

New life of recycled rare earth-oxides powders for lighting applications.

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Abstract. In this work we analysed the optical and structural properties of Ce:YAG regenerated phosphors. The concentrate resulted as the final product of an industrial recycling process of waste electrical and electronic equipment (WEEE), and in particular fluorescent powders coming from spent lamps treatment plant. The waste pristine materials were re-utilized without any further purification and or separation process as starting materials to obtain a YAG matrix ($\text{Y}_2\text{Al}_5\text{O}_{12}$) doped with Cerium ions. We tested out the recovered concentrate against commercial Ce:YAG phosphors comparing their structural and optical properties by means of XRD measurements and steady time and time resolved luminescence. The analysis reveals that the new phosphors obtained by scrap powder have the same crystal structure as the commercial reference sample and comparable optical properties. In particular, the Ce-related emission efficiency has a quantum yield of about 0.75 when excited at 450 nm, in good agreement with our reference sample and with the one of commercial powder presently exploited in white LED. This achievement strongly suggests the possibility of a new life for the exhausted phosphors and a possible step forward to a complete circular process for lighting equipment.

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Introduction

Nowadays there is a spreading technological interest in the increase of efficiency of light sources. If one considers the revolution in lighting technology, both in concept, design and light systems, the society is dealing with in the late decades (from the first years of 2000's), the growing interest in the field is easily understood. According to McKinsey [1], the global market share of alternatives lighting sources as Light Emitting Devices (LEDs) and Compact Fluorescence Lights (CFLs), will raise from few percentage of the global market share in 2010 to almost 90% in the 2020. In particular, LED systems are foreseen to cover up to 70% of the lighting market, increasing from the current value of about US\$26 billion (2017) to more than US\$72 billion in 2020. The expected increase of LED exploitation has a great relevance in terms of environmental impacts, a reduction of



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25% of traditional incandescent lamps by substitution with alternative sources corresponds to saving more than 180 million tons of CO₂ emitted.[1],[2]

The main drawback in LED and CFL technology is that LED and CFL systems make a large use of phosphors as emitting sources [3]. The latter are mainly represented by Rare Earths Elements (REE) based compounds, a requirement that can have potential impact on the economical point of view, due to potential supply disruption of raw materials and to elevated cost of their initial refining process. Currently, white emission in LED technologies (WLED) is achieved by using up or down conversion of phosphor emission. For WLEDs, phosphor down-conversion is most commonly based on a blue or near-ultraviolet LED combined with a yellow-emitting phosphor, or a combination of different phosphors to produce a broad energy distribution [4]. The phosphor(s) may be incorporated into the LED package, or may be located remotely. Fluorescent lamps (CFL) also exploit phosphors' down-conversion, the fluorescent powders being deposited on the lamp bulb and excited by the emission of the mercury vapour. In both the cases, Ce doped Yttrium Aluminium Garnet (Ce:YAG) represents the phosphor of choice for its spectral properties. The ubiquity of Ce:YAG phosphors in commercial devices is related to their very simple and cost-effective fabrication, as well as their long term stability, which is related to the high melting point and stable thermal and chemical properties of the system. However, the supply of REE, such as Ce and Y in Ce:YAG phosphors, to European industry completely relies on China, the main world producer of REE compounds, and such a dependence of the supply chain represents a potential disruptive economic threat. Indeed, the concentrated supply of REE, where a portion of about 99 % and 87 % for heavy and light REE, respectively, are currently sourced from China, has resulted in a supply chain for European end-users that is not sufficiently robust when considering high capital investments in modern technologies. [3] Although different alternatives to RE based phosphors were already proposed to Ce:YAG phosphors (organics, hybrids, nanodots) [5]-[14], the use of rare earths seems still with the higher potential solution to easy implementation in solid state lighting devices.

In order to reduce this threatening dependence on China REE supply, European industry must develop novel "REE-free" technologies and/or reduce the REE waste and increase its capability to re-use and recycle them. An archetypal example in this respect is the supply chain of Aluminium in Italy, where no mines of raw materials are present and the whole national production of Al relies on recycling politics. The aim of this paper is to demonstrate a possible low cost way to exploit REE waste of CFL as secondary source of phosphors.

LED waste is classified by the 2012/19/EU Directive as a Waste Electrical and Electronic Equipment (WEEE). The recycling processes, widely applied by the European recyclers, are mainly addressed at the recovery of major commodity fractions (e.g. plastics, glass), with still high amounts of landfilled materials. However, the presently un-recycled residual fraction contains many strategic elements at concentration even higher than primary ores like Rare Earths (such as Yttrium, Lutetium, and Europium). Consequently, the current management strategy of end of life LED/CFL lighting devices determines two potentially extremely negative impacts, a dangerous contamination of the environment and the neglected extraction of critical raw materials. The methods for Yttrium and other REE extraction, described by patents and scientific articles [15]-[17], are based on hydrometallurgical and pyrometallurgical processes. Pyrometallurgical extraction requires high consumption of energy, has very high environmental impact due to gaseous emissions and requests high capital investments, so that being unsustainable for the European SMEs recyclers. For this reason hydrometallurgical processes are generally preferred, but there are still a few drawbacks, the main one for Yttrium, REE and Indium recovery from target waste being the too high energy consumption for the production of high purity products.

In this scenario, the present work deals with the possibility to re-use the Ce:YAG fine fraction residue of the hydrometallurgical treatment from spent lamps without any further chemical purification/separation or extraction as starting material to obtain new phosphors for WLED emission, thus promoting a low cost process for secondary sources' supply with virtual no impact on the environment.

Experimental

Two sets of Cerium doped YAG samples have been prepared; for the preparation of set 1 (YAG1), waste powders from the industrial plant of the Relight srl have been utilized.[18] The chemical composition is reported in table 1, evidencing the large contribution of Yttrium oxide (86.12%), and minor contributions of Europium oxide (5.98%) and Gadolinium oxide (2.98%).

The starting oxides were dissolved in nitric acid to convert them into corresponding nitrates. The powder was dissolved in 600 ml of 0,4 mol/l solution of the Nitric acid. The solution was agitated for 8 hours at temperature of 50 °C. The pH was monitored and, when needed to preserve pH in the range of 4.5-5.0, concentrated nitric acid was added.

Since in the starting oxides there was an excess of europium oxide and a lack of aluminium and cerium ions, pure $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Aldrich), and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich) was added in the stoichiometric amount to obtain the right molar ratio.

The second set (YAG2) was obtained starting from pure nitrates; Pure $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Aldrich), $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich) and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich) were utilized.

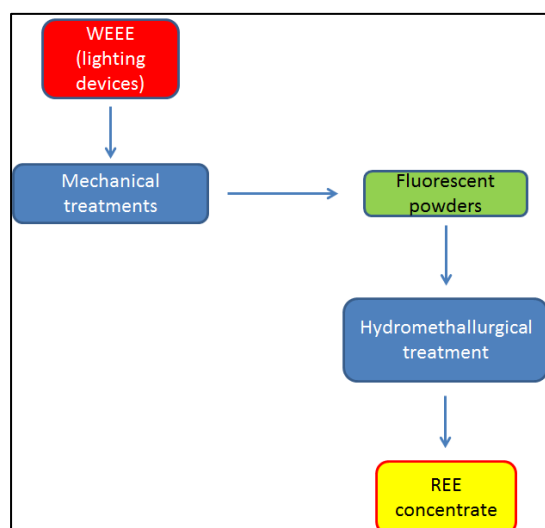
For both the synthesis the nitrate salts were dissolved in 80 ml of deionized water and acetic acid was then added as complexing agent. These metal salts were dissolved at a molar ratio, Y:Al, of 3:5, respectively. Ce was added to obtain a concentration of 1.0 at. %.

Each solution was heated with stirring at 60°C for 1 hour. Then, ethylene glycol was added to the solution until it became a gel. Successively it was dried at about 100°C for three days and calcined at 1250 °C, each sample for 12 hours.

X-ray diffraction patterns were collected by using a Seifert X3000 diffractometer with a θ - θ Bragg-Brentano geometry with Cu-K α wavelength.

Steady state photoluminescence (SSPL) measurements were performed using the filtered light from a laser driven Xenon lamp (EQ- 99-X) with a final bandwidth of about 1 nm, while time resolved luminescence (TRPL) measurements were performed using an optical parametric oscillator with a frequency doubler device, pumped by the third harmonic (355 nm) of a pulsed Nd:YAG laser (Quanta-Ray Pro 730). The excitation pulse width at half-maximum was 8 ns with 10Hz of repetition rate, and spectral bandwidth less than 0.3 cm⁻¹. The collected signal was dispersed by a spectrograph (ARC-SpectraPro 300i) with a spectral bandpass <2.5 nm and detected by a gateable intensified CCD (PI MAX Princeton Inst.). The preparation of a white LED from waste powders has been obtained by drop casting a suspension of the YAG1 powder in a methanol solution over a blue LED (OSRAM Golden DRAGON, LD W5SM) with main emission at 460 nm.

Table 1 atomic percentage of REE oxides in scrap powders. The scheme of the extraction process of the REE concentrate is also reported on the left



<u>Material</u>	<u>atomic content</u> (%)
Lanthanum oxide	0.02
Cerium oxide	0.96
Europium oxide	5.98
Terbium oxide	0.73
Yttrium oxide	86.12
Gadolinium oxide	2.98
others	3.21

Results and Discussion

Figure 1 reports the XRD diffraction pattern of the Ce:YAG samples obtained from scraps (YAG1) and from pure/commercial starting materials (YAG2). The spectra are in agreement with the JCPDS card: 79-1892/1 relative to the YAG structure. Low intensities peaks at about $2\theta = 28^\circ$ e 47° reveals the presence of minor phase impurities, most probably $\text{Al}_2\text{Y}_4\text{O}_9$ in both the samples, due to the relative low temperature synthesis. It is worth nothing that minor peaks related to the presence Y_2O_3 , YAlO_3 and Ce_2O_3 are observed.

The Scherrer analysis has been performed to have an estimation of the average dimension of the nanocrystals. According to the equation:

$$D = \frac{0.89K_\alpha}{\beta \cos \theta}$$

where β is the line broadening at half maximum in radians observed in the experimental spectrum at $2\theta = 18.10^\circ$ and $K_\alpha = 0.1540$ nm. The average dimension of the nanocrystals can be estimated for the two set of samples between 40 and 50 nm.

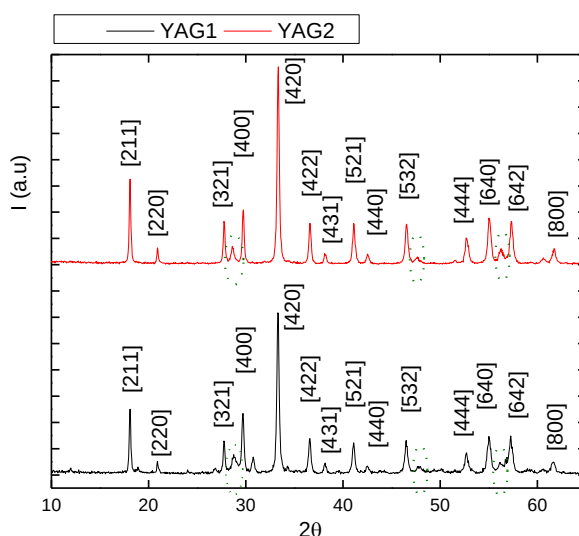


Figure 1 - XRD diffraction pattern of sample YAG1 (obtained from scraps) and YAG2 (from pure starting compounds). Peak indexes of the YAG phase are indicated, the peaks from secondary phases are indicated with green dotted circles

The emission spectra of the two samples, excited at 450 nm, are almost overlapped, a further indication of the close resemblance of the crystallographic structure (**Figure 2**) of the two set of samples because of the well-known effect on the emission properties of the crystal field (see in following). Indeed, we observed only a small broadening of the emission band towards the lower spectral energy side in scrap YAG1 sample as compared to our YAG2 reference. The emission band peaked at about 450 nm arises from Ce^{3+} ions and is related to the recombinations from the 5d levels to the fundamental doubly split 4f levels $^2F_{5/2}$ and $^2F_{7/2}$ [19]. Generally, the effect of local crystal field surrounding the Ce^{3+} ion affects the position of the 5d levels, while is rather weak on the 4f states due to the shielding effect of the outer 5p and 6s electrons [19]. Since the starting scrap powders of YAG1 contain Gd oxide and Ce doped Gadolinium Aluminium Garnet could be formed during the synthesis (even though at a concentration level below the sensitivity threshold of XRD measurements). Indeed, the emission of Ce^{3+} ions is redshifted in Ce:GdAG as compared to Ce:YAG [20],[21].

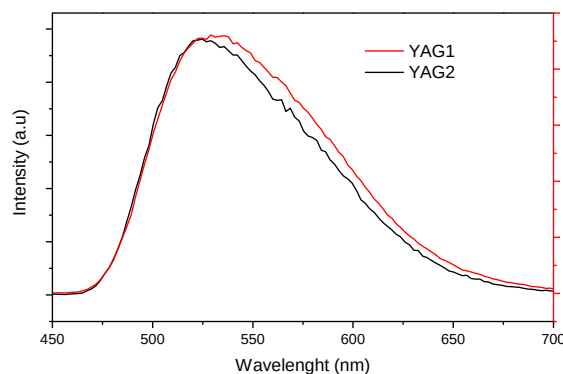


**Figure 2 - Steady time photoluminescence spectra of YAG1 and YAG2 samples.
Excitation wavelength: 450 nm**

Despite the presence of Ce:GdAG phase and the low quantum efficiency of radiative recombinations of Ce in Ce:GdAG, no substantial decrease of efficiency in recovered YAG1 samples was observed with respect to our reference sample (YAG2). The quantum yield of the emission was evaluated according to the following equation [22]:

$$QY = QY_R \frac{I}{I_R} \frac{OD_R}{OD} \frac{n^2}{n_R^2}$$

where the subscript R refers to our reference (Coumarin 540, C6), I is the PL intensity excited at 450 nm, OD indicates the optical density (that is the absorbance) which was evaluated at 450 nm, and n refers to the refractive index (at 450 nm) of the samples (ethanol for the C6 reference solution) [22]. We estimated a quantum efficiency of about 0.75 for both the samples, gathering a 17% decrease as compared to commercial bulk samples, where the QY is of about 0.9 [19], [23]. As we discuss in the following, we ascribe the reported decrease of QY to the nanosized dimensions of our samples, instead of to the presence of impurities or defects.

To go further in the characterization of the samples, we recorded time resolved luminescence of both the samples excited at 450 nm. The spectra, reported in **Figure 3**, and the time decays monitored at the peak position (550 nm) are very similar for both the samples. We also verified that the spectral profile did not change when recorded at different delays from the excitation pulse down to 150 ns time delay. This is a further proof that the recombinations take place from the same Ce^{3+} emitting site and no secondary emissions and/or charging phenomena to other centers are observed.

The decay kinetics can be well represented by a multiexponential decay model by assuming two different decays. In this model, the PL intensity at a certain time t is the sum of individual single-exponential decays[22]:

$$I(t) = \sum_{i=1}^n \alpha_i \times e^{-t/\tau_i}$$

where τ_i are the decay times and α_i their amplitudes at time $t = 0$ (n is the number of decays, $n=2$ in the present case).

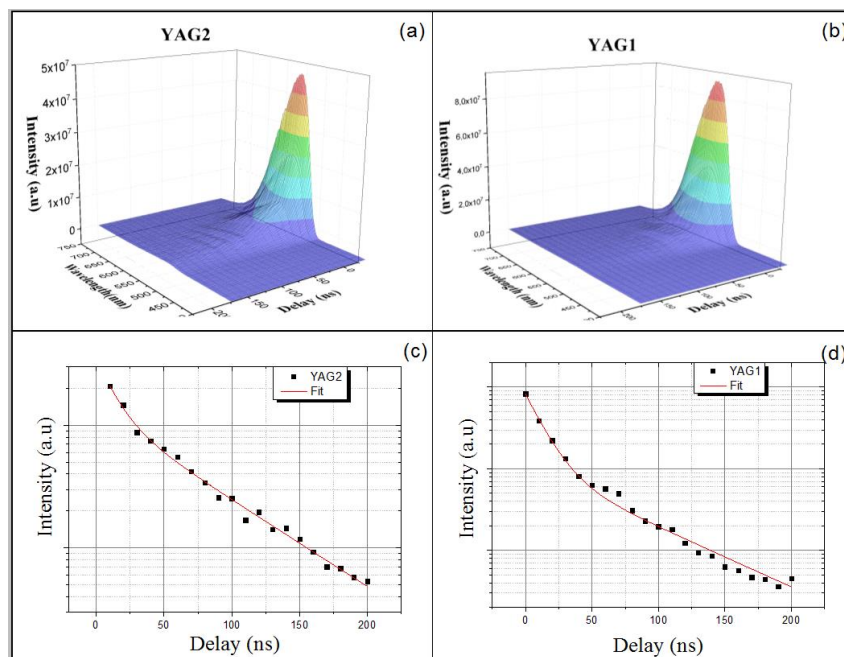


Figure 3 Time resolved luminescence spectra from YAG1 and YAG2 samples. In panels a) and b) the full decay spectra are reported; in panels b) and c) the time decay evolution is reported monitored at 550 nm. Excitation wavelength: 450 nm

The presence of two time decays is indicative of two recombination paths, with estimated time decays of 8 ns and 65 ns for the faster and slower component respectively (**Figure 3**). Since the spectral profile did not change during the decay, we can hypothesize that there are two different mechanisms of depletion of the emitting centers. The slow decay is in good agreement with literature data of Ce³⁺ decays of about 60-70 ns in bulk YAG matrices. Typically, this time decay is well represented by a single exponential decay [23]. In our case, however, we have two decays, and the second fast one could be related to some non-radiative channels depleting the Ce³⁺ excited level. Therefore we propose to assign the slow recombination channel of our samples to “bulk” recombination and the faster one to recombination at Ce³⁺ sites close to the surface. The proposed assignment is supported by the estimated nanosize dimensions of our samples, being the powders constituted by nanoparticles with mean average diameter of about 45 nm. At nanoscale, due to the surface-to-volume ratio, the contribution of surface centers, including both radiative and non-radiative paths, became relevant. The non-radiative path can be related to the presence of OH group at the surface, or, more generally, to the presence of surface defects. Another possibility is the formation of Cerium clusters at the surface, related to the higher ionic radius of Ce³⁺ (1.034 Å) with respect to Y³⁺ (0.880 Å). We would like to point out that the mechanism leading to the presence of a faster decay, responsible of the smaller QY estimated with respect to bulk samples, is the preparation procedure that settles the nanosized dimensions of our crystals. Indeed, we retrieved the same time decay plot in both the samples, the scrap recovered YAG1 and our reference YAG2, both prepared with the same procedure described in the experimental section.

To evaluate the weight of the surface contribution we estimated the fractional contribution f_i of each time decay. It also represents the contribution of each component to the steady-state intensity, allowing comparing time resolved and steady state spectra. The fractional contribution is defined as follows [22]:

$$f_i = \frac{\alpha_i \tau_i}{\sum_j \alpha_j \tau_j}$$

As extracted from the previous equation, the fractional contribution of the fast surface de-excitation accounts for 28% and 20% of the overall emission of YAG1 and YAG2, respectively. We also estimated the average lifetime $\langle t \rangle$, defined as a weighted mean of gathered data by assuming a multiexponential decay model [22], where the contribution of each decay to the average decay is weighted. The average lifetime $\langle t \rangle$, for a double-exponential decay, can be defined accordingly:

$$\langle t \rangle = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2} = f_1 \tau_1 + f_2 \tau_2$$

The data indicate that there is a very slightly difference among YAG1 and YAG2 with average lifetime of 48 ns and 54 ns, respectively.

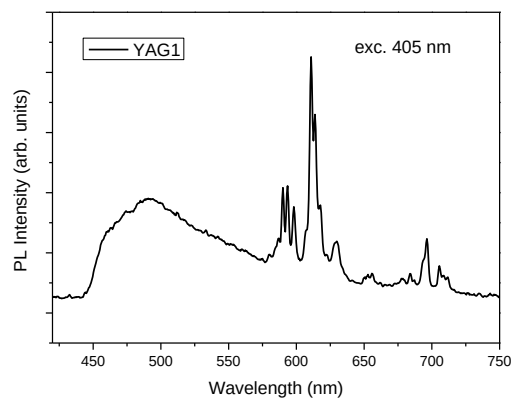


Figure 4 Steady time photoluminescence spectrum of YAG1 sample. Excitation wavelength: 405 nm.

To characterize further the scrap powders, we investigated the possible presence of impurities by exciting at 405 nm. Indeed, aiming to exploit our recycled powders as possible secondary source of phosphors in lighting applications, the typical excitation is in the 400-450 nm range. When exciting at smaller wavelengths, the emission contribution of possible impurities can be detected. It is worth nothing that the presence of impurities is not always detrimental, but can be exploited to change the emission properties of the phosphors. Actually, by exciting YAG1 sample at higher energy, besides the recombination from Ce^{3+} ions, still observed but with decreased efficiency, we gathered the emission from Eu^{3+} ions. Those ions are embedded in the YAG1 matrix but could not be excited a larger wavelengths. In this framework, **Figure 4** reports the emission spectra excited at 405 nm, where additional narrow bands with respect to the broad Cerium emission are clearly evident. The main peaks, centered at 590 nm, 610 nm and 710 nm, are assigned to the recombination $^5\text{D} \rightarrow ^7\text{F}_j$, $j=1,2$ and 4 respectively of Eu^{3+} .

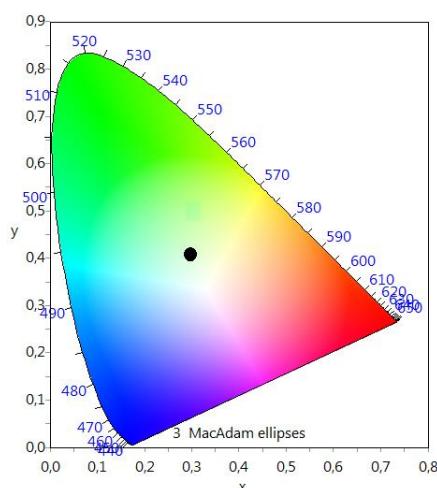


Figure 5 - CIE diagrams of YAG1 sample. The spectrum contains also the residual component of the 460 nm line of a commercial LED

Finally, in order to prove the effective possibility to reutilize the obtained phosphor, a blue led (emission at 460 nm) was covered with a thin layer of YAG1 by drop casting the powder dispersed in ethanol solution. As expected, the emitted spectra presents the emission of the YAG1 phosphors coupled with a strong residual component of the electro-emitted radiation by the LED (CIE coordinates: $x=0.3041$, $y=0.4095$). The CIE spectrum, reported in **Figure 5**, evidences the perceived white light, and indicates the way we can re-use the waste of CFL or display systems.

Conclusions

In this work we demonstrated that Ce:YAG regenerated phosphors synthesized starting from scrap powders derived by an industrial recycling process of waste electrical and electronic equipment from exhausted CFL can find new applications in lighting field as secondary sources of phosphors. The samples were synthesized by following a nitrate-based low temperature procedures that allows to prepare crystalline nanoparticles of about 45 nm in diameter. The regenerated powders have a quite high quantum yield (0.75), only 17% lower than commercial bulk samples, and comparable to the one of samples produced by the same synthesis but starting from commercial powders. We realized a white LED device by drop casting the powders dispersed in ethanol on a commercial blue LED. The optimal optical performances and the good quality of the white light perceived in a model lighting application strongly suggest the possibility of a new life for the waste regenerated phosphors and a possible step forward to a complete circular process for displays and CFL.

References

- [1] McKinsey & Company Lighting the Way: *Perspectives on the Global Lighting Market* 2nd edn; (2012);
- [2] Evstratyeva, K Market Overview for Global LED Industry: 2013–2018 (Strategies Unlimited/Pennwell, 2014).
- [3] Report “Critical raw materials for the EU” by ad-hoc working group on defining critical raw materials of Raw Materials Supply Group. May 2014-
http://ec.europa.eu/enterprise/policies/raw-materials/critical/index_en.htm
- [4] National Research Council. 2013. *Assessment of Advanced Solid-State Lighting*. Washington, DC: The National Academies Press.
- [5] Luridiana, A, Pretta, G, Chiriu, D, Carbonaro, CM, Corpino, R, Secci, F, Frongia, A, Stagi, L, Ricci, PC 2016 *RSC Advances*, 6 (26), pp. 22111-22120
- [6] Chiriu, D, Stagi, L, Carbonaro, CM, Ricci, PC 2016 *Physica Status Solidi (C) Current Topics in Solid State Physics*, 13 (10-12)
- [7] Chiriu, D, Stagi, L, Carbonaro, CM, Ricci, PC 2016 *Physica Status Solidi (C) Current Topics in Solid State Physics*, 13 (10-12), pp. 989-997.
- [8] Chiriu, D, Stagi, L, Carbonaro, CM, Corpino, R, Casula, M.F., Ricci, PC 2016 *Materials Research Bulletin*, 77, pp. 15-22
- [9] Carbonaro CM,, Ricci PC, Grandi S, Marceddu M, Corpino R, Salis M, Anedda A, 2012 *RSC Advances*, 2 (5), pp. 1905-1912
- [10] Carbonaro, C.M., Orrù, F., Ricci, P.C., Ardu, A., Corpino, R., Chiriu, D., Angius, F., Mura, A., Cannas, C. 2016 *Microporous and Mesoporous Materials* 225, pp 432-439
- [11] Ricci, PC, Carbonaro CM, Casu, A, Cannas C, Corpino R, Stagi L., Anedda A, 2011 *J. Mater. Chem.* 21 (21), pp. 7771-7776 .
- [12] Kim, T-H, Chung, D-Y, Ku, J, Song, I, Sul, S, Kim, D-H, Cho, K.-S., Choi, B.L., Min Kim, J., Hwang, S., Kim, K. 2013 *Nature Commun.* 24, 2637 .
- [13] Choi, MK, Yang, J, Kang, K, Kim, DC, Choi, C., Park, C, Kim, SJ, Chae, SI, Kim, T-H, Kim, JH, Hyeon, T, Kim, D-H 2015 *Nature Comm.* , 6, art. no. 7149.
- [14] Wei, W, Xu, H, You, Q, Cheng, Q, Liu, C, Zou, L, Liu, X, Liu, J, Cao, Y-C, Zheng, G 2016 *Mater and Design*, 91, pp. 165-170
- [15] Beolchini F, Fonti V, Dell’anno A, Rocchetti L, Vegliò F 2012 *Waste manage* 32, 949-956
- [16] Cui J, Zhang L. 2008 *J. Hazard Mater* 158, 228-256
- [17] Zhifeng L Patent (2015) CN103191903 (B) “Method for recycling waste LCD (liquid crystal display) panels”
- [18] Innocenzi, V, Michelis, ID, Sgarioto, S, Gotta, D, Kopacek, B, Veglio, F 2016, *Electronics goes green* 2016+, 7829831.
- [19] He, X, Liu X, Li R, Yang B, Yu K, Zeng M, Yu R 2016 *Sci. Rep.* ; 6: 22238.
- [20] Joshi C, Yadav P, Moharil SV 2014 *Trans. Electrical and electronics Materials*, 15, 69-72
- [21] Tien T Y, Gibbons EF, DeLosh RG, Zacmanidis P J, Smith DE, and H. Stadler L 1973 *J. Electrochem. Soc.*, 120, 278
- [22] Lakowicz JR, *Principles of Fluorescence Spectroscopy*, 2nd Ed., Kluwer Academic, 1999
- [23] Gorrotxategi P, Consonni M, Gasse A 2015 *J. Solid State Light.* 2:1