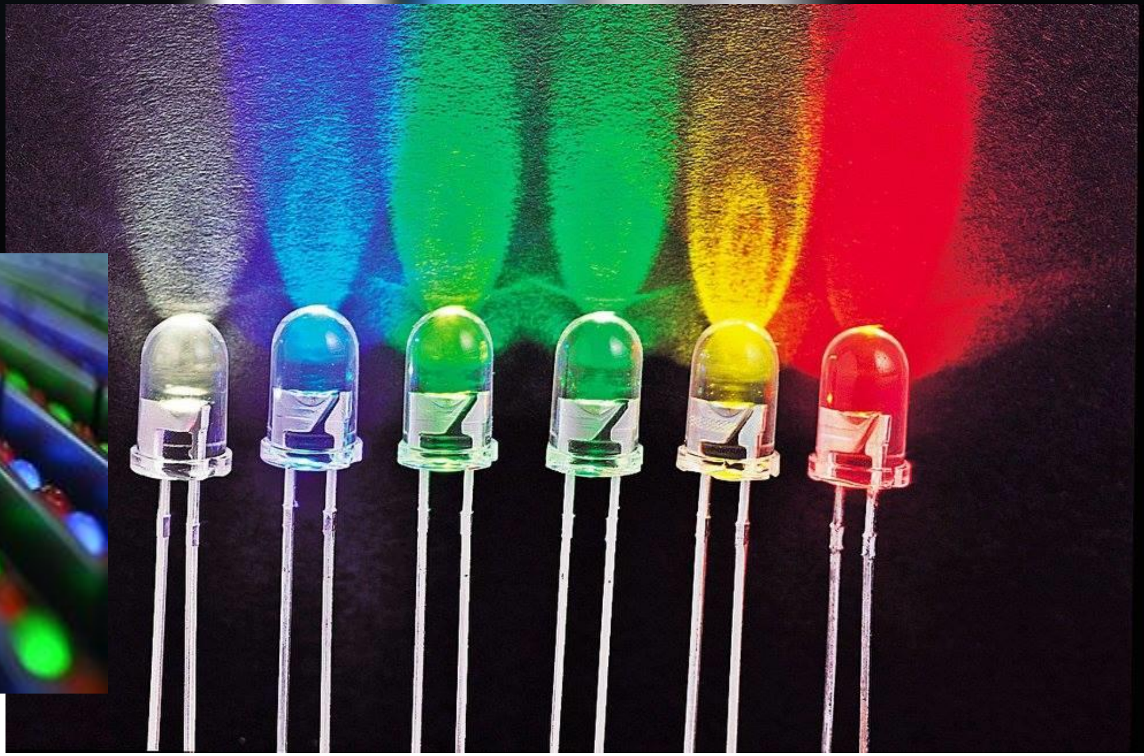
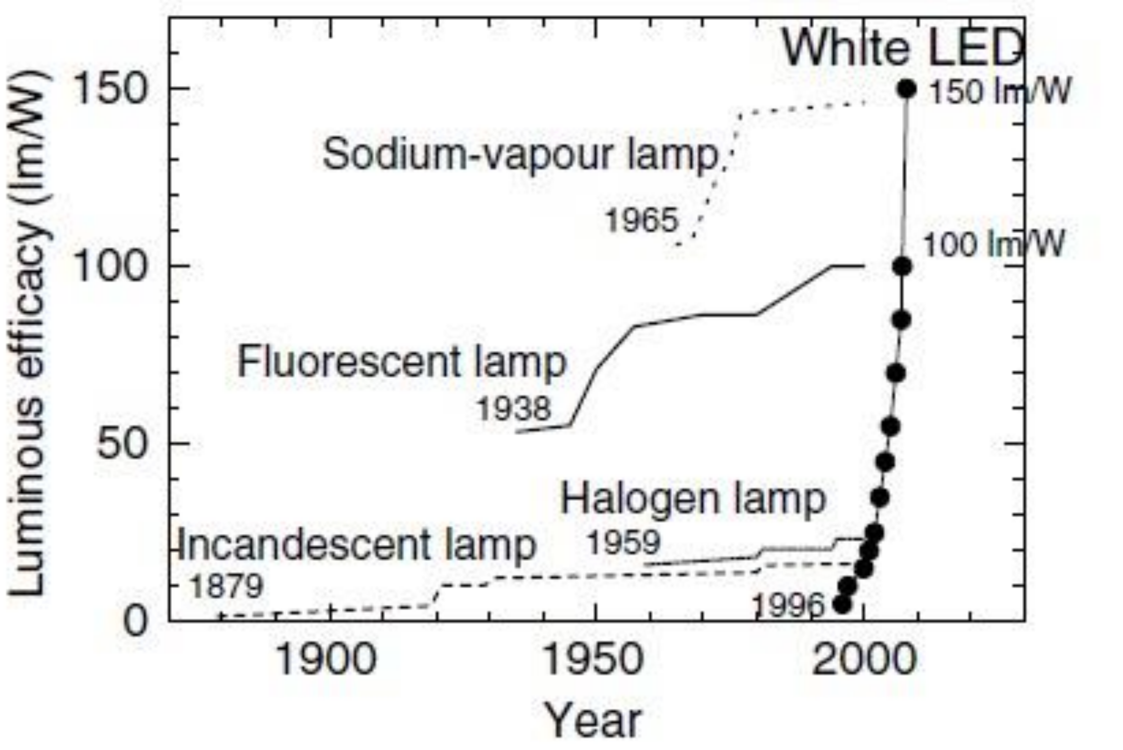
LED technology and LED phosphors

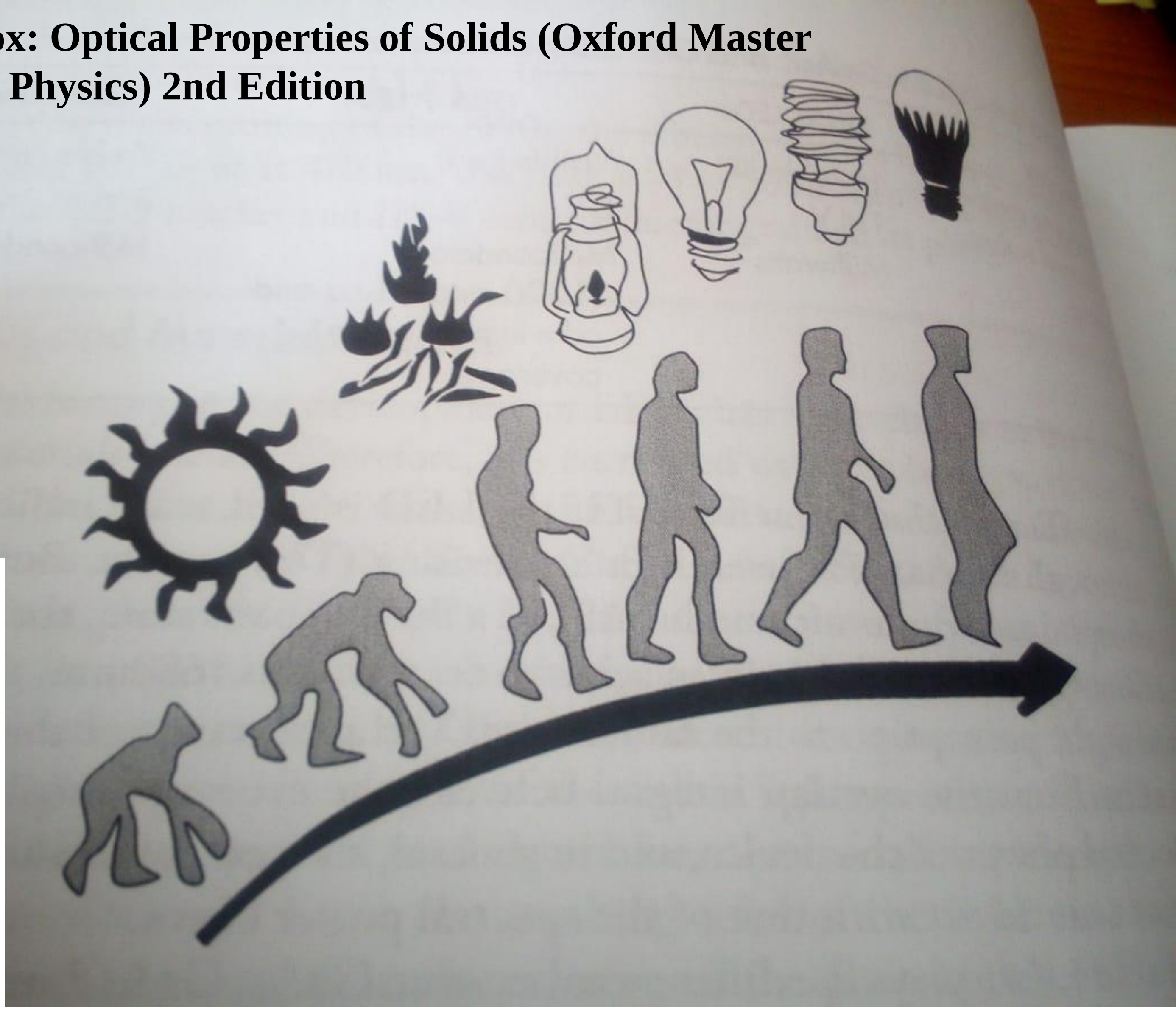


Outline

- Introduction to LEDs
- Short history
- Basic parameters + definitions
- Circadian light source
- Phosphor used nowadays
- Eu^{2+}-doped ternary sulfides
- Two centres circadian sources

Mark Fox: Optical Properties of Solids (Oxford Master Series in Physics) 2nd Edition

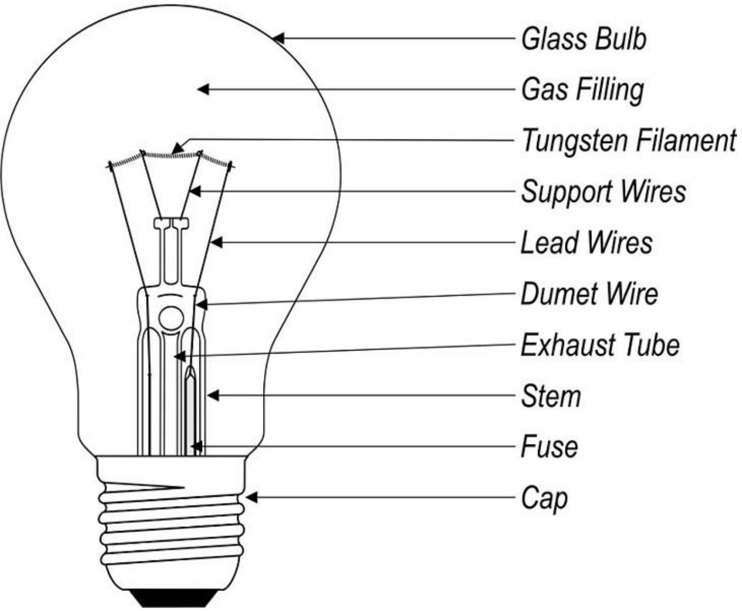




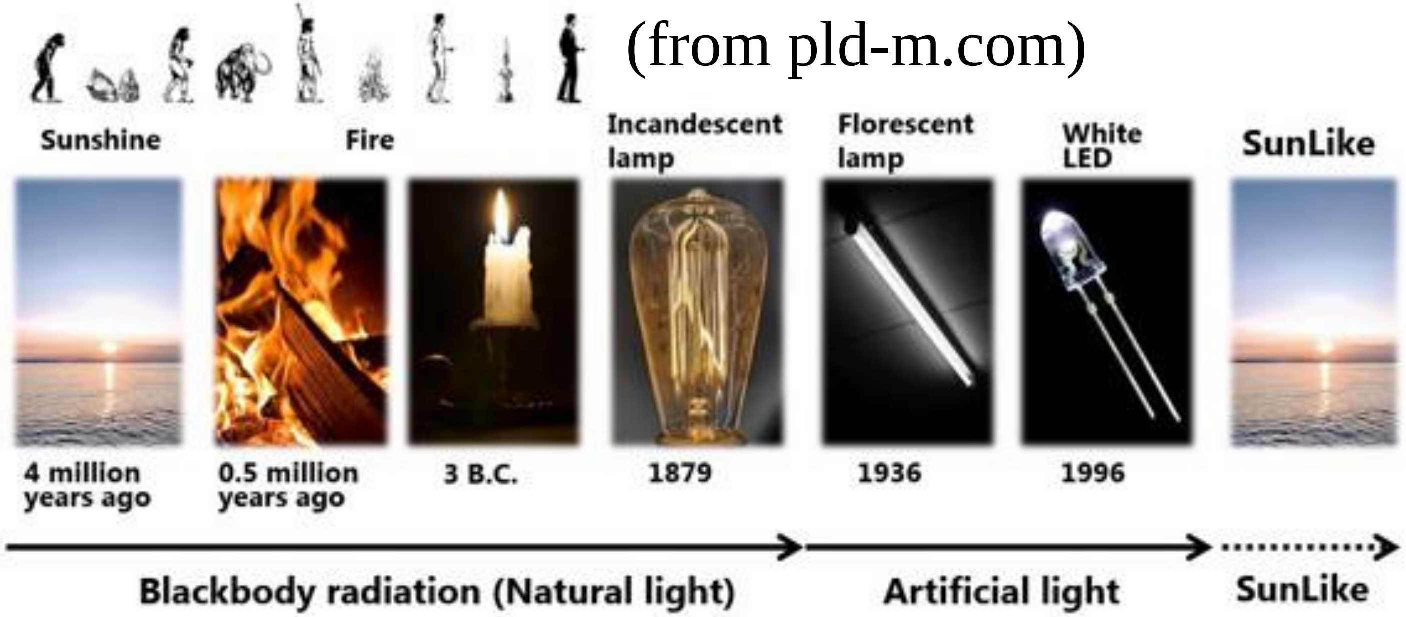
Lighting evolution → energy savings

History of light bulbs

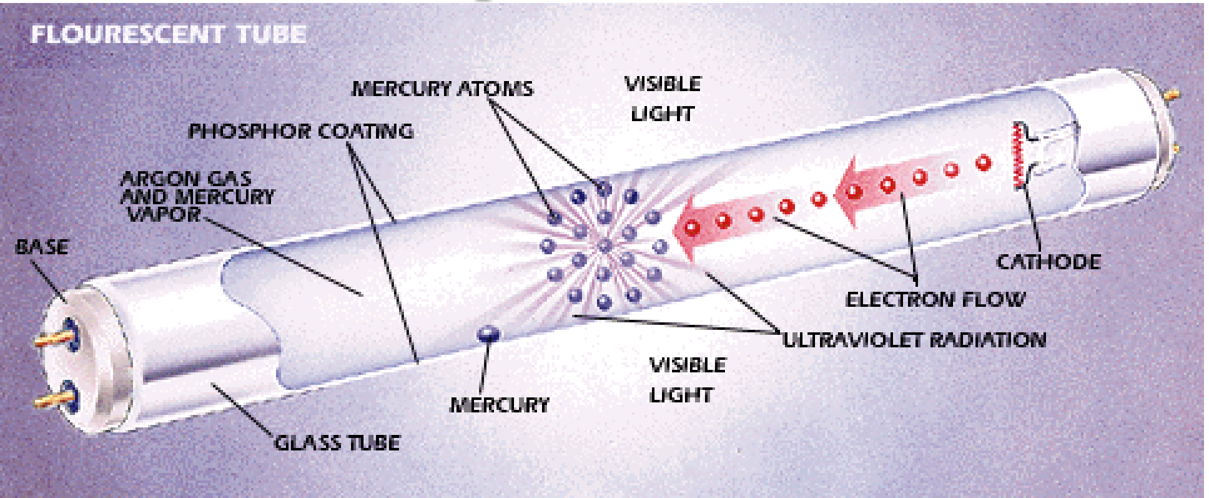
*incandescent lamp (from lamptech.co.uk)

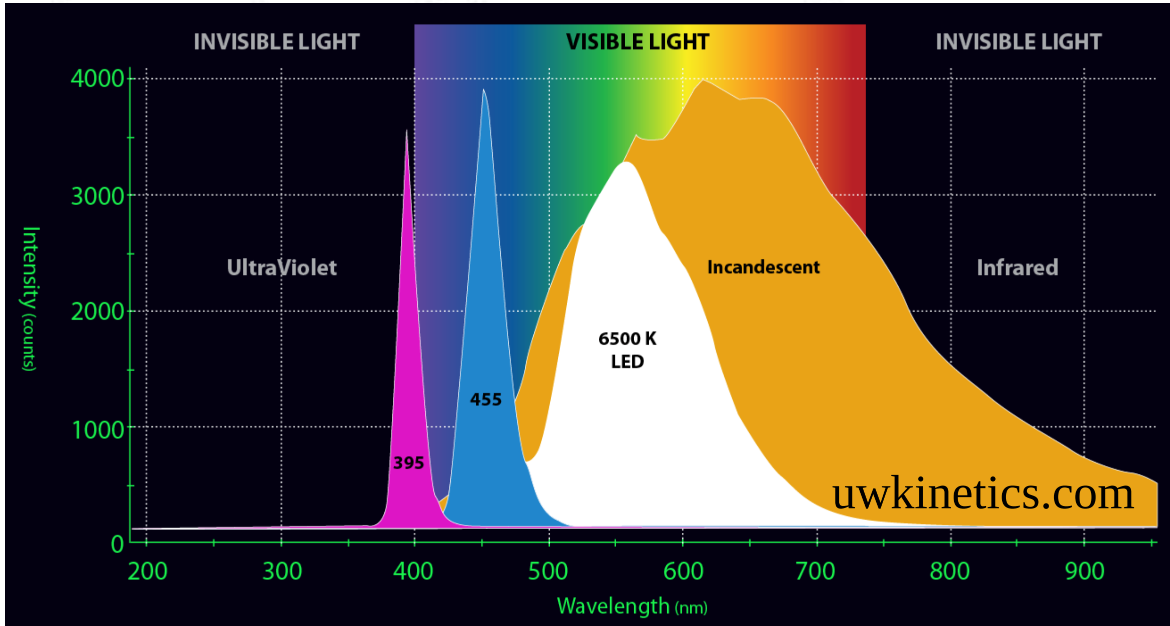


(from pld-m.com)



*fluorescent lamp (from ustr.sancaleve.com)





Short history of LEDs

- **Electroluminescence in semiconductors** discovered in 1907 by Joseph Henry Round in a piece of silicon carbide (SiC) → The weak light emission hampered further research;

- 1960s III-V semiconductors synthesized and the **first practical (red) LED built** (Nick Holonyak Jr – Godfather of the LED);

- 1990s, **green, yellow and red LEDs available** (better growth process of III-V semiconductors);

- No efficient blue or UV LEDs due to problems with the growth and doping of nitride materials;

- This technological´deficit resolved in 1995 by Shuji Nakamura (Nichia Chemical Industries Corporation) by the invention of **very efficient and intense blue LEDs based on the InGaN/GaN system**;

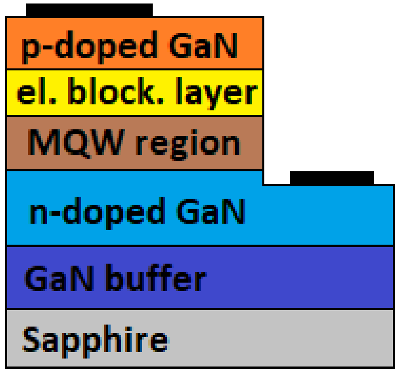
- **Breakthrough in materials science** – great innovation in lighting and display technology we still experience today;

Main applications of InGaN/GaN nitrides – not only LEDs

InGaN/GaN

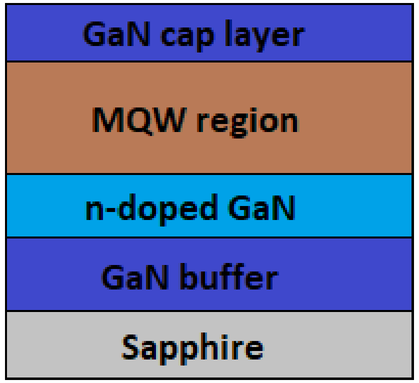
LED structures

- Sapphire substrate
- Both types of doping
- Minimize piezoelectric field (non-polar growth)
- Limited number of quantum wells (usually 5)
- Strong overall PL
- Surface hon wavelength



Scintillators

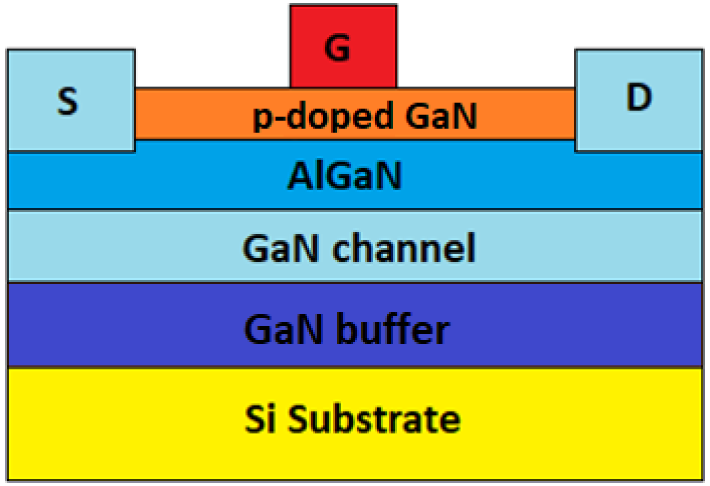
- Sapphire substrate
- n-type doping
- Minimize piezoelectric field (non-polar growth)
- As many quantum wells as possible (up to 70)
- PL without defect bands
- Fast response



AlGaN/GaN

High Electron Mobility Transistors

- Si or SiC substrates
- Maximize piezoelectric field (polar growth)
- High breakdown voltage
- High temperature resistivity



What is LED lighting technology? Basic definitions

*A **light-emitting diode** (LED) is a semiconductor device that emits visible light when an electric current passes through it.

***Solid-state lighting** (SSL) is a technology in which LEDs replace conventional incandescent and fluorescent lamps for general lighting purposes.

*An **LED light bulb** is a SSL device that fits in standard screw-in connections but uses LEDs to produce light.

*Recent advances in LED technology have made it possible for LEDs to produce **white light** as well (so called **white LEDs**).

* The most sophisticated control strategies are designed to manipulate the **circadian rhythm** of room occupants → lighting settings are programmed and shifts in color temperature and light level can be pre-set → **circadian white LED sources**

White LED – how the white color is achieved?

*4 different approaches can be considered in order to **generate white light** from LEDs:

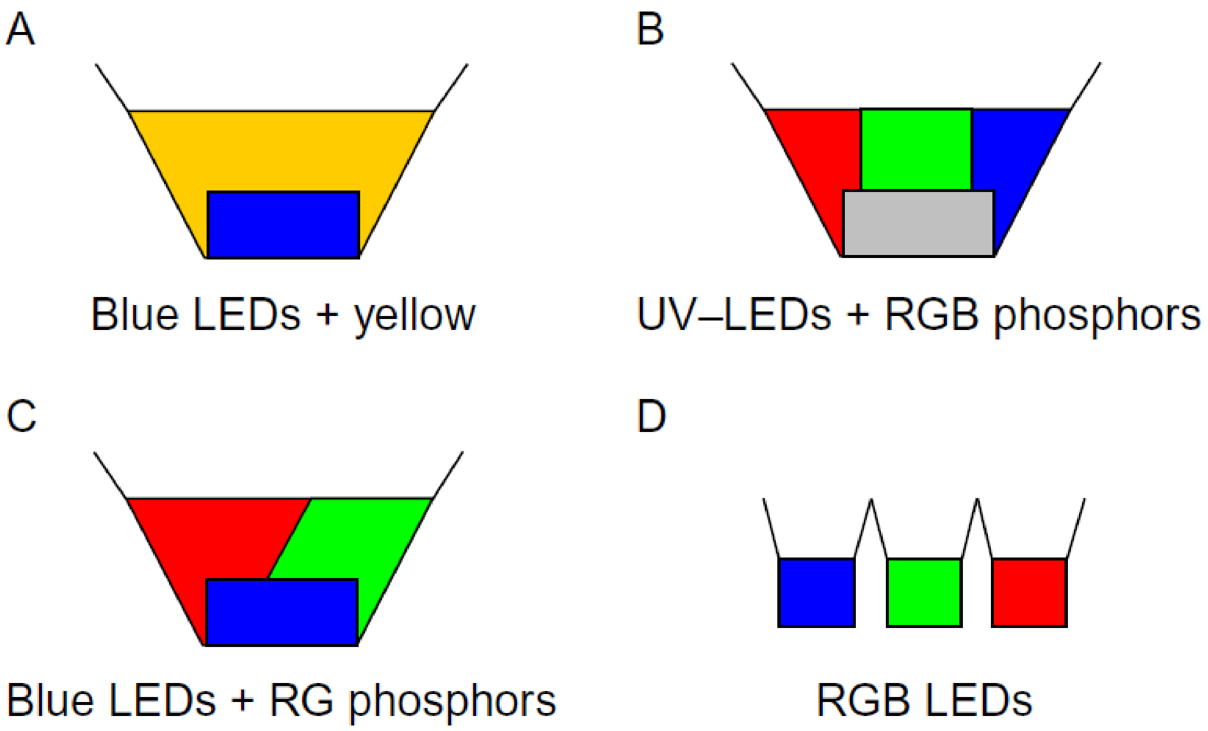
(A) white light is obtained using a **blue LED to excite a yellow phosphor**;

(B) white light is obtained using an **UV LED to excite red–green–blue (RGB) phosphors**

(C) White light is obtained using using a **blue LED to excite red–green (RG) phosphors**

(D) White light is obtained by **mixing reds, greens, and blues, ie, RGB, LEDs**;

M. Sato et al. Rare Earth-Doped Phosphors for White Light-Emitting Diodes, 2016.



Type (D) can create not only white colors but also **various colors**, although electronic tuning is complicated to require different driving currents for different color LEDs

(A), (B), (C) – so called **phosphor-converted LEDs (pc-LEDs)**

The advantages of LED lighting systems

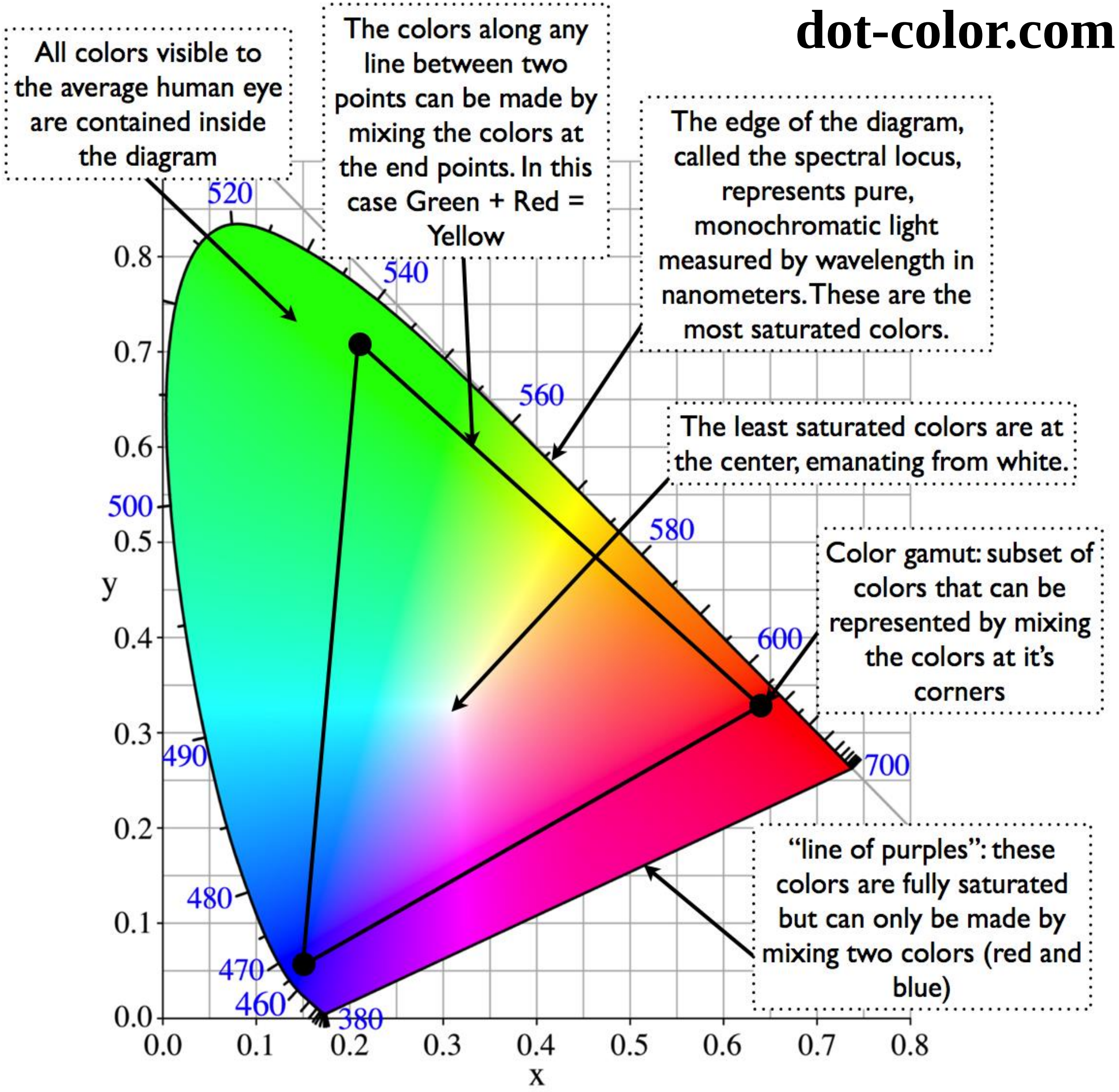
***Energy efficiency (> 200 lm/W)**;
*Possibility of **safe battery-driven** operation;
*Emission of **light of an intended color** without using color filters;
***Decreased heat generation** (LED beam is without any infrared content);
*Environment friendliness (**free of hazardous substances**);
*Elimination of **noise pollution** by avoiding the humming, flickering and headaches;
***higher reliability**;
***extended lifetime** of LEDs → 60,000 h as opposed to 1000 – 2000 h for incandescent lamps and about 5000 – 1000 h for compact fluorescent lights);
***long-term cost-effectiveness** (absence of moving parts, LED provides a high breakage and vibration resistance);
*instant **switching ON/OFF**, suitability for frequent on-off cycling applications;
*equipment size and weight reduction due to small LED form factor, adjustment flexibility;
*elimination of **sun phantom effect**;
*extensive applications;

LED technology – CIE color space

-CIE 1931 color spaces → first defined quantitative links between **distributions of wavelengths in the electromagnetic visible spectrum**, and **physiologically perceived ´colors in human color vision;**

-mathematical relationships are **essential tools for color management** (color inks, illuminated displays, and recording devices, e. g. digital cameras);

-CIE 1931 RGB color space and CIE 1931 XYZ color space created by the **International Commission on Illumination (CIE)** in 1931;
- results of **series of experiments** done in the late 1920s by W. D. Wright and J. Guild;

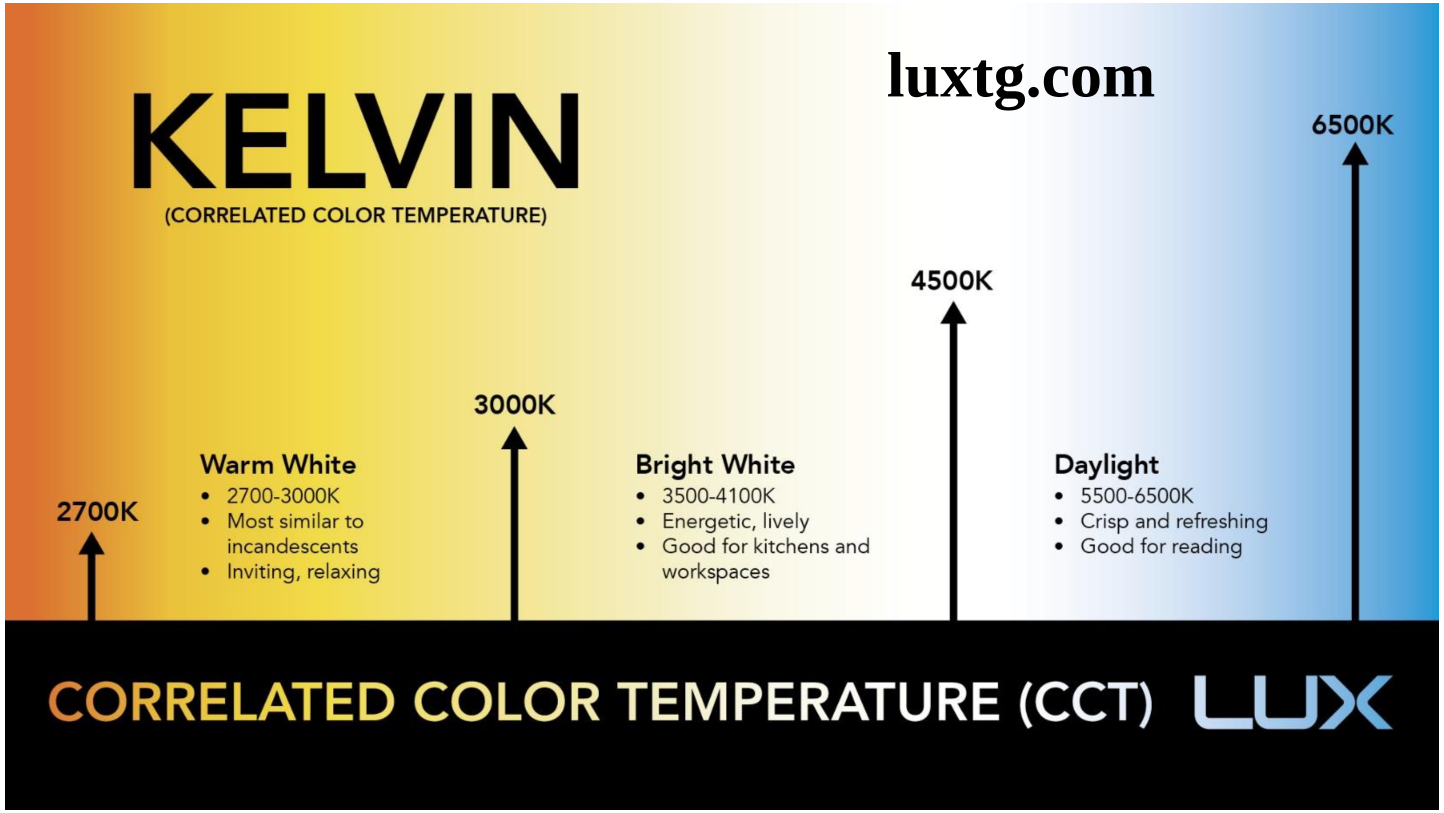


Anatomy of a CIE Chromaticity Diagram

Correlated Color Temperature (CCT)

The absolute temperature of a blackbody whose chromaticity most nearly resembles that of the light source. (Illuminating Engineering Society of North America Definition)

*specification of the color appearance of the light emitted by a lamp, relating its color to the color of light from a reference source when heated to a particular temperature in K;
*lamps with CCT < 3200 K considered "**warm" sources**, CCT > 4000 K **"cool" appearance**;



A popular feature for LED smart bulbs is **adjustable CCT** bulbs. They are also often called **tunable** LED smart bulbs or **circadian sources.**

Color rendering index (CRI)

*the most useful **measure of a light source's color characteristics;**
*measure of a light source's ability to show **object colors "realistically" or "naturally"** compared to a familiar reference source (e. g. incandescent light or daylight);
*calculated from the differences in the chromaticities of eight CIE standard color samples (CIE 1995) when illuminated by a light source and by a reference illuminant of the same correlated color temperature (CCT);
*the smaller the average difference in chromaticities, the higher the CRI
*CRI of 100 represents the **maximum value**;
*Lower CRI values → some colors may **appear unnatural** when illuminated by the lamp;
*Incandescent lamps → CRI > 95,
*Cool white fluorescent lamps → CRI ~ 62

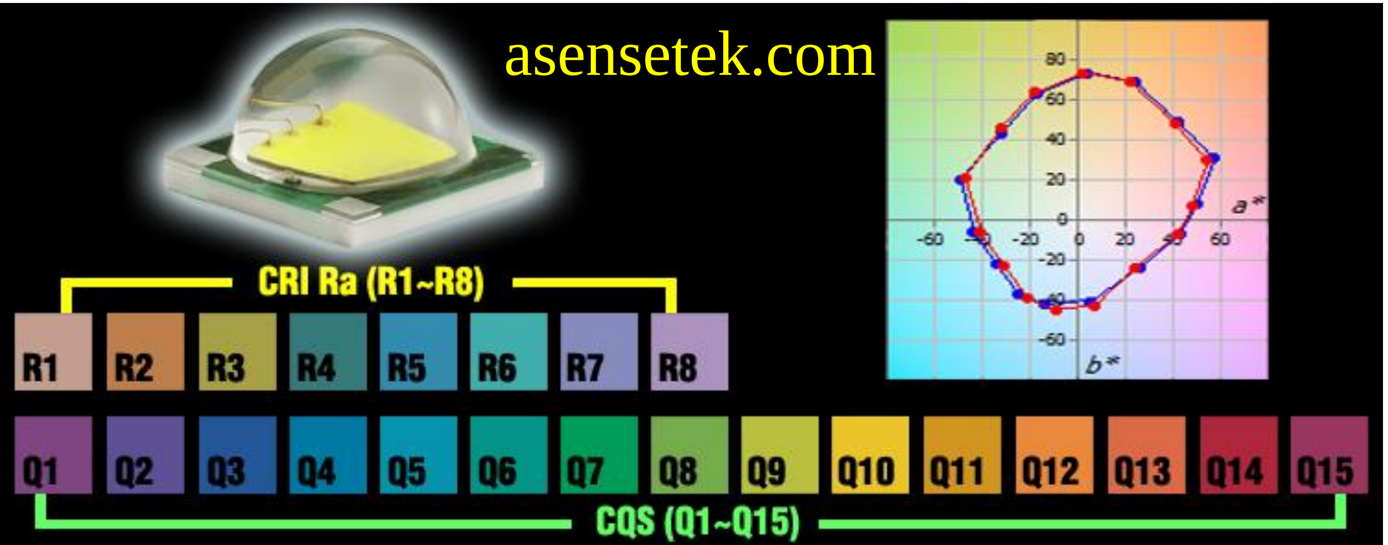
85 -100 CRI = Excellent color rendition
75 - 85 CRI = Very Good color rendition
65 - 75 CRI = Good color rendition
55 - 65 CRI = Fair color rendition
0 – 55 CRI = Poor color rendition

luxtg.com

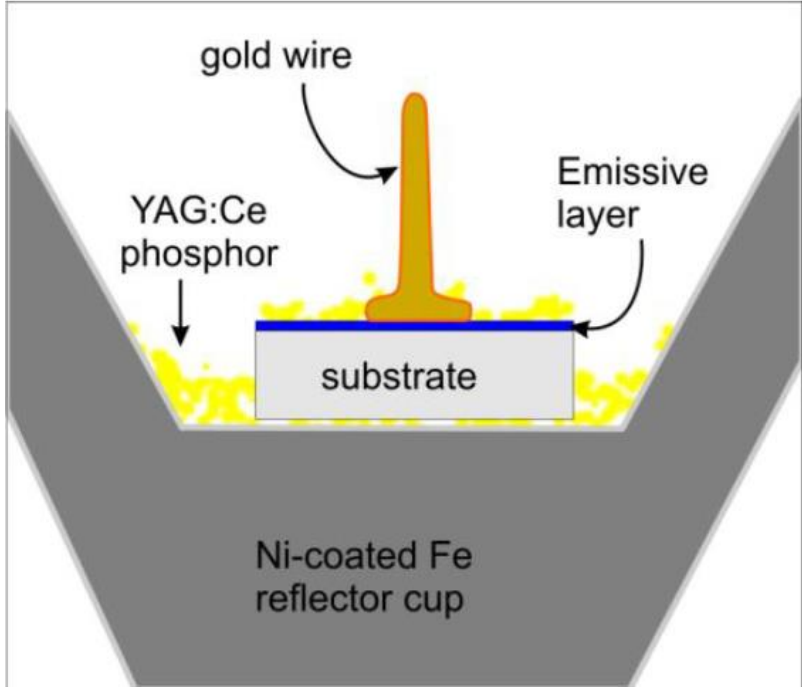
Color quality scale (CQS) – improvement of CRI

*CRI has been shown to have **deficiencies** when applied to **white LEDs**
*restricted scope of CRI unnecessarily penalizes some light sources with desirable color qualities

* CQS is a test samples method that compares the appearance of a set of reflective samples when illuminated by the test lamp
* CQS uses a larger set of reflective samples, all of high chroma, and combines the color differences of the samples with a root-mean-square
* The scale of the CQS is converted to span zero to 100 and the uniform object space and chromatic adaptation transform used in the calculations are updated;



Requirements for the phosphors to be used in LEDs



*The **emission spectrum** appropriate for the given application;

*The phosphor **excitable** by nearUV or blue LED;

*The **quantum efficiency (QE)** as high as possible (> 90%!);

*The luminescent properties **thermally stable** within the working temperature range (150 °C);

*The luminescence should **decay sufficiently fast** (to prevent saturation effects);

*Only **chemically stable** phosphors can be used (conformal coating stability issues can be resolved to a great extent);

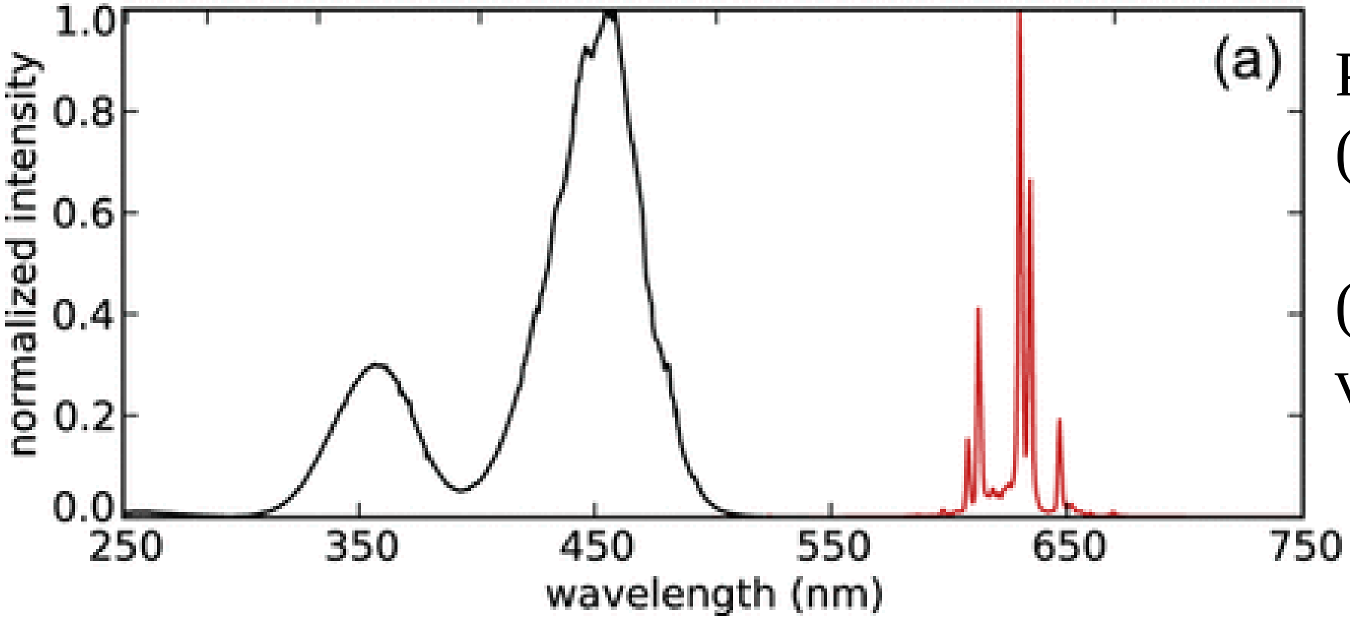
***Price**

LED technology in LCD displays – different story?

* if white LEDs are to be used in displays (e. g. backlight liquid crystal displays (LCD)), very pure (saturated) primary colors (RGB), corresponding with narrow emission bands are needed!

* the broadband phosphor do a poor job in obtaining saturated primaries in displays → large portion of the emitted light needs to be filtered → low energy efficiency

*the development of phosphors with narrow green and red emission bands is of technological importance – for example **$K_2SiF_6:Mn^{4+}$** is of a great importance:



PL excitation (Em = 630 nm) and emission (Ex = 455 nm) spectra of $K_2SiF_6:Mn^{4+}$

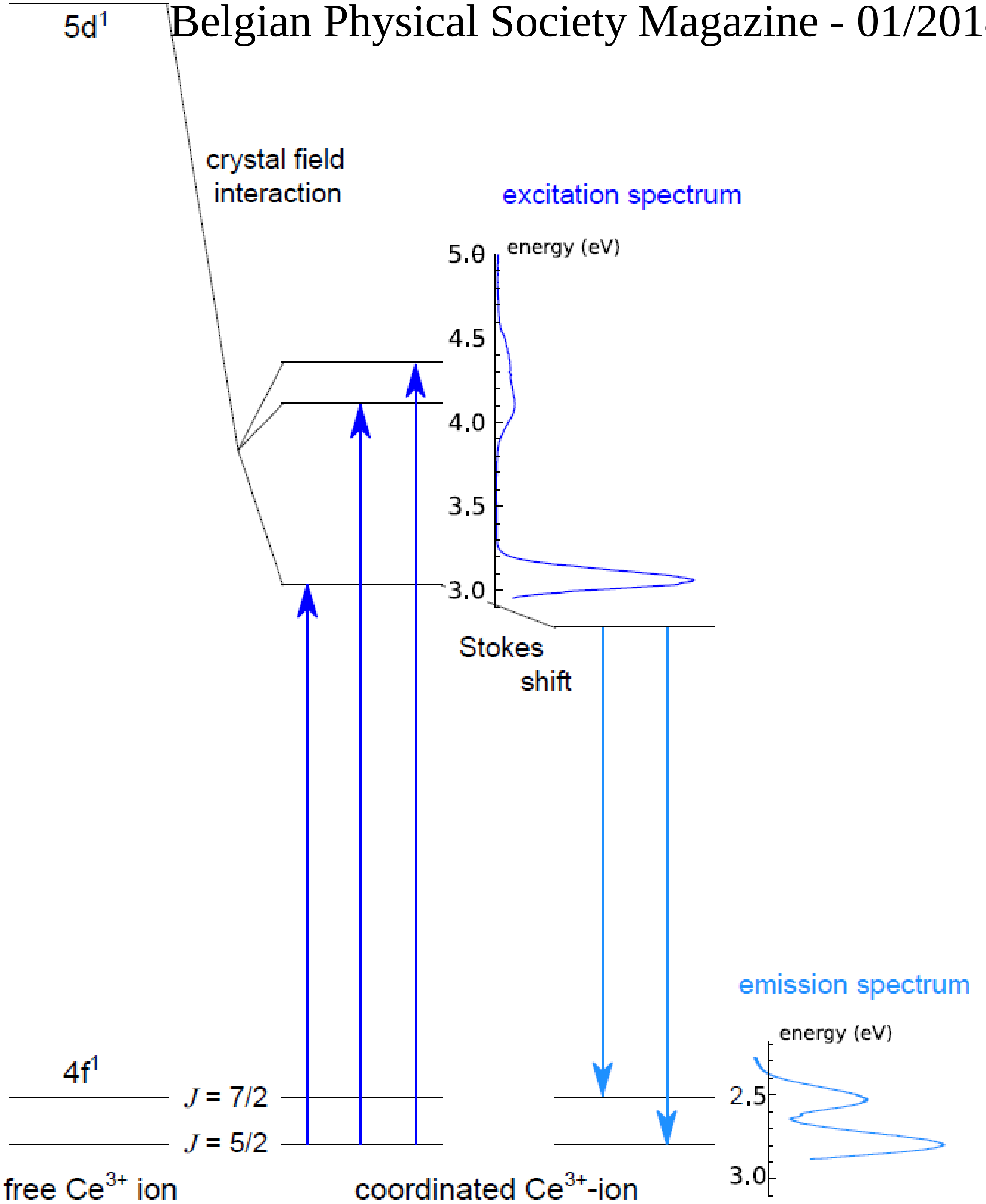
(after ECS J. Solid State Sci. Technol. 2016 vol. 5 no. 1 R3040-R3048)

Ce^{3+}-doped phosphors for LED applications

- **ground state** of Ce^{3+} → two spin orbit split levels, $^2F_{5/2}$, $^2F_{7/2}$, about 0.25 eV apart + insensitive to the crystal field;
- **excited state** → one 5d electron in addition to the empty 4f shell;
- free Ce^{3+} ion the energy difference **6.12 eV**;
- if Ce^{3+} incorporated in a host lattice, both a **splitting** as well as a **shift** of the 5d levels barycenter takes place

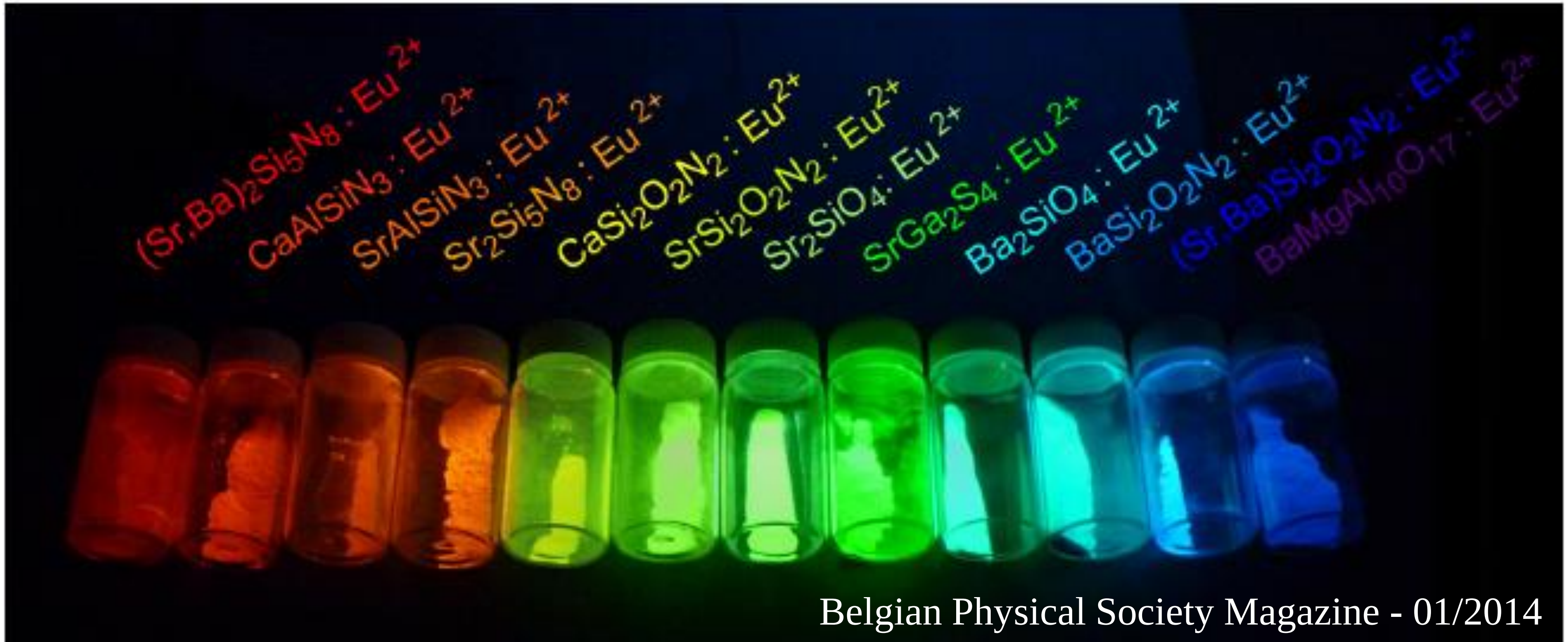
an overall **redshift** which drags the $4f^1 \rightarrow 5d^1$ transition in the UVA or VIS spectral range;

- the magnitude of both effects largely dependent on the **bonding distance** of the lanthanide ion;



Eu^{2+}-doped phosphors for LED applications

- half filled $4f^7$ shell in the ground state → only one spin-orbit level (**$^8S_{7/2}$**), yielding emission bands containing **only one component**;
- Eu^{2+} feature **more narrow emission compared to Ce^{3+}** (better suited for display applications);
- the energy difference $4f^7$ and $4f^65d$ smaller compared to Ce^{3+}, **longer wavelength emission** can be achieved by the Eu^{2+} ion by **selecting appropriate host crystals**;
- this is in contrast to Ce^{3+} for which efficient red emitting phosphors are **difficult** to make;



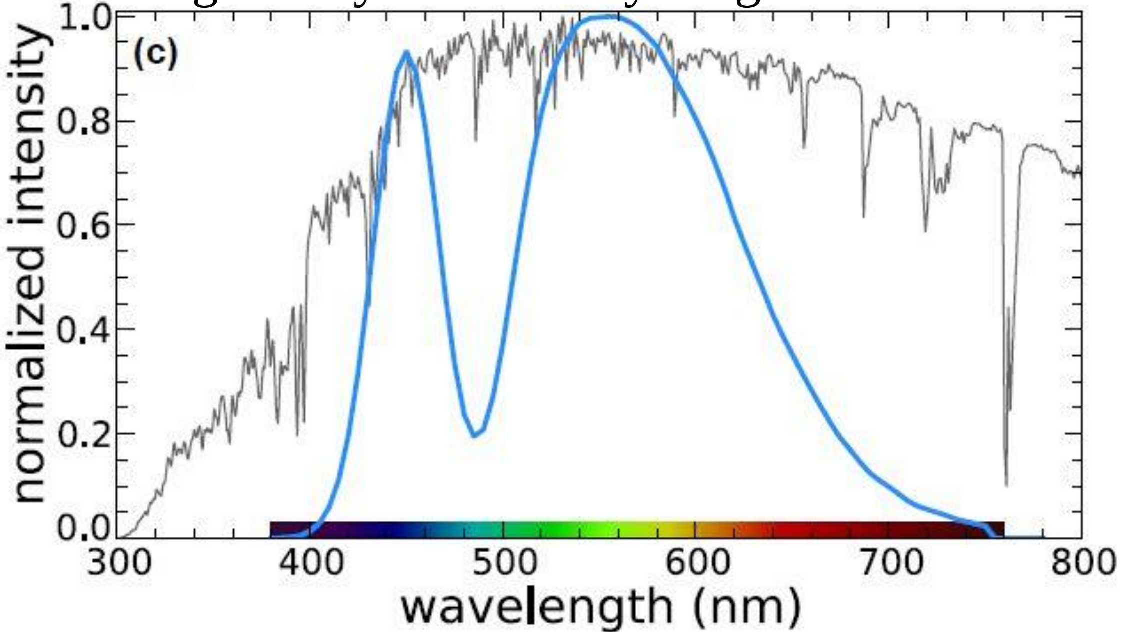
Belgian Physical Society Magazine - 01/2014

YAG:Ce^{3+} - the most common white LED phosphor

*reported already in 1967 with its primary use in **cathode ray tubes**;
*extremely **broad emission** band with a FWHM > 100 nm;
*The yellow emission from YAG:Ce + blue LED radiation → white light with a daylight-like **CCT (> 4000 K)** and reasonable color rendering (**CRI ~70 - 80**) → used in many applications
*the absorption and emission transitions **parity and spin allowed** → strong absorption of blue LEDs and a fast decay time that prevents saturation quenching;
*The QE of YAG:Ce under blue LED excitation **>85%, even at 200 °C**
*YAG:Ce do not degrade under blue LED excitation or moisture conditions
*the synthesis of YAG:Ce is relatively straightforward and cheap

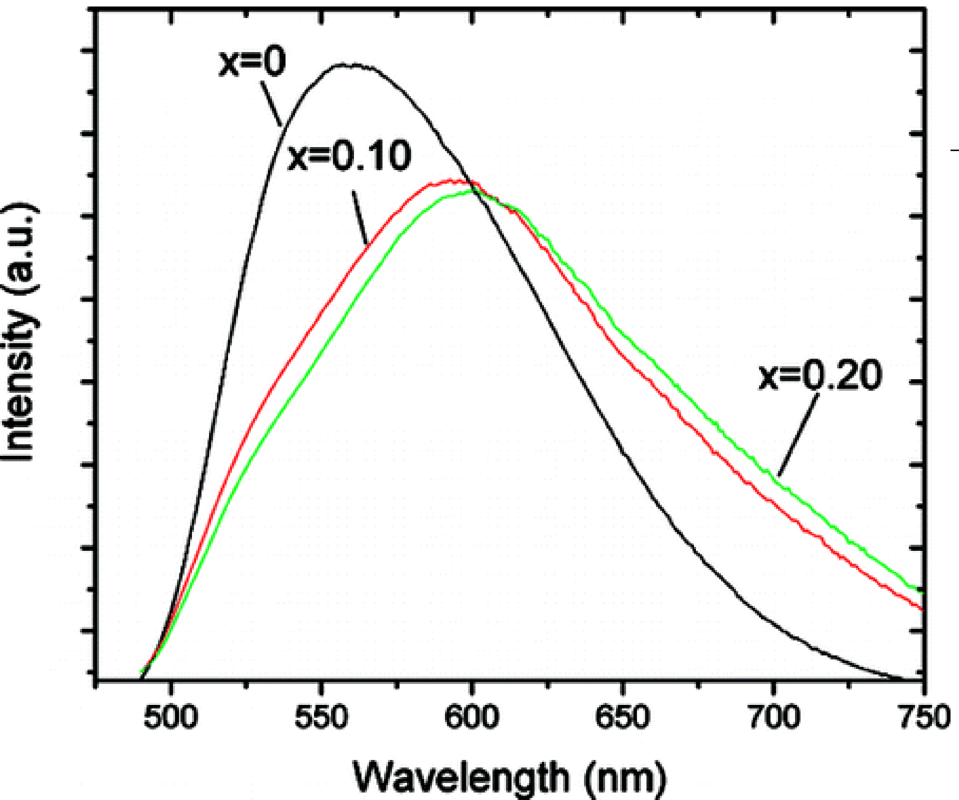
*One deficiency for pc-LEDs that use only YAG:Ce is that they are limited to high CCTs and lower CRIs, due to a lack of a red spectral component;

Belgian Physical Society Magazine - 01/2014

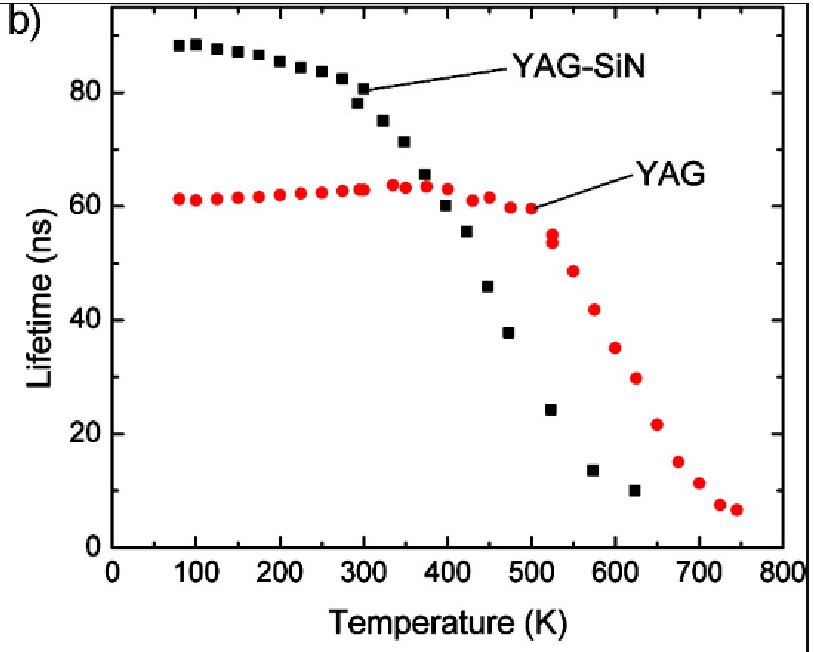


How to improve YAG:Ce^{3+}-based LEDs?

- possibility to redshift the Ce^{3+} $5d^1 \rightarrow 4f^1$ emission through Gd^{3+} substitution of Y^{3+} or Mg^{2+}-Si^{4+} substitution for Al^{3+}(octahedral)-Al^{3+}(tetrahedral) - cost of efficiency at high temperatures ☹
- there has been progress finding silicate garnet phosphors with Ce^{3+} emission maxima ranging from 505 - 605 nm with room temperature QEs comparable to YAG:Ce
- furthermore, replacing Al^{3+}(tetrahedral)-O^{2-} with Si^{4+}-N^{3-} in the garnets leads to an additional red component in the emission spectra due to Ce3+ ions coordinated by N^{3-}



However, any orange–red garnet still has stronger high temperature quenching compared to YAG:Ce



A. A. Setlur, W. J. Heward, M. E. Hannah, and U. Happek, Chem. Mater., 20, 6277 (2008).

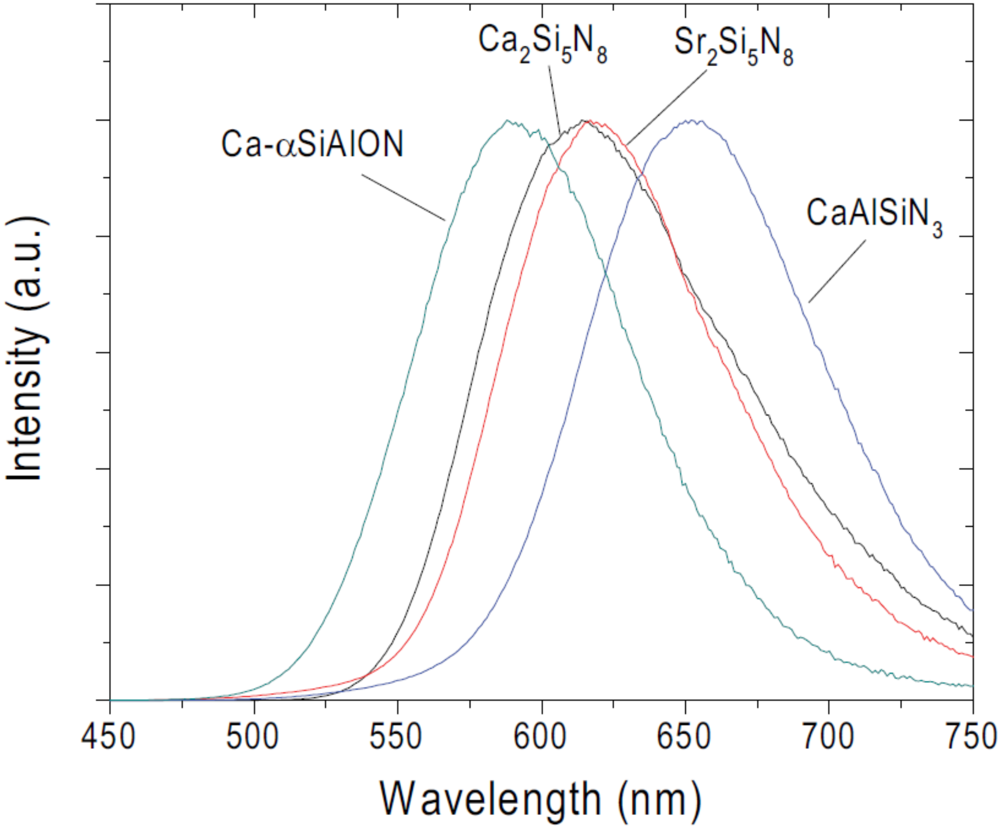
Nitride and oxynitride phosphors for white LEDs

*efficient phosphors family **$MSi_2O_2N_2:Eu^{2+}$ (M = Ca^{2+}, Sr^{2+}, Ba^{2+})** → emission ranges from ~498 nm for $BaSi_2O_2N_2:Eu^{2+}$ to ~560 nm to $CaSi_2O_2N_2:Eu^{2+}$

*QE > 85% at T >200 °C for the green **Eu^{2+}-doped $SrSi_2O_2N_2$** phosphor

* another important family of materials are based upon **Eu^{2+}-doped $CaAlSiN_3$** hosts

* **$CaAlSiN_3:Eu^{2+}$** phosphors (~ 650 nm emission) and QE > 85% beyond 200 °C



*phosphor blends of **YAG:Ce and $CaAlSiN_3:Eu^{2+}$** combined with blue LEDs can be used for high CRI, warm white lamps;

*it is also possible to use **all-nitride phosphor blends** to make pcLEDs that cover a full range of CCTs at CRI > 90

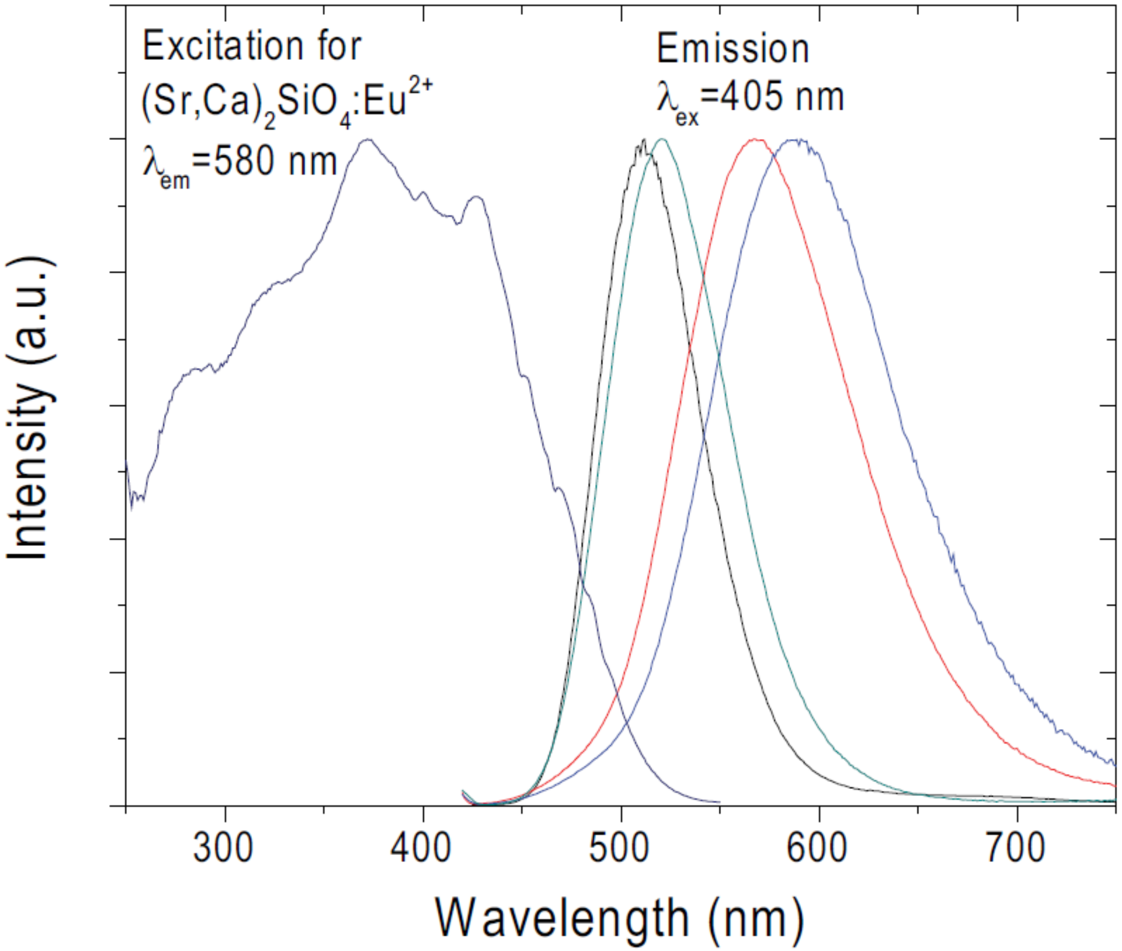
(Anant A. Setlur: The Electrochemical Society Interface • Winter 2009)

$M_2SiO_4:Eu^{2+}$ ($M = Ba^{2+}, Sr^{2+}, Ca^{2+}$)

*$Ba_2SiO_4:Eu^{2+}$ peaks at ~ 505 nm, and Sr^{2+}/Ca^{2+} substitution leads to a redshift in the emission ~ 585-590 nm

*the excitation generally peaking in the violet and deep

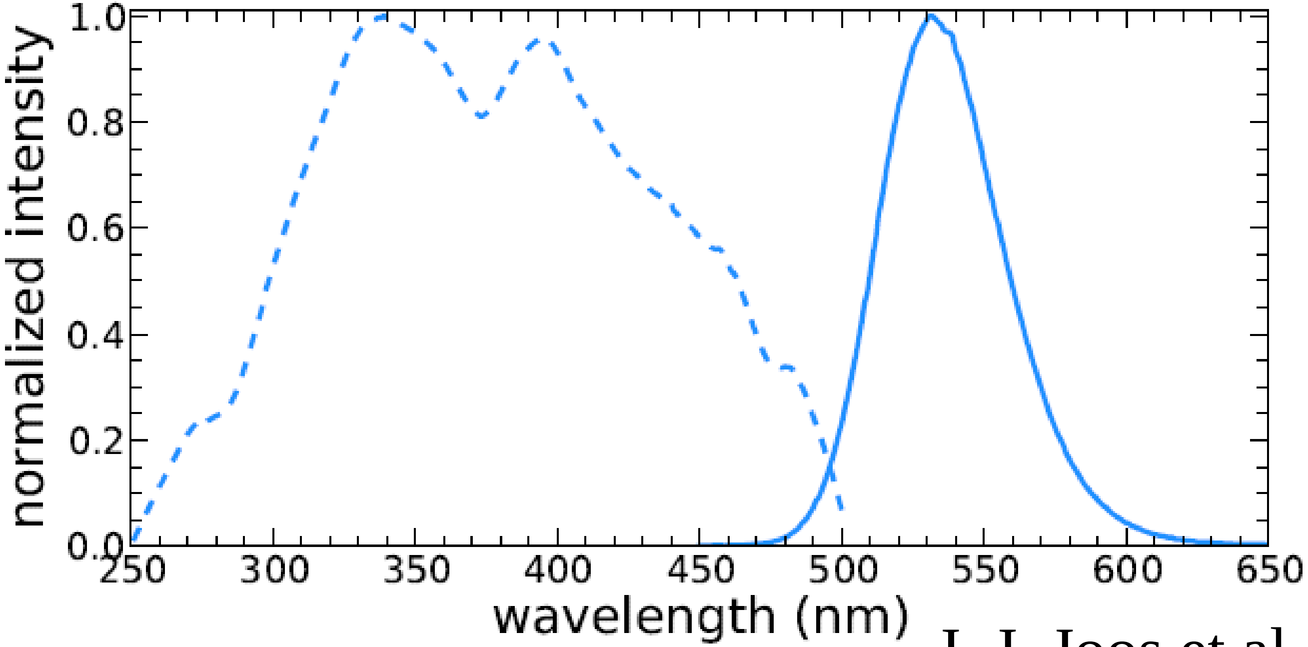
* drawback is the relatively strong quenching → QE(150 °C)/QE(RT) = 60-65%

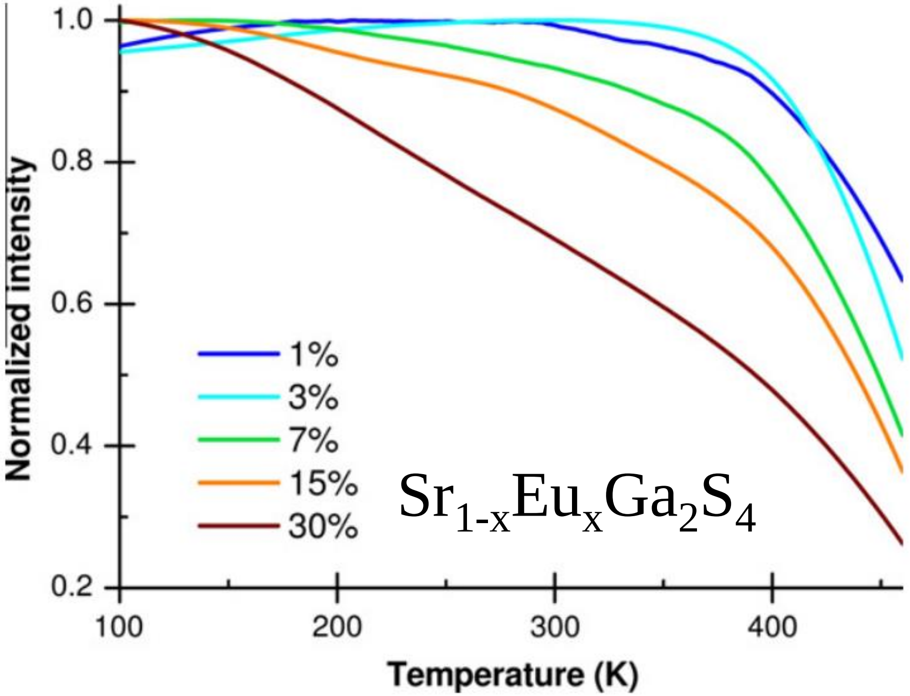


T. L. Barry, J. Electrochem. Soc., 115, 1181 (1968); G. Blasse, W. L. Wanmaker, J. W. Ter Vrugt, and A. Bril, Philips Res. Rept., 23, 189 (1968).

$SrGa_2S_4:Eu^{2+}$ - a bright green phosphor

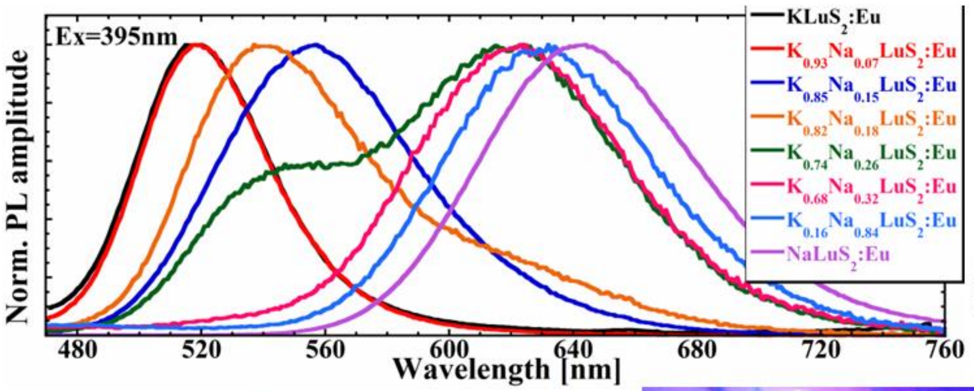
* The emission band is sufficiently narrow for the use as green primary in displays without color filtering;
* The phosphors can be excited efficiently by both blue, violet or near ultraviolet light sources;
* The short lifetime of the Eu^{2+} (~ 450 ns) prevents saturation effects at intense excitation fluxes;
* The (high) efficiency insensitive to temperatures in the operational range

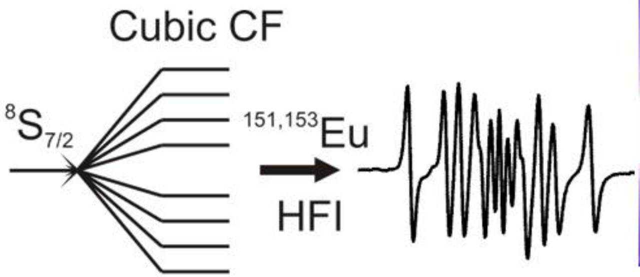


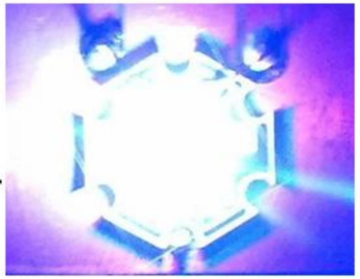


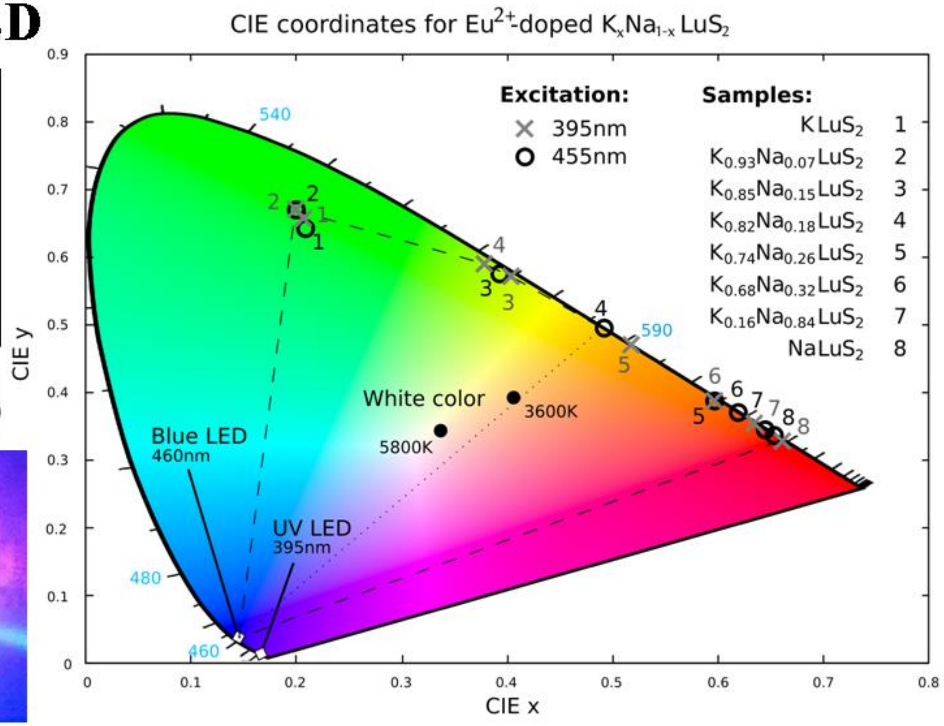
J. J. Joos et al., Opt. Mater. 34:1902-1907 (2012).

$K_xNa_{1-x}LuS_2:Eu^{2+}$ for circadian white LED









Tunable Eu^{2+} emission in $K_xNa_{1-x}LuS_2$ phosphors for circadian LEDs

V. Jarý, L. Havlák, E.
Mihóková, J. Bárta, M
Buryi, V. Laguta, M.
Rejman, M. Nikl

Fyzikální ústav
Akademie věd ČR, v. v. i.

Aim – to construct a circadian light source

a white light source which is able to vary CCT temperature of white light during the daytime (more blue part in the morning, more red part in the evening!)

Two excitation diode needed – nearUV (390 nm) and blue (455 nm)

Their mutual intensity ratio enables to tune the temperature of white light

National patent number 305254, 1. 7. 2015; Lubomír Havlák, Vítězslav Jarý, Martin Nikl, Jan Bárta:

Phosphores $(Li_cNa_dK_eRb_fCs_g)(La_hGd_iLu_jY_k)_{1-a}Eu_aS_{2-b}$ for solid state lightnings

Samples sets

$RbLaS_2$:Eu (0.05%)
$RbGdS_2$:Eu (0.05%)
$RbLuS_2$:Eu (0.05%)
$RbYS_2$:Eu (0.05%)

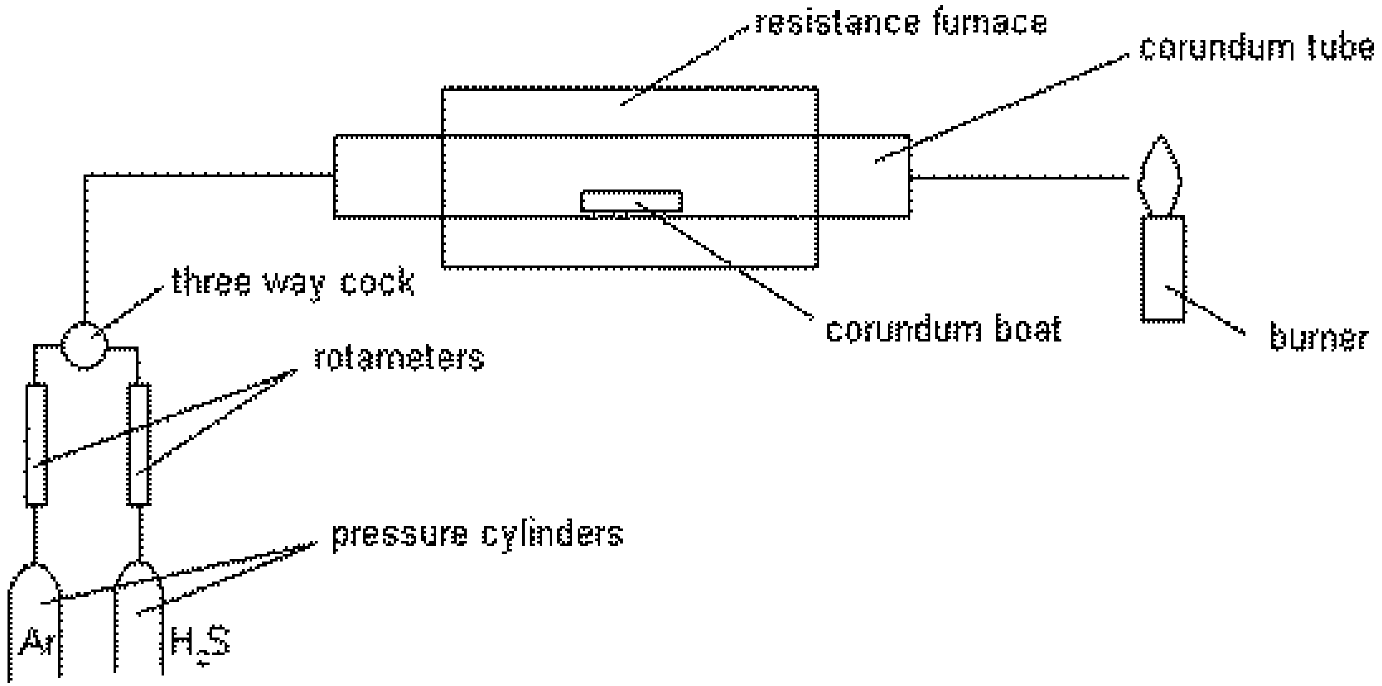
$KLaS_2$:Eu (0.05%)
$KGdS_2$:Eu (0.05%)
$KLuS_2$:Eu (0.05%)
KYS_2:Eu (0.05%)

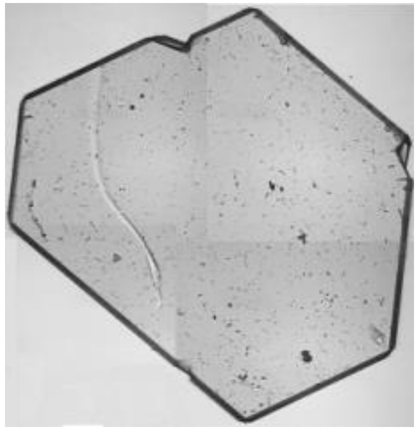
$NaLaS_2$:Eu (0.05%)
$NaGdS_2$:Eu (0.05%)
$NaLuS_2$:Eu (0.05%)
$NaYS_2$:Eu (0.05%)

$KLuS_2$:Eu (0.05%)
$K_{0.93}Na_{0.07}LuS_2$ (0.05%)
$K_{0.85}Na_{0.15}LuS_2$ (0.05%)
$K_{0.82}Na_{0.18}LuS_2$ (0.05%)
$K_{0.74}Na_{0.26}LuS_2$ (0.05%)
$K_{0.68}Na_{0.32}LuS_2$ (0.05%)
$K_{0.16}Na_{0.84}LuS_2$ (0.05%)
$NaLuS_2$:Eu (0.05%)

Composition deduced from diffraction and XRF data!

Sample preparation





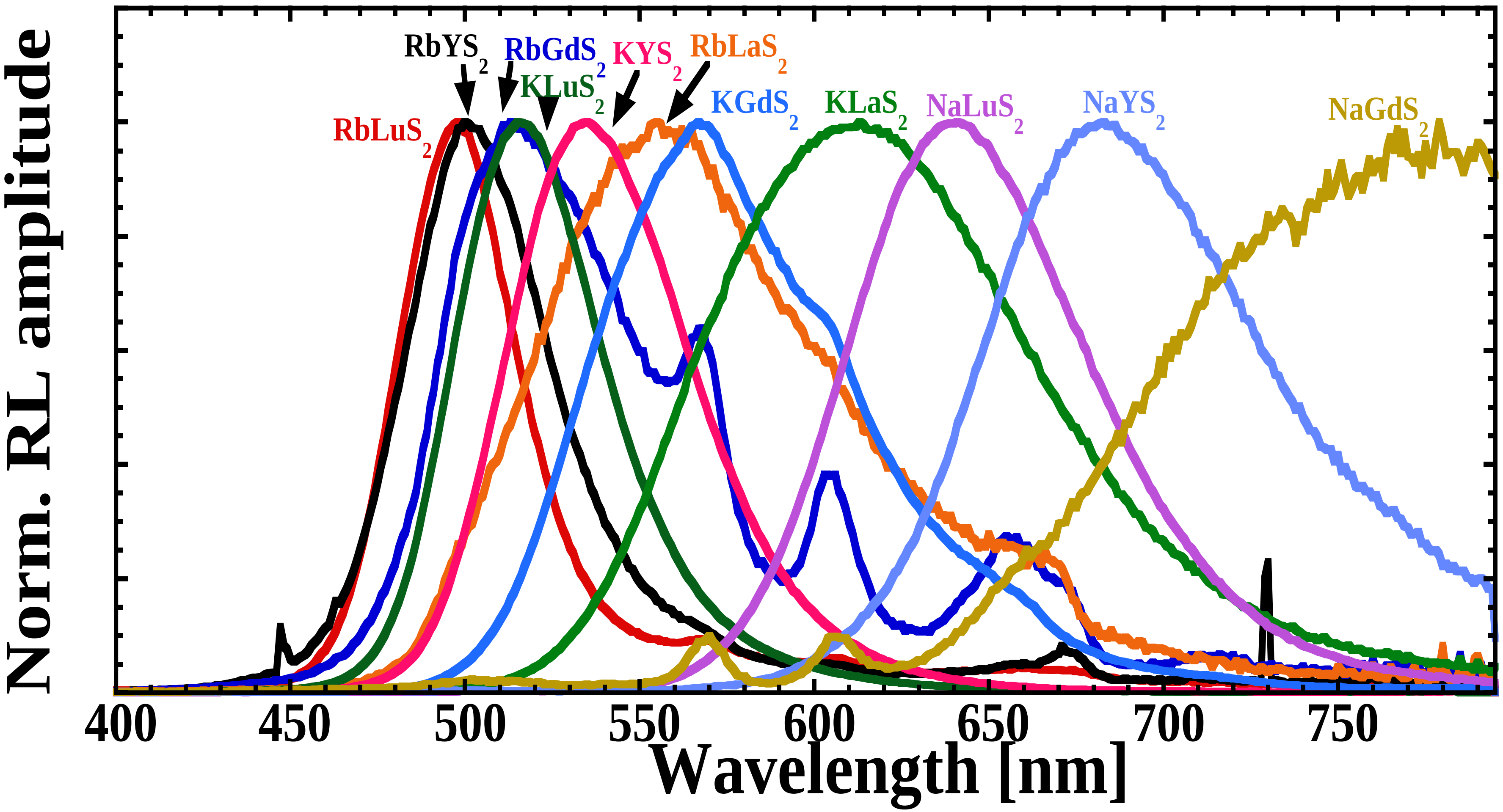
A_2CO_3 (l) + Ln_2O_3 (s) + $4H_2S$ (g) → $2ALnS_2$ (s) + $4H_2O$ (g) + CO_2(g)

A_2CO_3 (l) + H_2S (g) → A_2S (l) + H_2O (g) + CO_2 (g)

1025 ^{o}C, 15 L/hour H_2S flow, 1-2 hour, abundance of A_2CO_3

L. Havlak et al., Acta Mater. 59, 6219–6227 (2011).

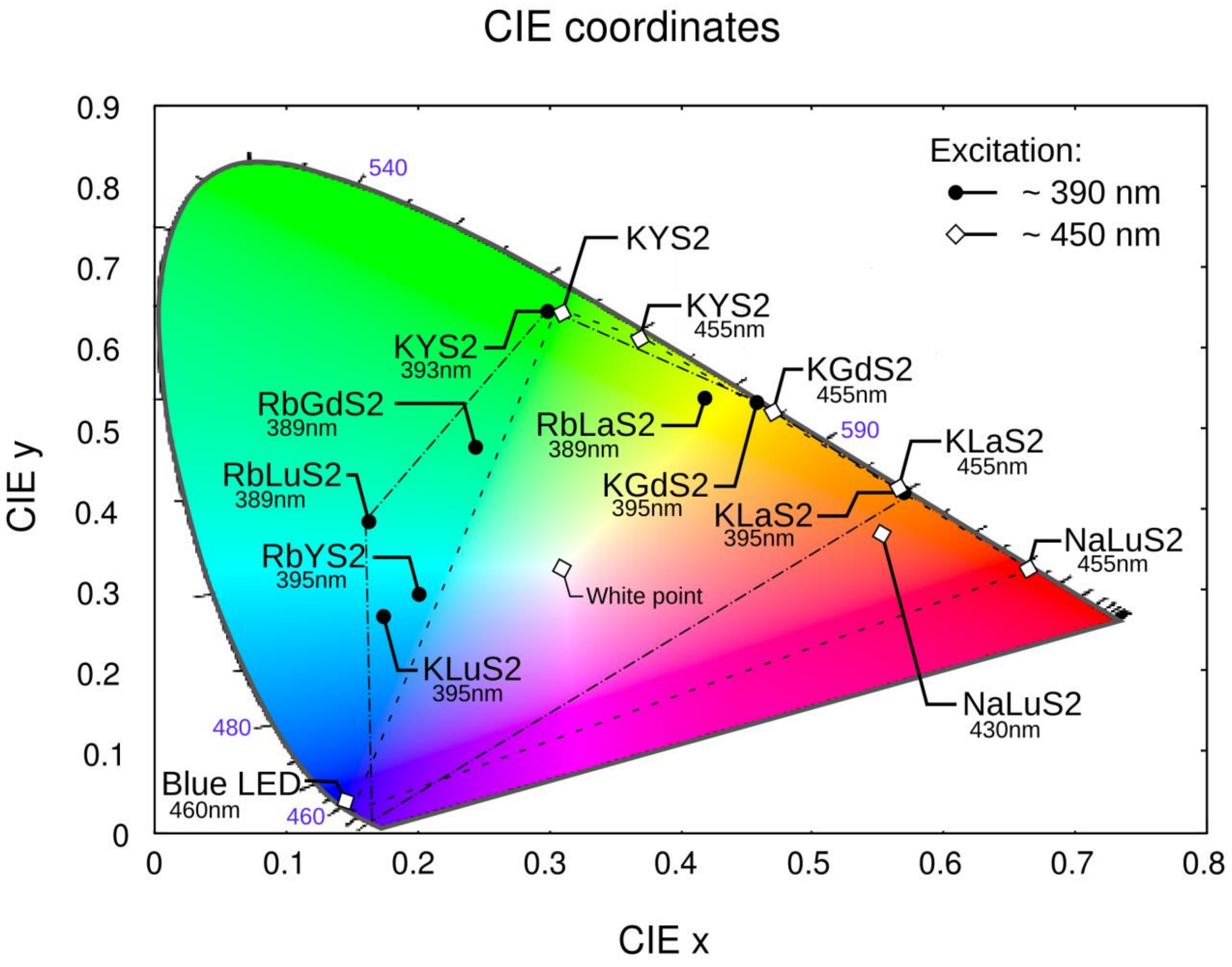
Review - RT RL spectra of Eu^{2+}



-RT RL spectra (40 kV, 15 mA X-ray) – ranging from **498 nm** ($RbLuS_2$) to **776 nm** ($NaGdS_2$)

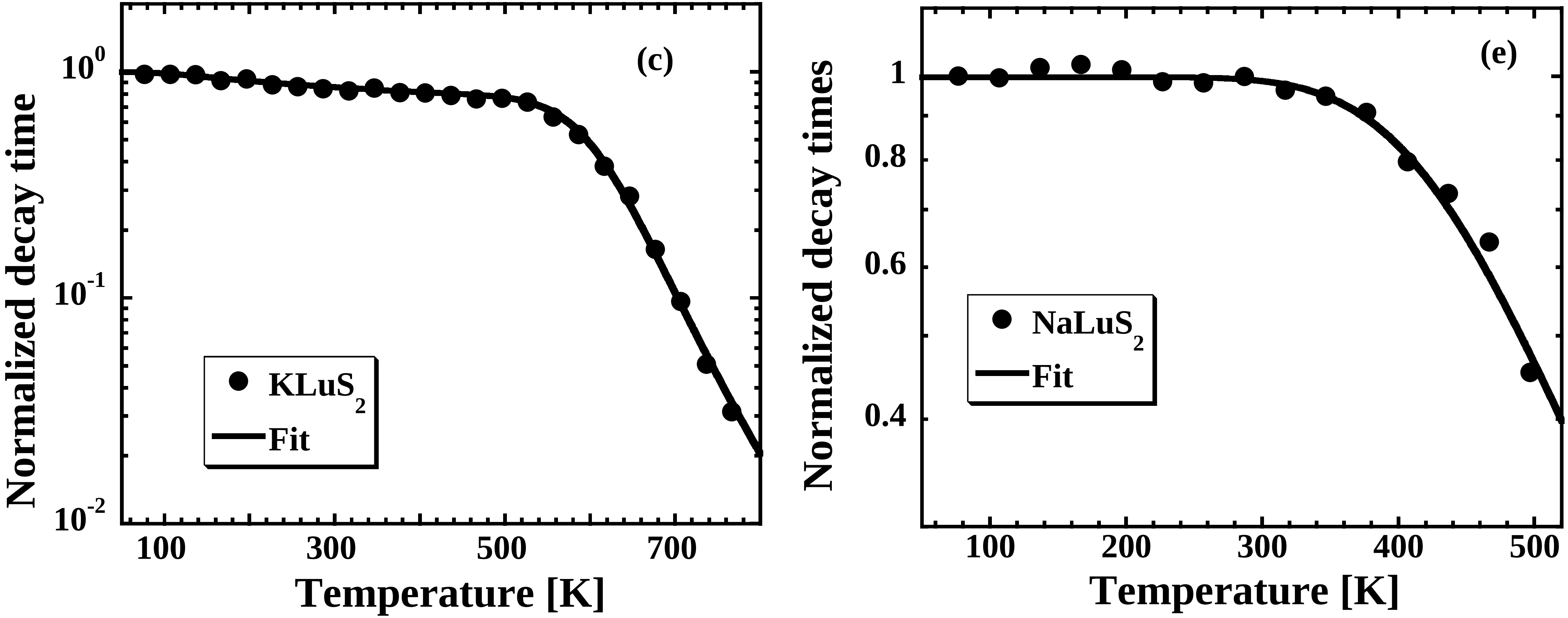
-Shift of the Eu^{2+} emission wavelength due to the **splitting of the excited state $4f^65d^1(^2D)$ by the local crystal field**

CIE coordinates



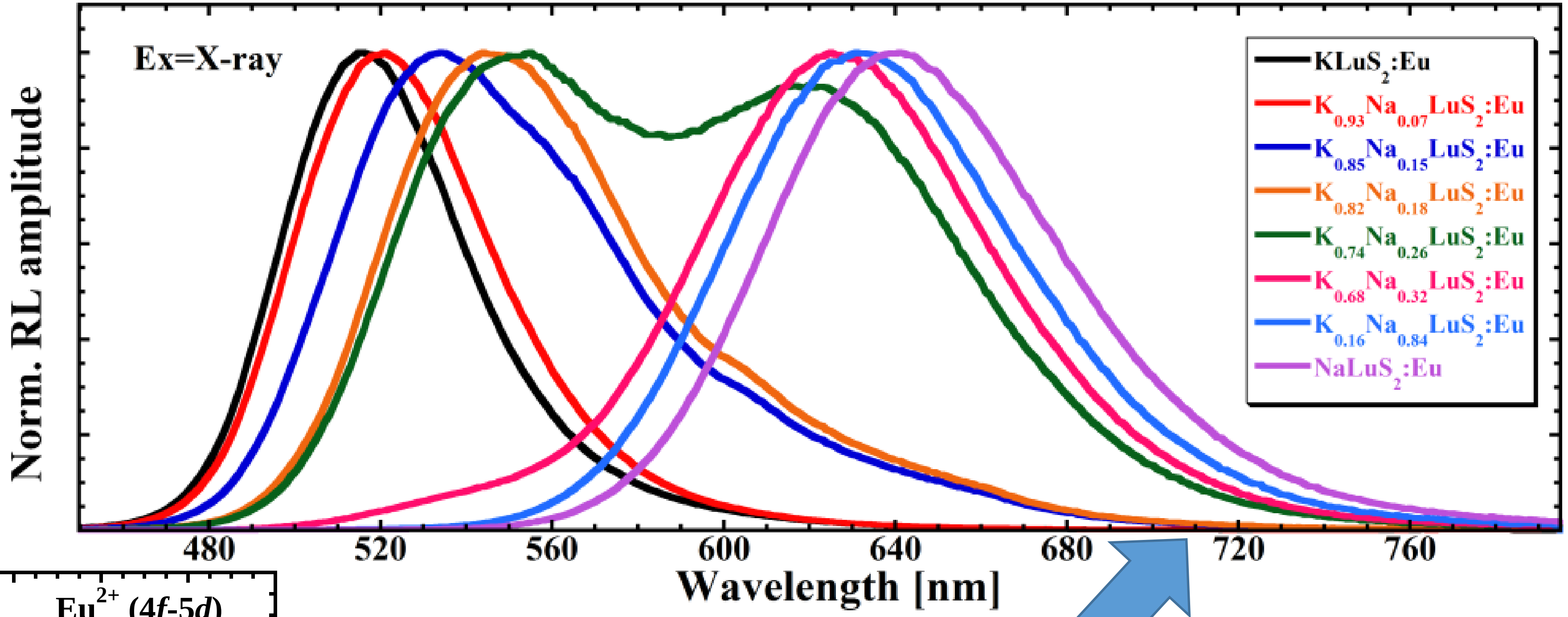
- **large area** of visible color space is covered
- $KLuS_2$, $RbYS_2$, $RbLuS_2$ under 395nm excitation provide good opportunity for **tuning white color CCT temperature**

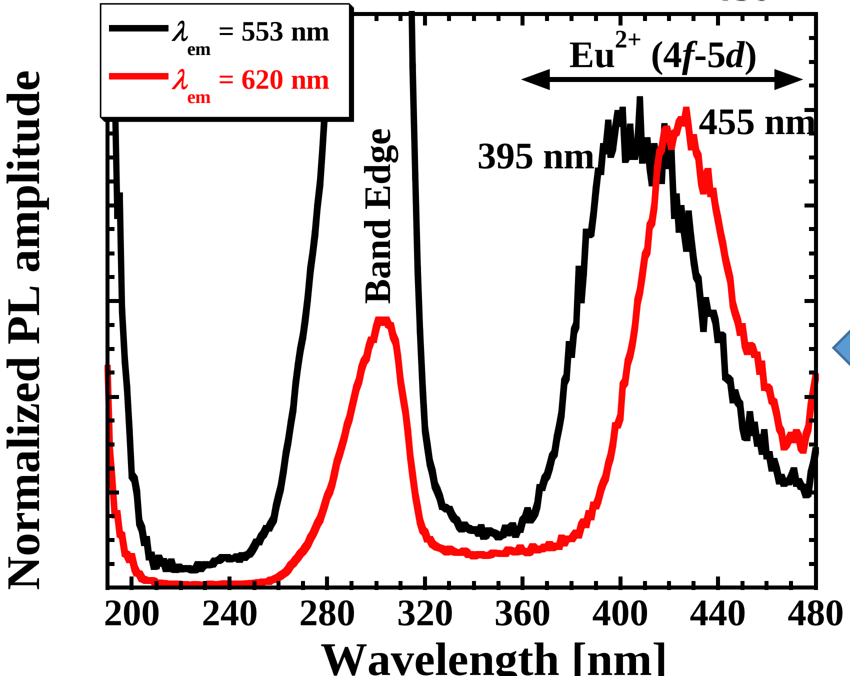
Temperature stability of $KLuS_2:Eu^{2+}$, $NaLuS_2:Eu^{2+}$



- cooperation with theoreticians on explaining intense and high temperature stable Eu^{2+} emission in these sulfides hosts in a frame of **electronic and band structure**

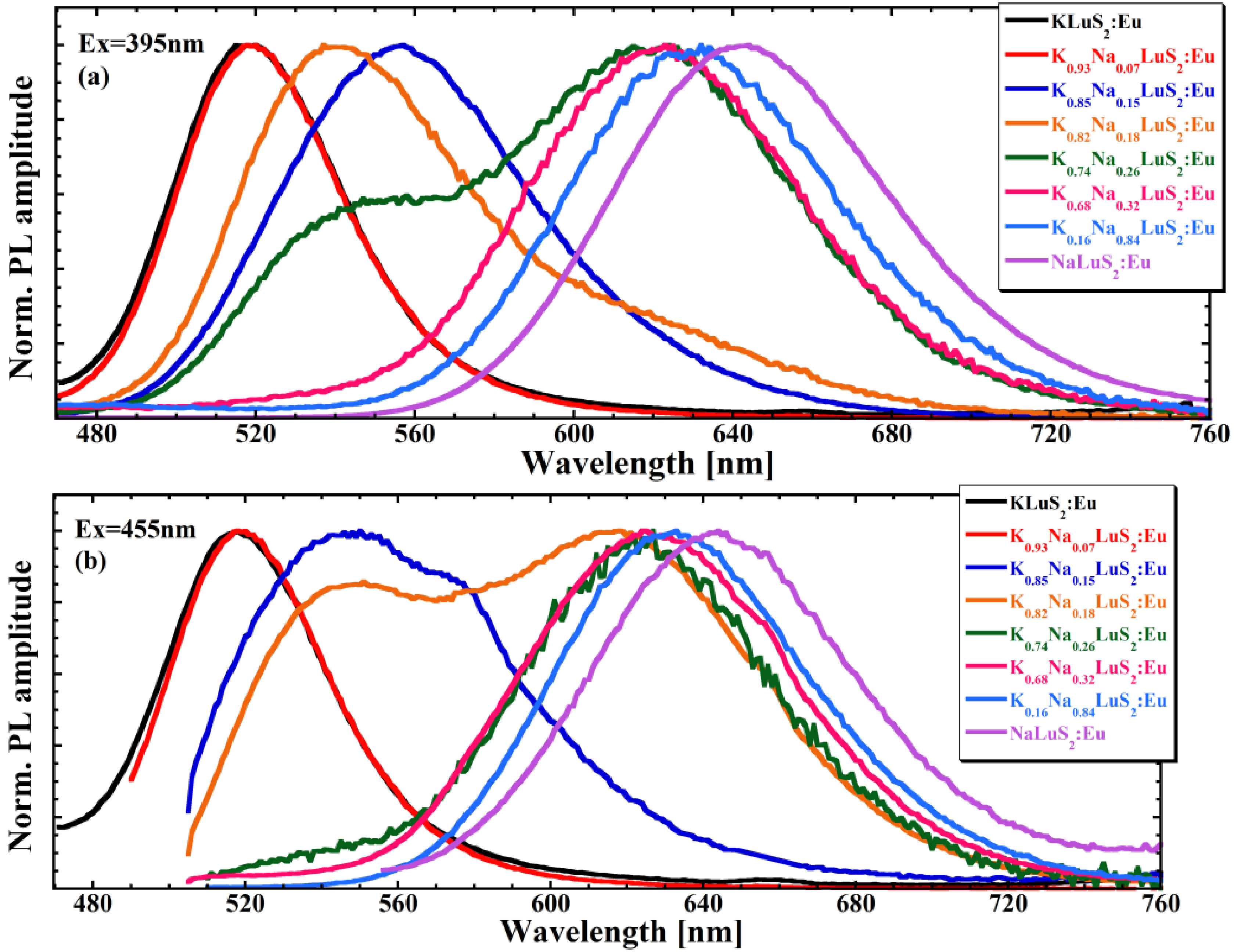
Another step - Eu^{2+}-doped $K_xNa_{1-x}LuS_2$ (x = 0 – 1)



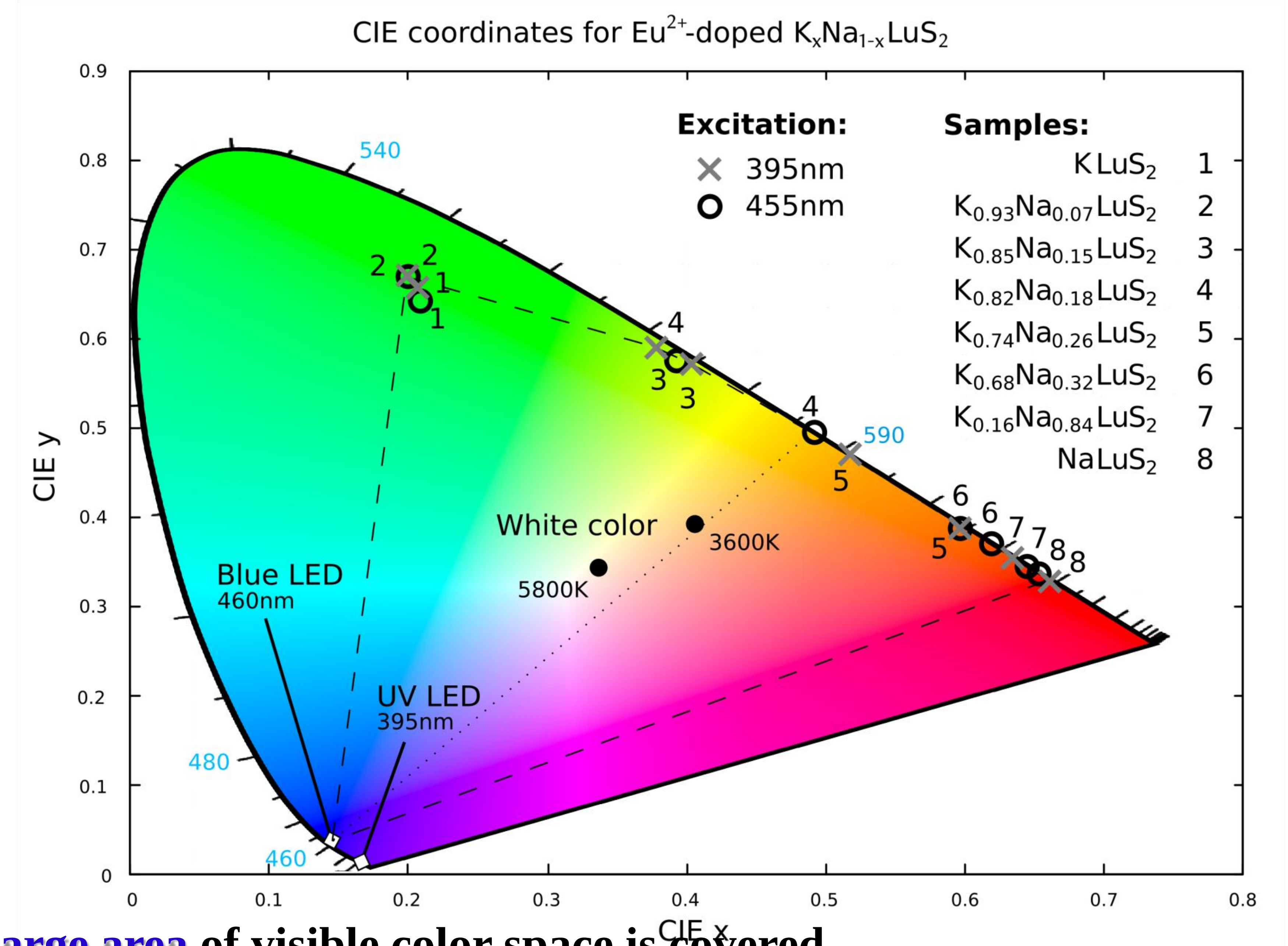


Broad emission in VIS well excitable with both nearUV and blue diode!

Eu^{2+}-doped $K_xNa_{1-x}LuS_2$ (x = 0 – 1): PL emission spectra

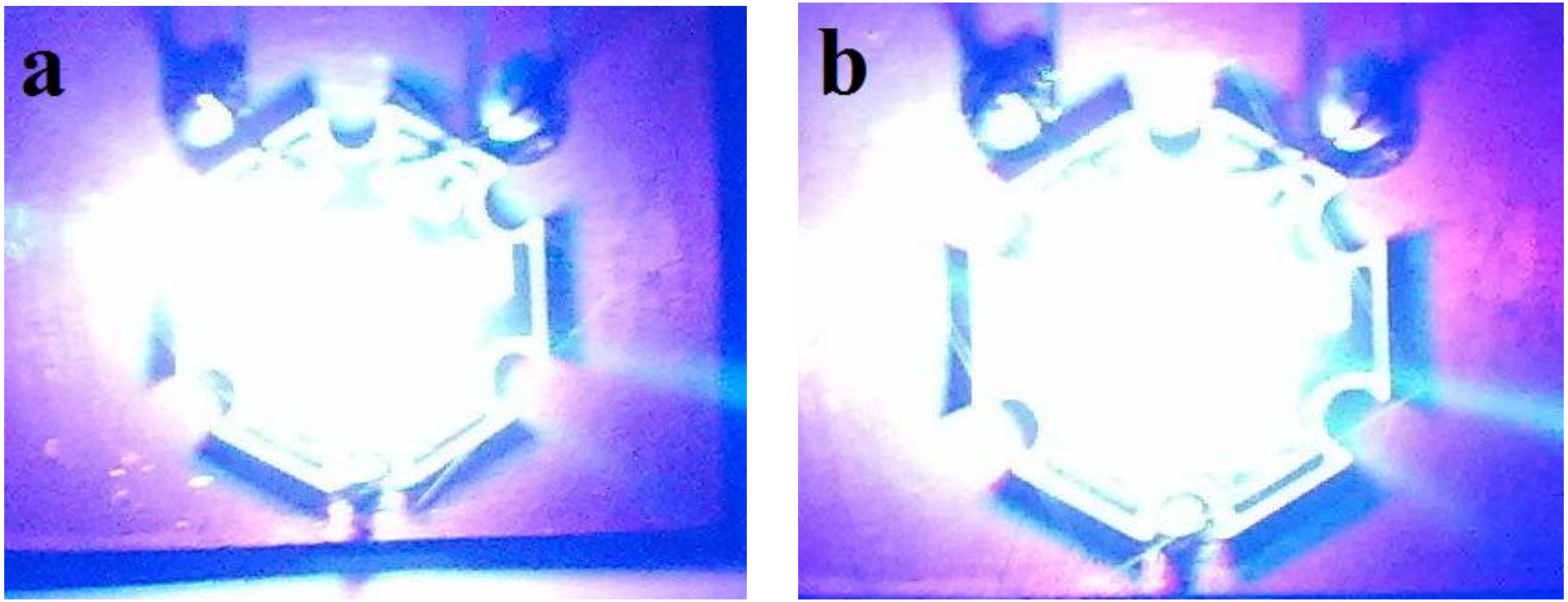


CIE coordinates $K_xNa_{1-x}LuS_2:Eu^{2+}$ (0.05%)



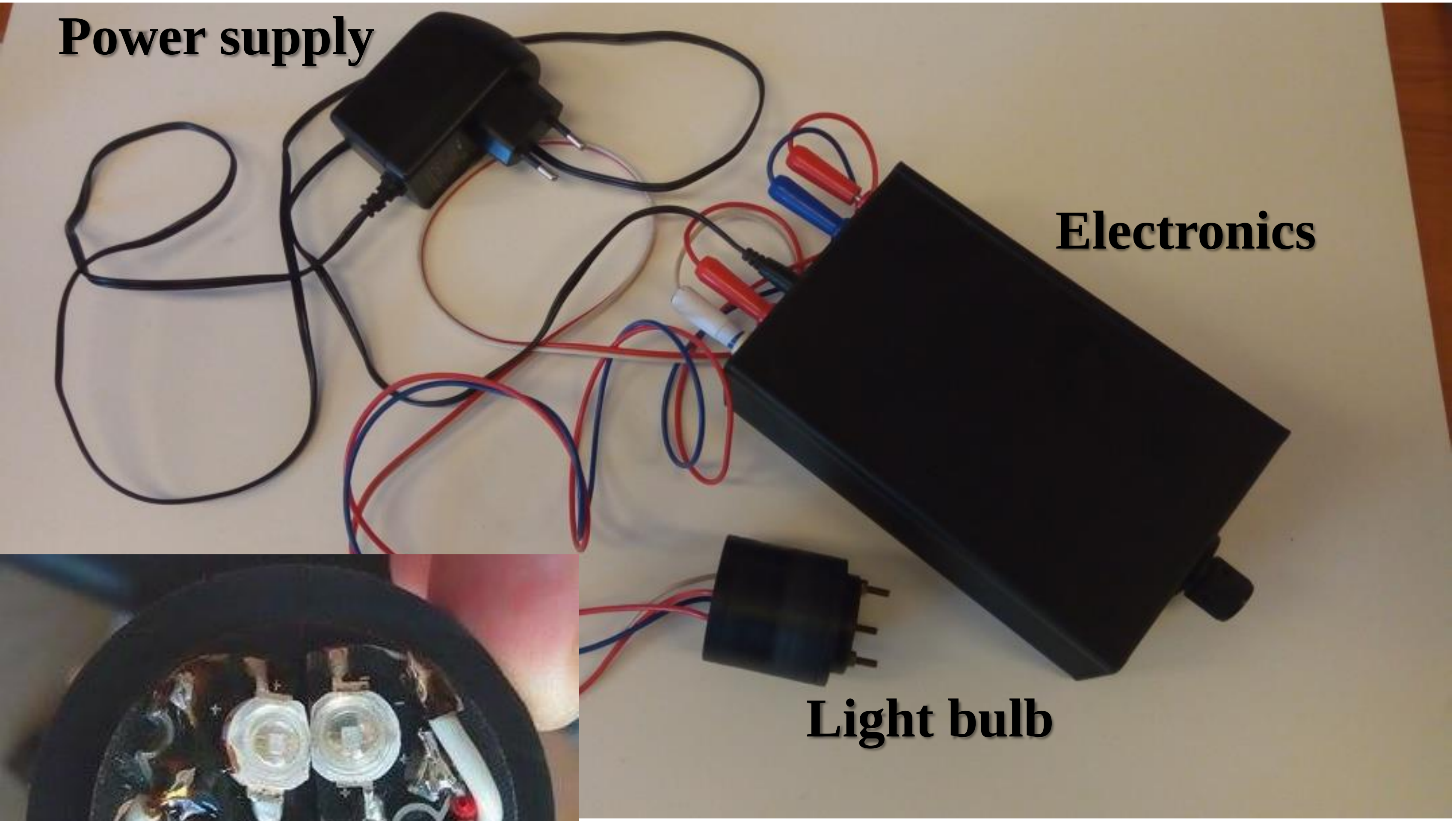
large area of visible color space is covered

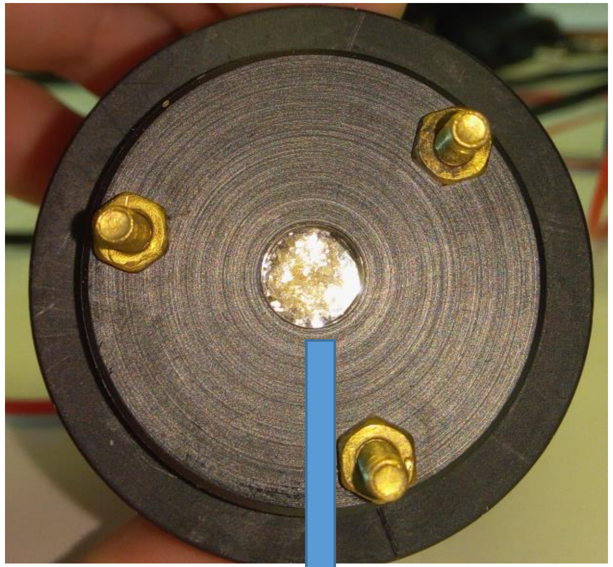
Real photos of $K_xNa_{1-x}LuS_2:Eu^{2+}$ (0.05%) emission



-photographs of **white emission** obtained by using 455 nm blue excitation diode covered by the layer of (a) $K_{0.82}Na_{0.18}LuS_2$:Eu (0.05%) and (b) $K_{0.74}Na_{0.26}LuS_2$:Eu (0.05%) phosphor.

Prototype of circadian light source

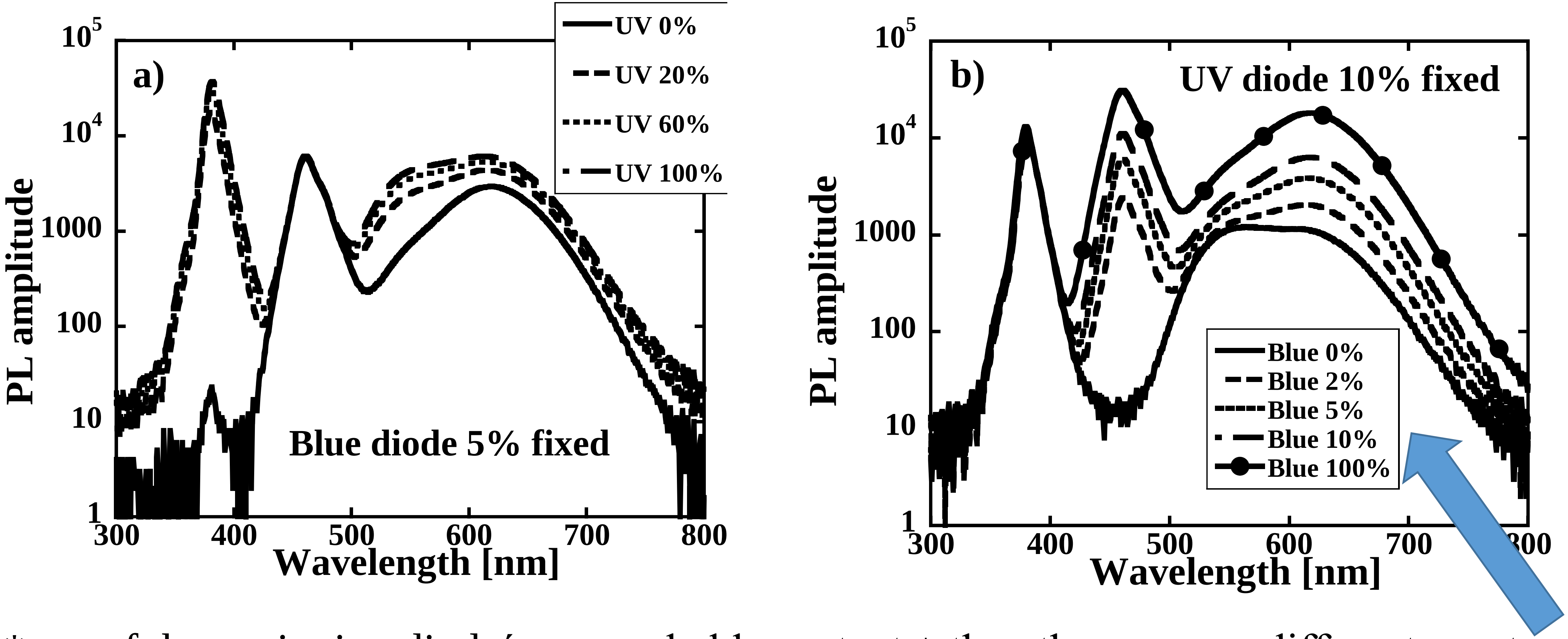




3x 385 nm 1 W diode +
1x 455 nm 3W diode

All LEDs meet in a place where phosphor is located

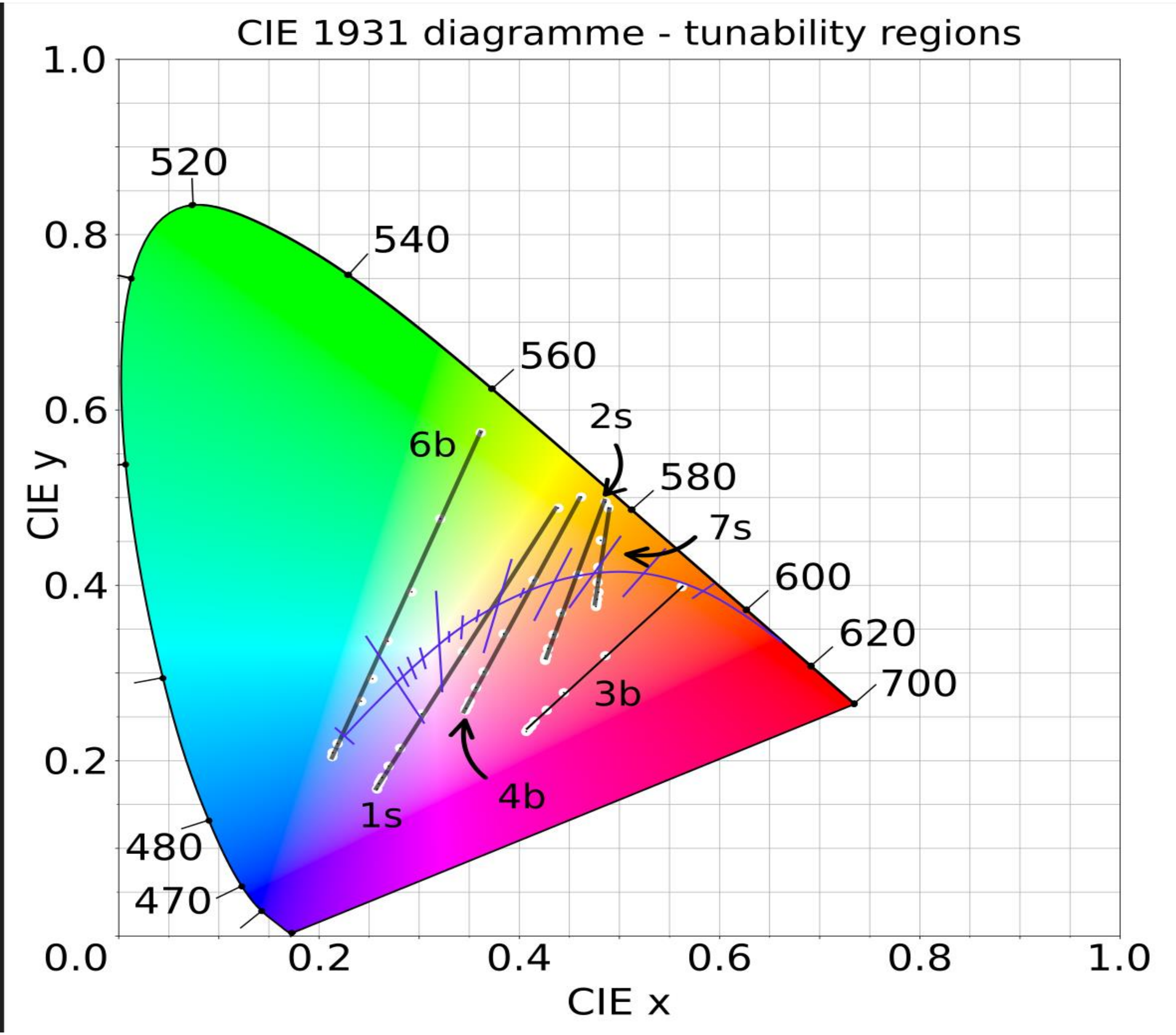
Overall emission spectra of light coming from circadian light source



*one of the excitation diode´s power held constant + the other vary → different spectra obtained

*by using SINGLE phosphor with SINGLE doping ($K_{0.8}Na_{0.2}LuS_2:Eu^{2+}$ (0.05%)) + two excitation diodes (385 nm, 455 nm), large area of color space can be covered and the spectra can be easily tuned to cover wide range of CCTs

Color properties of resulting white light - the tunability regions



*6b = $K_{0.85}Na_{0.15}LuS_2:Eu^{2+}$ (40% nearUV)

*1s = $K_{0.65}Na_{0.35}LuS_2:Eu^{2+}$ (100% nearUV)

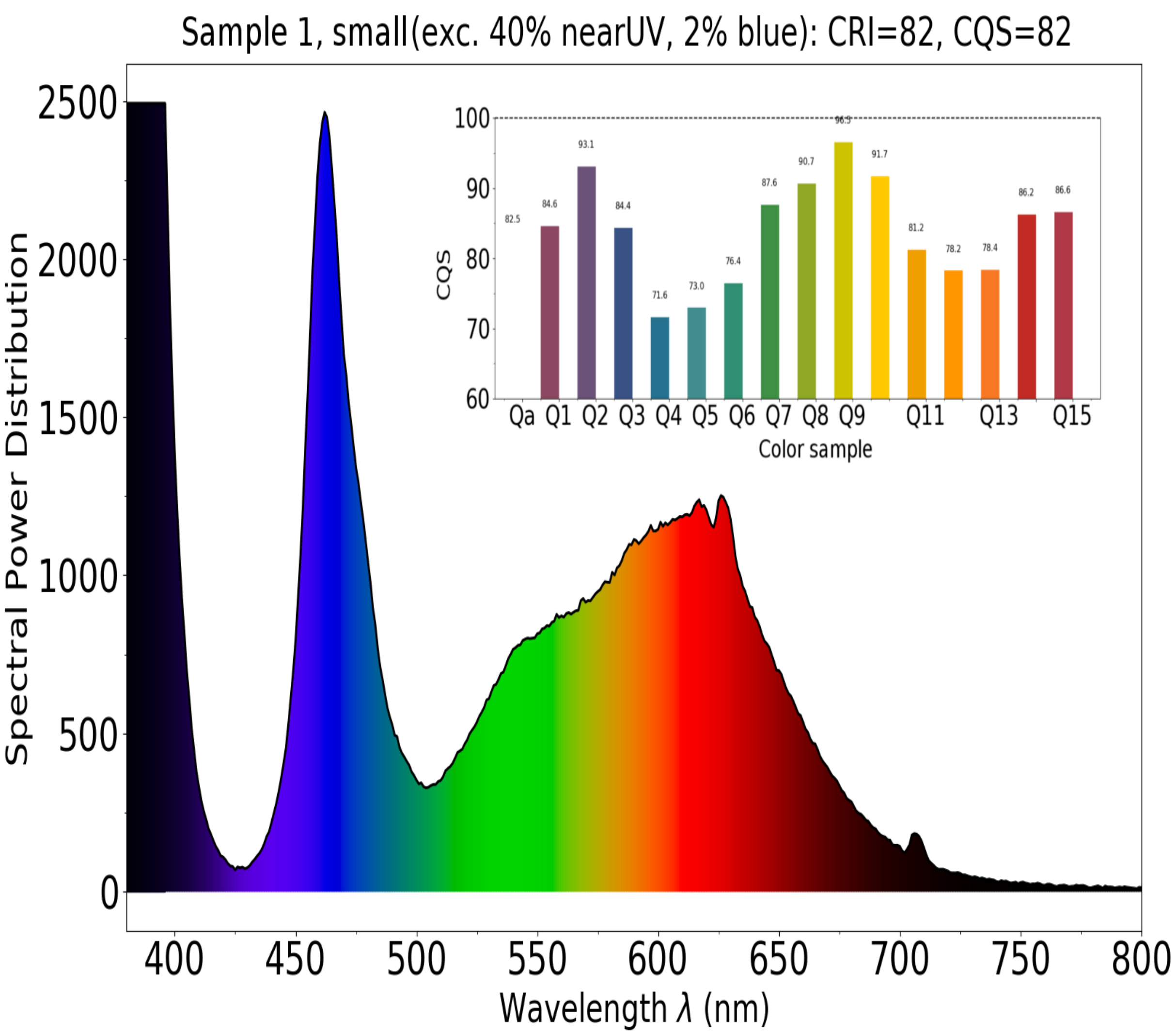
*4b = $K_{0.8}Na_{0.2}LuS_2:Eu^{2+}$ (60% nearUV)

*3b = $K_{0.75}Na_{0.25}LuS_2:Eu^{2+}$ (60% nearUV)

*7s = $K_{0.86}Na_{0.14}LuS_2:Eu^{2+}$ (40% nearUV)

*2s = $K_{0.74}Na_{0.26}LuS_2:Eu^{2+}$ (60% nearUV)

Color properties of resulting white light



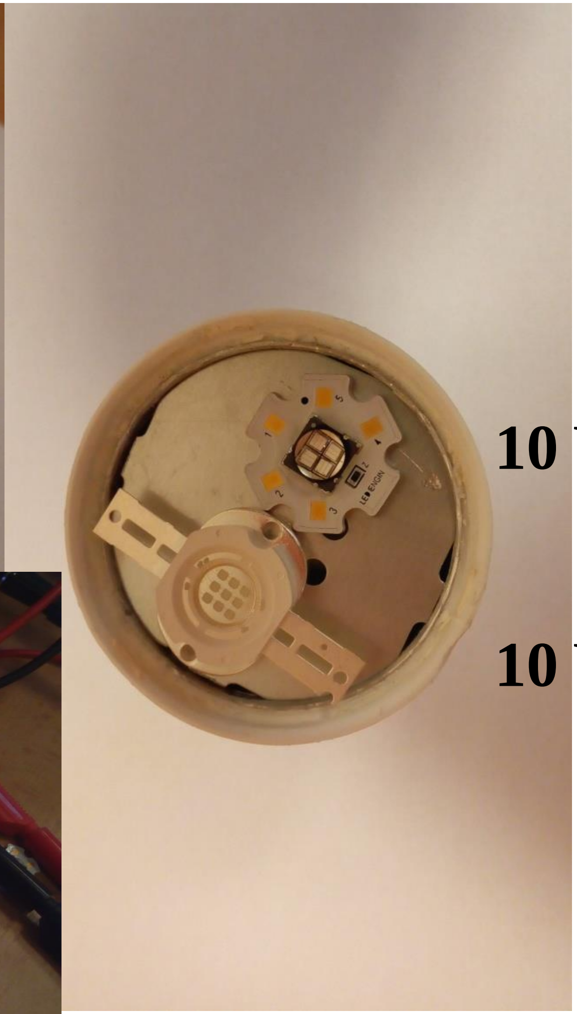
- Obtained mixed spectrum with **highest CQS metric** from sample $K_{0.65}Na_{0.35}LuS_2:Eu^{2+}$ (0.05%) under mixed excitation (nearUV 40%, blue 2%);

- 10 out of 15 samples have CQS > 80, (maximum value is 97).

Color properties of resulting white light

Sample*	NearUV [%]	Blue [%]	CIE-x	CIE-y	CQS	CRI	CCT
1 (small)	40	2	0.331	0.296	82.5	82.3	5595
1 (small)	60	2	0.338	0.308	82.4	84.6	5197
1 (small)	80	2	0.343	0.316	82.4	86.1	4970
1 (small)	100	2	0.350	0.327	82.2	87.2	4722
1 (small)	20	2	0.317	0.272	81.4	75.0	6840
1 (small)	100	5	0.309	0.258	80.2	70.6	8019
2 (small)	100	2	0.467	0.423	78.8	81.2	2704
2 (small)	80	2	0.464	0.418	78.7	82.0	2691
2 (small)	60	2	0.462	0.413	78.5	82.5	2681
2 (small)	40	2	0.460	0.407	78.3	83.0	2671
2 (small)	20	2	0.453	0.392	77.3	83.3	2635
2 (small)	100	5	0.451	0.382	76.4	82.6	2591
4 (big)	10	2	0.388	0.343	76.0	82.8	3507
2 (small)	10	2	0.446	0.374	75.9	80.9	2587
2 (small)	80	5	0.448	0.375	75.7	81.5	2567
4 (big)	20	2	0.404	0.375	75.6	80.3	3420
4 (big)	20	5	0.376	0.316	75.6	80.6	3607
4 (big)	40	5	0.385	0.337	75.6	82.7	3536
4 (big)	60	5	0.390	0.347	75.5	82.8	3508
4 (big)	80	5	0.393	0.355	75.4	82.3	3483
4 (big)	100	5	0.398	0.364	75.3	81.2	3462
4 (big)	80	10	0.373	0.311	75.3	80.4	3655
2 (small)	60	5	0.446	0.371	75.2	80.6	2550
4 (big)	100	10	0.377	0.320	75.1	81.5	3615

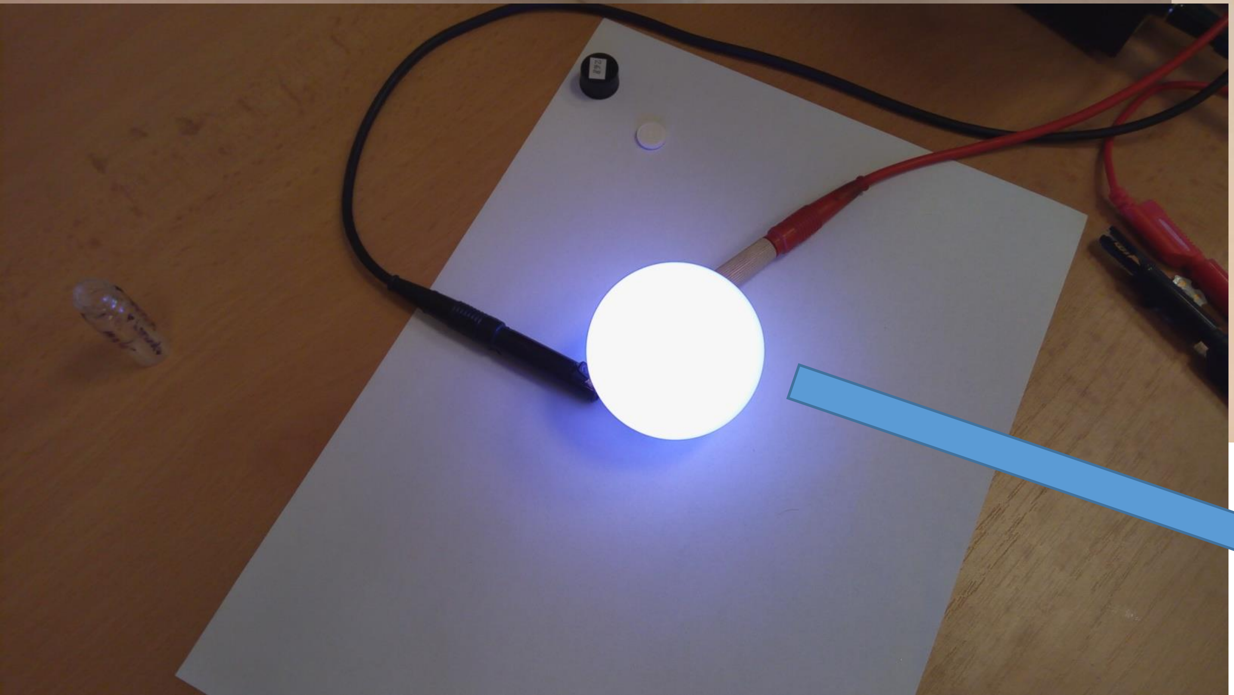
High power white LED based on two diodes + $K_xNa_{1-x}LuS_2:Eu^{2+}$ (0.05%)



10 W UV LED (385 nm)

10 W blue LED (455 nm)

Phosphor placed on both UV and blue LED



White light emission

Novel concept for tunable white LEDs based on UV excitation

-Single host material with two different luminescent centres, **A1 and A2**

-Single UV excitation (**LED at 360 nm**) – centre **A1** is excited and emits light

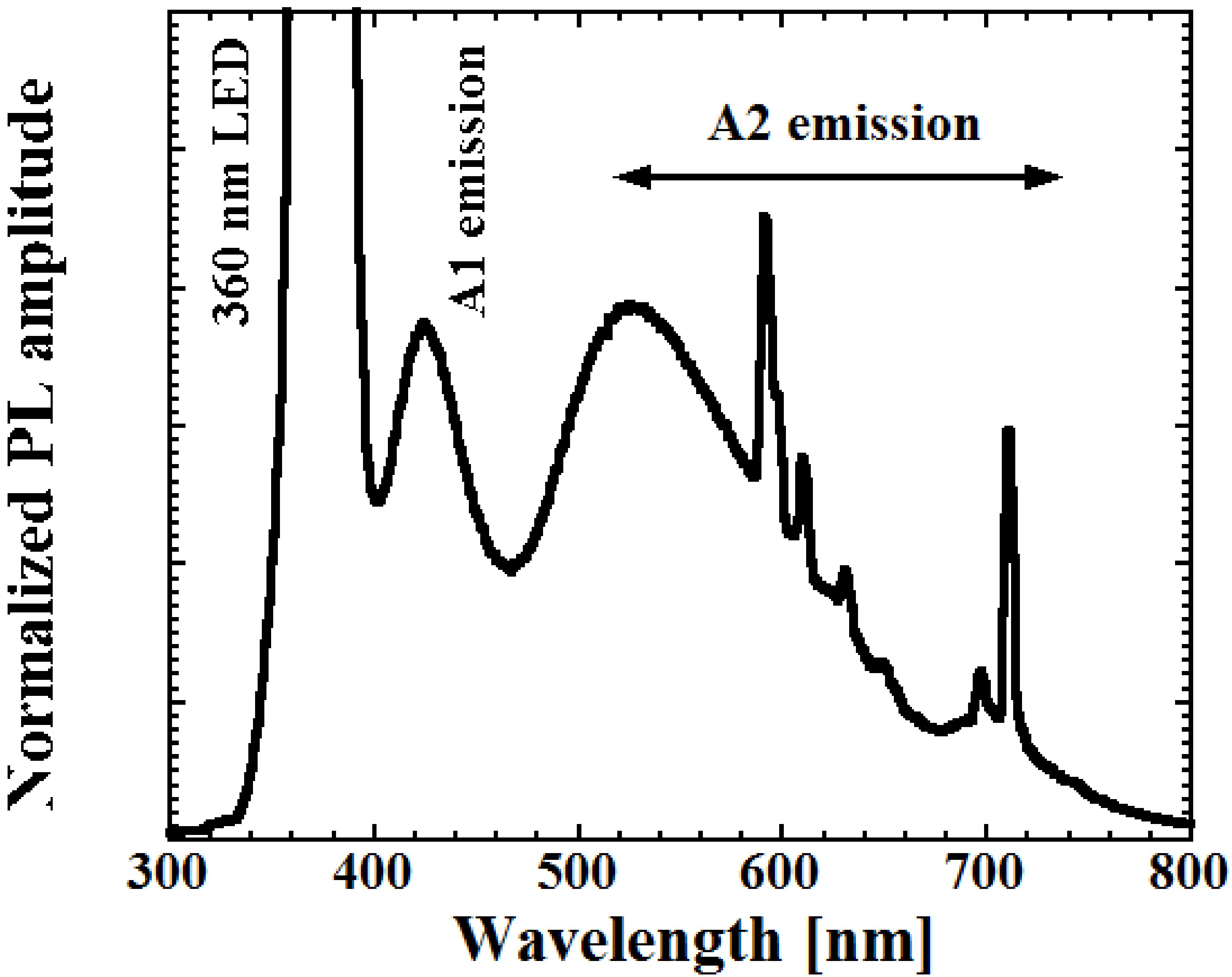
-Part of **A1**´s emission is absorbed by **A2** which emits at lower energies

-Only by single excitation at 360 nm, white light can be obtained in this manner

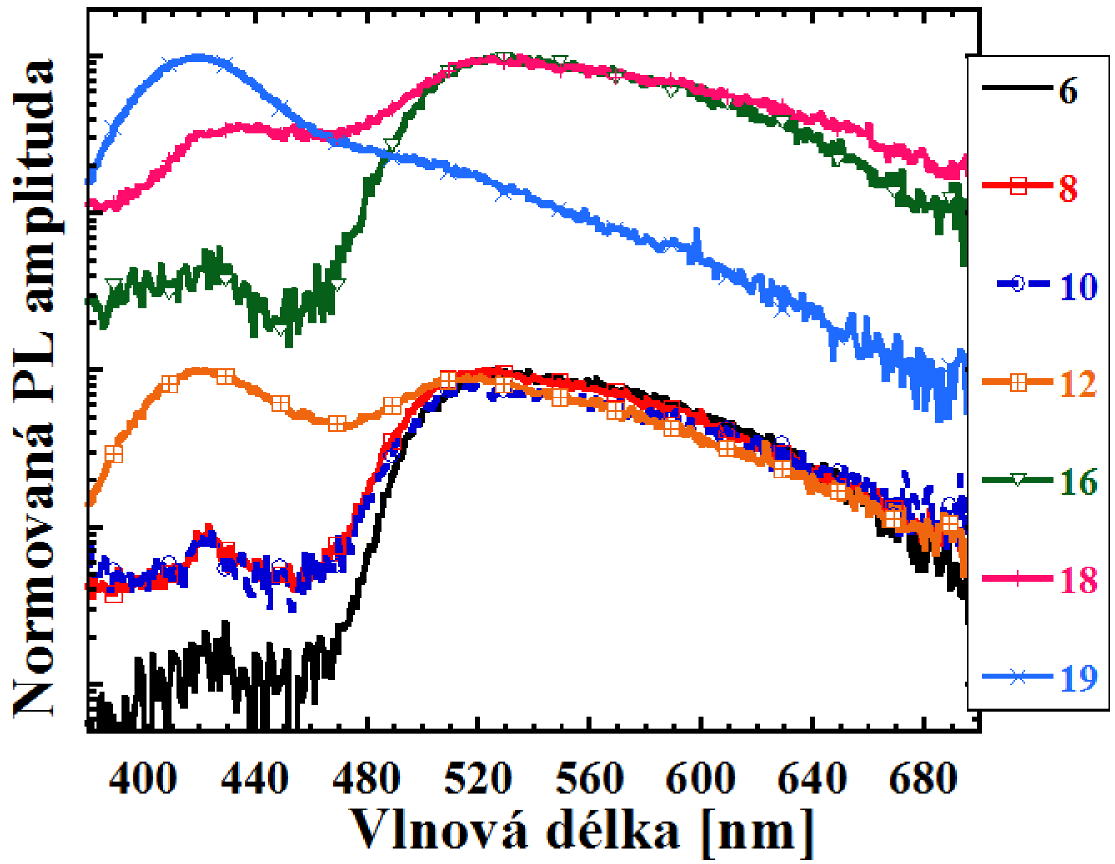
-Different CCT temperatures can be reached just by using different **A1**, **A2** concentrations and by chemical modification of a host

-These phosphors developed at the Institute of Physics, Czech Academy of Sciences

Optical properties – emission spectra under 360 nm excictation - example

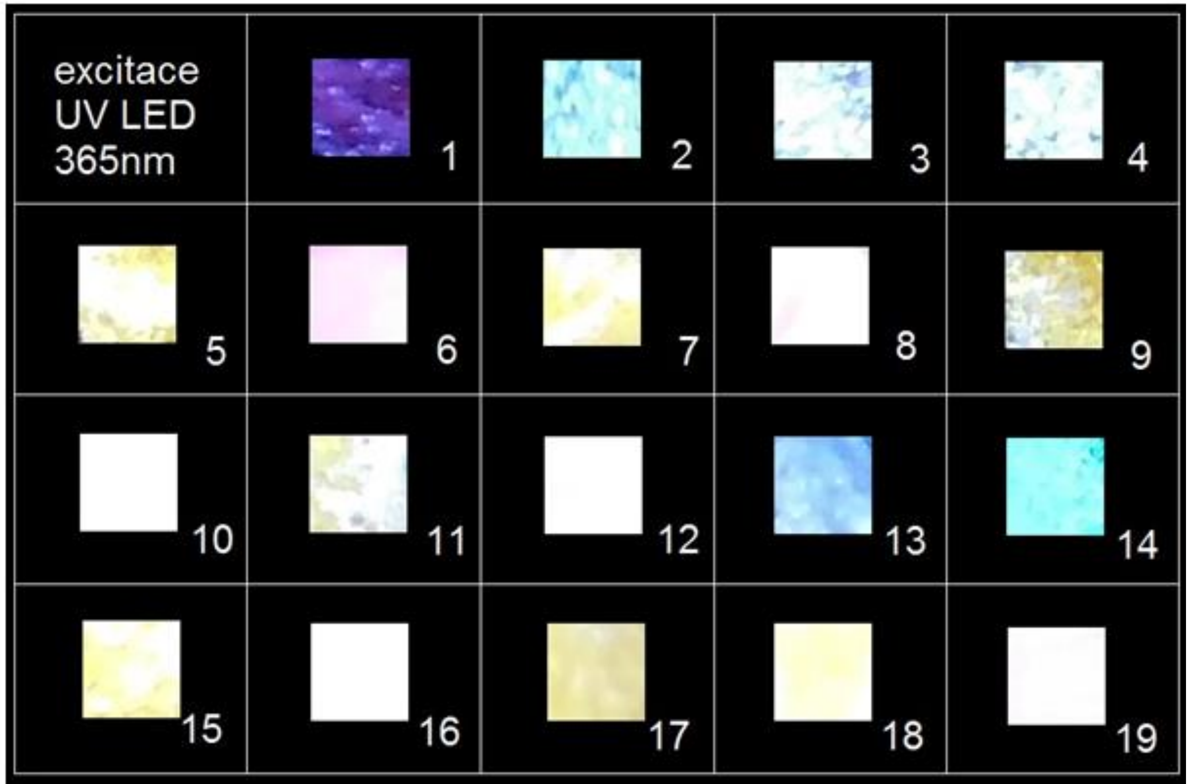


Examples of tunability – different A1, A2 concentration

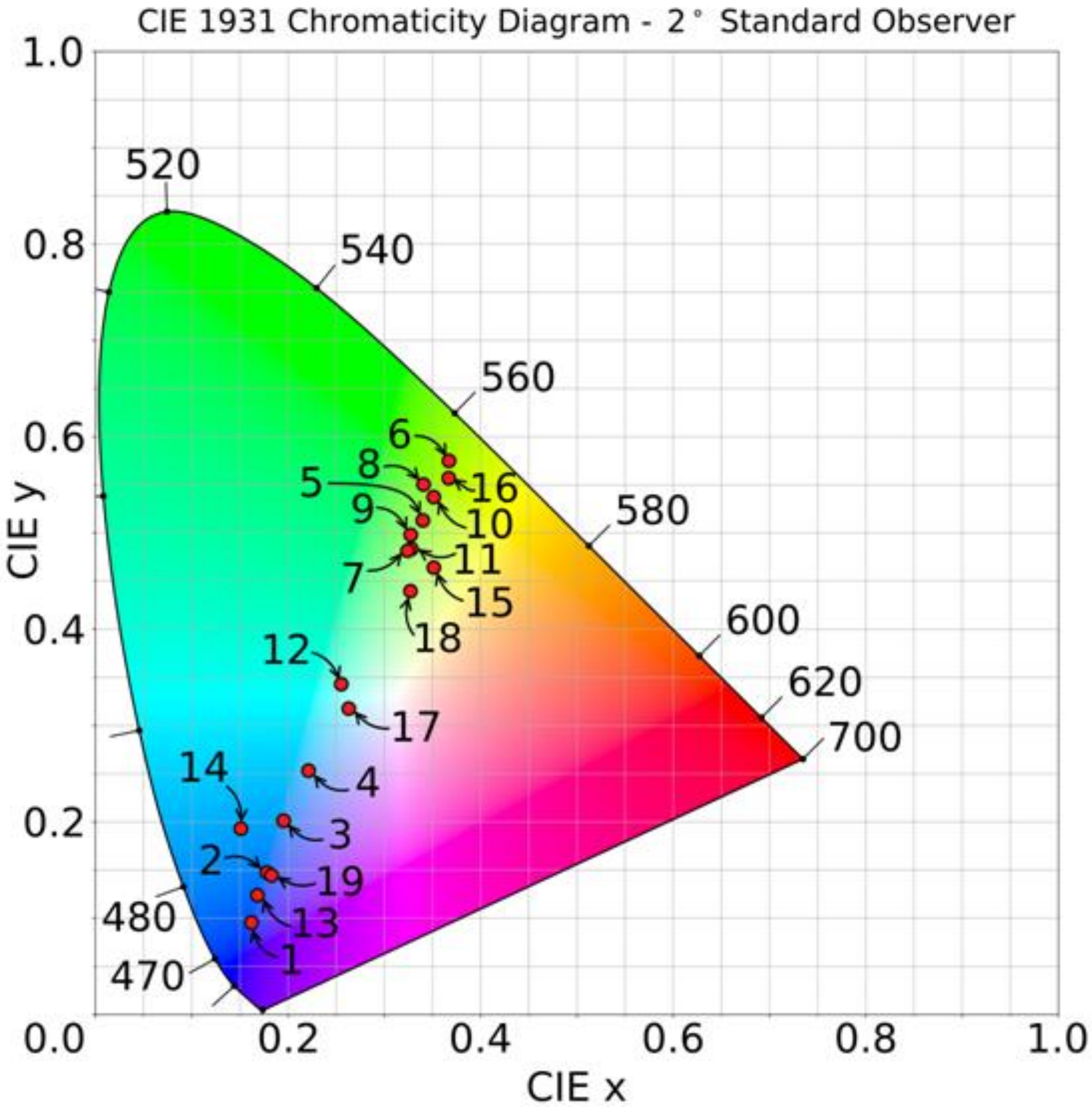


Examples of emission spectra of phosphors excited by 360 nm light as a function of A1, A2 concentration

Resulting outcome colours obtained by using real 365 nm excitation LED + our phosphors with different A1, A2 content



CIE coorinates – large area of visible space covered



Changes given only by varying A1, A2 concentration within one host under single 360 nm excitation

Conclusions

- Basic principles of LED technology were introduced;
- Fundamental parameters of pc-LEDs were defined and explained;
- Quantities used for light sources´ description were discussed;
- A selection of white LED phosphors was described;
- A circadian light source based on Eu^{2+}-doped (K;Na)LuS_2 is fully investigated;
- A principle of circadian light source operation based on two emission centres suggested;

LED in a bathroom → water temperature indicator ☺

KZLIDEA company