PHOTOLUMINESCENCE FUNDAMENTALS MATERIALS CHARACTERIZATION AND APPLICATIONS

A general narrative review with emphasis on rare earth activated inorganic phosphors

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Abstract

Photoluminescence (PL) is a correlation of optical absorption to radiative relaxation in molecules, semiconductor nanocrystals and activated inorganic solids. The present narrative review reports some physical principles, synthesis, characterization and applications with particular emphasis on rare earth activated phosphors. The revision include PL, and thermoluminescence, three of context absorption or structure and eight are not in scope. The revision also includes the comparison of the same material activated by Ce^{3+} (silicate and $KBaPO_4$) with Tb^{3+} (barium silicate) and Bi (BaS). Increasing relative intensity is observed in the $KBaPO_4$ study from 1 to 10 mol% Ce^{3+} and Y_2O_3 activated with erbium shows the difference between stimulated trap release and prompt emission. Source reported wavelengths, chromaticity and concentration effects are taken into account, as are incomplete articles and internal inconsistencies. These results are useful for wavelength conversion and selection of candidates but do not necessarily give a rank for quantum yield, thermal stability or device efficiency. Phase and valence confirmation, calibrated photon yield, time resolved spectroscopy and application testing are essential for reliable translation.

Keywords: Photoluminescence, rare earth ions, inorganic phosphors, quantum yield, energy transfer, optical characterization, solid state lighting is key.

1 Introduction

Fluorescence of molecules, semiconductor crystals, defects and intentionally doped inorganic hosts is a case where light emission after optical absorption is encountered. These systems, while different chemically, are similar in that there is a competition between the processes generating photons and processes dissipating the excitation by other channels. Thus, the photoluminescence (PL) has two functions, useful optical output and as a probe of the electronic structure and relaxation pathways of matter. It cannot be interpreted considering one of the functions only. A bright spectrum is not a general certificate of performance, but instead a measurement of a material in a specific experimental setup. [1] The bibliography supplied is focused on rare earth activated phosphors for lighting. Examples of such representative materials include Tb^{3+} and Eu^{3+} and Dy^{3+} activated $Ba_2Sr_2Al_2O_7$ [2], mixture of $SrMg_2Al_{16}O_{27}$ activated by mixed activator [3], Tb^{3+} activated ZrO_2 [4] and borate systems doped with Tb^{3+} or Ce^{3+} [5, 6, 7]. These studies give impetus to a general consideration of the interaction between the emitting centre and its host. They also demonstrate how seemingly identical emission colours can have different origins, implying different transitions, excitation mechanisms and local environments. Other examples of hosts

included are Tb^{3+} activated $MgSrAl_{10}O_{17}$ [8] and Sr_2BO_3Cl [9] which further illustrate the variety of aluminate and borate related hosts included in the literature provided. A general review should not be limited to the cataloguing of host compositions. It should describe which observations are important to a mechanism and which properties are similar between laboratories and which other measurements would be required to make an application case strong. In this paper, therefore, we connect the basic photophysics, the families of materials, synthesis, the spectroscopy and the requirements of application. The most attention is focused on rare earth phosphors since they dominate the sources supplied; organic emitters and semiconductor nanocrystals are included to place this emphasis in the broader context of PL.

2 Scope and literature approach

The new selective narrative review has been updated by reviewing the paper on PL,TL and other allied area. All attachments were checked for title and physical quantity of attachment. The earlier literature with its evidence limitations remains from the manuscript provided. This is a selective narrative review; no exhaustive search of databases or pooled estimate/meta-analysis is claimed. Extraction of nominal composition, activator, synthesis, excitation and emission wavelengths, concentration dependent intensity, optical gaps and evidence limitations. The text encoding was unreadable for some OCR and visual inspection were used. Values were taken from source text and tables, and no spectra were digitized or experimental data was collected. The reattached Y_2O_3:Er^{3+} thermoluminescence paper is a re-use of reference [14] and thus will not be re-entered. Seven new relevant articles are referenced [46-52]. Previous references not included amongst the current attachments are still considered evidence and have not been independently revalidated.

3 Physical basis of photoluminescence

3.1 Excitation and relaxation

When the energy of the incident photon is right and the appropriate selection rules are obeyed, an incident photon can raise a system from a lower electronic state to a higher allowed one. Excitation may then be relaxed by one of the following processes: vibrational cooling, internal conversion, intersystem crossing, migration of excitation, carrier trapping and photon emission. These pathways are often illustrated in molecules by a Jablonski diagram, and in semiconductors by a band/defect level diagram. Rare earth centres are characterized by their multiplets in the host [1]. The energy of the photons is related to the wavelength of the photons by $E = hc/\lambda$, where h is called Planck's constant, c is the speed of light and λ is the wavelength. The emission may take place at a longer wavelength than the absorption because some of the energy that causes the excitation is lost prior to the decay. This separation is known as the Stokes shift. A large value will influence reabsorption and optical extraction, while a large swing also will result in higher energy losses during the wavelength conversion process. If one is not sure that the excitation is more than one step, or if there is no other source of energy to account for anti-Stokes emission, then it should not be assumed. [1]

3.2 Fluorescence phosphorescence and delayed emission

Fluorescence is most often used for molecular emitters where it describes a radiative transition between two states of the same spin multiplicity, in this case between the lowest excited singlet state and the ground singlet state. Spin multiplicity is often involved in phosphorescence, usually with a change from a triplet state to the singlet ground state, and it is often slower. These differences are in terms of transition character and not a lifetime boundary. Delayed fluorescence may occur when a triplet state populated state returns to an emissive singlet state. The route can be harnessed by the design of the molecule, as in the case of thermally activated delayed fluorescence [11]. Phosphor is a term used to describe a luminescent substance and is not necessarily a reference to molecular phosphorescence. Long radiative lifetime is not the only mechanism for persistent luminescence in inorganic solids, trapping and release of carriers also play a role. Thermoluminescence (TL) is different from steady state PL, and involves heating to release emission after the energy has been stored. In the provided $Sr_2B_2O_5$:Tb^{3+} opening page, the glow-curve reported by Chen shows a trap depth of 0.570 eV [13]. This fitted TL parameter is NOT a PL quantum yield or a thermal-quenching activation energy. The supplied $Sr_2B_2O_5$ study is for prompt PL [31] and the retained Y_2O_3:Er study is for TL analysis [14].A more detailed

example of trap is supplied by the complete $Y_2O_3:Er^{3+}$ thermoluminescence paper [14]. The nominal 1–5 mol% Er^{3+} series was achieved by urea-assisted combustion. The glow maximum of the largest TL signal under 254 nm irradiation and 7 °C s^{-1} is reported for 2 mol% Er^{3+} (115.97 °C) while reported glow maxima are 113.54 and 117.56 °C for 1 and 3 mol% Er^{3+}, respectively. The glow shape analysis and fitted components result in activation energies of 0.71–1.14 eV and 101.73 and 124.36 °C, respectively. These results describe stored charge, and thermally stimulated release, not prompt PL lifetime, photon yield or PL thermal quenching barrier. This 2 mol% TL maximum does not contradict a different study on $Y2O3:Er^{3+}$ [25] for which a maximum of 3 mol% PL was reported.

3.3 Quantum yield and lifetime

The efficiency of photoluminescence ΦPL is the ratio between the number of emitted photons and the number of absorbed excitation photons. In the case of one emissive population, kr and knr are the first order radiative and nonradiative rate constants so that $\Phi PL = kr/(kr + knr)$ and $\tau = 1/(kr + knr)$. These relationships indicate that high yield can either be due to increase in radiative emission or less nonradiative loss or both. Under the same conditions, the rates of yield and life time for the same population can be estimated as $kr = \Phi PL/\tau$, $knr = (1 - \Phi PL)/\tau$ [12, 1]. These expressions are simplified models. Multiexponential decay/excitational dependent kinetics can result from several sites, several traps and several transfer pathways within a heterogeneous material. The fitted average lifetime is then model- and weighting-dependent. This dependence is hidden by only reporting a single fitted number. A minimum of the following should be presented with the lifetime: fitting function, instrument response treatment, residual behaviour and definition of the reported average. [1]

4 Material families and emitting centers

Material family	Principal emitting state	Useful attributes	Common limitations
Rare earth phosphors	Localized 4f states or 5d to 4f transitions	Colour control through activator and host; chemically robust host options	Quenching, weak absorption for some ions, processing demands
Transition metal phosphors	Crystal field dependent d states	Broad host controlled colour range	Oxidation state and coordination sensitivity
Semiconductors and quantum dots	Carrier or exciton recombination; defect states	Size and composition tuning; integration with devices	Surface traps, charging, environmental sensitivity
Organic molecules and polymers	Molecular singlet and triplet states	Chemical design flexibility and solution processing	Aggregation, oxygen sensitivity and photobleaching
Defect and carbon based emitters	Localized defect or surface states	Potentially accessible synthesis and functionalization	Ambiguous emitting species and heterogeneous populations

Table 1 compares the different families of photoluminescent materials.

4.1 Rare earth activated inorganic phosphors

Inorganic phosphors activated by rare earths are also used. Rare earth activated inorganic phosphors are also employed. The structural sites and the chemical environment are supplied by the host and the emissive states are supplied or modified by the dopant. Rare earth 4f–4f lines can be rather sharp, as the 4f electrons are well protected by the outer shells by trivalent rare earth ions. Host effects still play a role via symmetry, site multiplicity, phonon coupling and charge compensation. The broadening of 5d-4f emission is often observed with Ce^{3+} and Eu^{2+} ions, since the interaction of the 5d states with their environment is stronger. So, the identity of an activator is not sufficient to determine a definite emission wavelength [1]. The full $SrAl_{12}O_{19}:Ce^{3+}$ report presents an excitation band between 280-380 nm with the peak at 331 nm as well as blue emission at 442 nm [15]. The reported CIE coordinates are (0.228, 0.040). There is no quenching threshold

with its relative intensity increasing throughout the 1–10 mol% series tested with the highest tested loading yielding the highest signal. This article has the number 2000099. Precursor naming, as well as written reaction, should be checked, and the occupation of one crystallographic position can only be confirmed by an asymmetric emission band. Tb^{3+} is a common green emitter, with the well-defined $^5D_4 \rightarrow {}^7F_5$ transition occurring in many hosts. The orange/red lines are commonly observed with Eu3+ associated with $^5D_0 \rightarrow {}^7F_J$. The relative intensities of the electric dipole and magnetic dipole transitions of Eu^{3+} can be used to probe some aspects of the local environment, but should not be regarded as complete crystallographic solution. Dy^{3+} can be a combination of blue and yellow bands, a near white chromaticity does not necessarily mean a continuous spectrum or good colour rendering. Eu^{3+} activated $Ca_{14}Al_{10}Zn_6O_{35}$ [1] and Ce3+ activated $Ca_{14}Al_{10}Zn_6O_{35}$ [17] provide examples of studies that have been conducted on different activators in the same nominal host composition. The study of $Ba_2Sr_2Al_2O_7$ mentions separate activation with Tb3+, Eu3+ and Dy3+ and colour selection by activator choice [2]. A supplied opening page lacks numerical spectral maxima which are not inferred here. $SrMg_2Al_{16}O_{27}$ has been reported to have green emission at 545 nm when excited at 353 nm for Tb^{3+} and Eu^{3+} emission lines at 597 and 614 nm when excited at 396 nm [3]. These data show colour selection in an aluminate host and do not necessarily indicate transfer between co-dopants, or improved device efficiency. The $BaAl_{12}O_{19}$ study has done the same for a transition metal activator, showing emission at 545 nm due to 380 nm excitation for the Tb3+ and a band at 550 nm due to 340 nm excitation for the Mn^{2+} [26]. Thus, near-coincidence of the emission maximums does not necessarily mean that the emitting states are the same. The emission of intra-4f lines is observed with Tb^{3+} and the response in Mn^{2+} is from the crystal field affected d states. The combustion preparation and structural characterization are supported by the $MgSrAl_{10}O_{17}$ excerpt, but gives no numerical emission maximum [8].The new aluminate evidence provides for activator comparisons to nominal $MgPbAl_{10}O_{17}$. It states the emission of Eu^{3+} at 592 nm and 618 nm in response to 396 nm excitation and the Dy^{3+} emission at 484 nm at 574 nm in response to 350 nm excitation on its opening page [33]. The 592 nm Eu^{3+} feature is referred to here as an orange-region line, not yellow as the source labels it. Qualitative colour quality, thermal performance and phase-purity statements are not possible to evaluate independently due only the first page available. Under the same excitation wavelength of 396 nm, $Ca_{12}Al_{14}O_{32}F_2$:Eu^{3+} also reported its emissions at 593 and 620 nm [24]. The title indicates combustion synthesis, but the abstract indicates a "wet chemical" route and the excerpt does not clarify the route.

4.2 Borates phosphates and oxide hosts:- Borates, phosphates, and oxide hosts are also available. Borate excerpts supplied by several report the green emission of Tb^{3+} under ultraviolet (UV) excitation. Under the 353 nm excitation, $Sr_2Mg(BO_3)_2$:Tb^{3+} exhibited 546 nm emission in the reported nominal concentration range of 0.2–2 mol% [5]. $LiBO_2$:Tb3+ gives 545 nm under 353 nm excitation [18], $LiSr_4(BO_3)_3$:Tb^{3+} gives 545 nm under 370 nm excitation [19], and Sr_2BO_3Cl:Tb^{3+} gives 546 nm under 380 nm excitation [9]. The full $Sr_2B_2O_5$ PL article is reported to emit at 545 nm when excited at 353 nm [31]. The similar green maxima are indicative of the Tb^{3+} emitting manifold while the different excitation wavelengths have relevance for matching a pump source. These reported wavelengths are the individual measurement conditions and not bandwidth or absorption-efficiency rankings. The abstract provided for $Ba_3Y(BO_3)_3$:Ce^{3+} indicates that it is suitable for the low temperature phase and that it exhibits emission peaks at 456 and 473 nm under 376 nm excitation [6]. The full $Ba_3Gd(BO_3)_3$:$Ce3^+$ paper, however, shows peaks at 488 and 501 nm when excited at 343 nm with the maximum relative PL intensity occurring at a nominal Ce^{3+} loading of 3 mol% [30]. This is in line with the host sensitive emission of Ce^{3+}, and due to the difference between the two in both preparation and measurement, the shift cannot be attributed to host alone. Moreover, the Ba3Gd paper describes the particle size in three different ways: 2.5 µm in the abstract and the conclusion, ~50 µm in the microscopy discussion, and 42.2 nm from line broadening. These values are not necessarily taken as a particle-size estimate. The first page of the $Sr_2Mg(BO_3)_2$:Tm^{3+} paper

describes blue emission around 450 nm upon UV excitation when the material is prepared in solid state [41]. There is no numerical value for the excitation wavelength, quantum yield, lifetime or thermal cycling result in that page. It expands the range of activators used, along with green Tb3+ emission in the same nominal host [5] but the excerpt cannot support the abstract's description of efficient and stable luminescence or environmental superiority. Phosphate examples further distinguish between: activator- and host-effects. $Ca_2PO_4Cl:Tb^{3+}$ is reported to emit at 545 nm under 380 nm excitation while Mn^{2+} in the same nominal host gives 591 nm under 405 nm excitation [21]. The Ca2PO4Cl:Dy3+ abstract supplied shows blue and yellow lines at about 482 and 573 nm, respectively when excited at 365 nm with a secondary excitation feature at 389 nm [20]. The blue–yellow combination is a starting point for colour design and in no way defines the quality of white light or the effectiveness of a device. Examples of oxide materials that were carried over from the original manuscript are $ZrO_2:Tb^{3+}$ [4] and nominal $Li_2Mg_{1-x}ZrO4:xTb^{3+}$ [23]. The latter is now backed up by a complete reattached article which describes the wet chemical preparation and dominant green emission at 543 nm, when it is excited at 380 nm with other emission lines reported at 488, 583 and 625 nm. The relative-intensity maximum occurs at nominal 2 mol% Tb^{3+}, and there is no indication that the notation in the paper's title corresponds to normalized site fractions. Two additional diffraction peaks described in the text qualify claims of phase purity, still a match with the reference pattern is not enough to solve them. The ZrO_2 comparability is still an inherited evidence in the opening page. The whole $KCaPO_4$ paper has presented Ce^{3+} blue-emitting (442 nm) and Eu^{3+} red-emitting (620 nm) with the 332 nm and 396 nm excitation, respectively [28]. It is reported by a $KNaPO_4$ opening-page excerpt that this maximum emission peak of Ce^{3+} is at 442 nm when excitation is at 330 nm and that of Eu^{3+} emission is at 620 nm with a maximum at 396 nm [29]. $KNaPO_4$ is kept as the nominal host label as its composition and phase assignment have not yet been confirmed and cannot be compared in detail. In addition, there are some inconsistencies of host names in the KCaPO4 article, descriptions of precursors and notation of temperatures so that the written procedure is not reproducible by itself. The first page of the $KSrPO_4:Ce^{3+}$, Eu^{3+} corresponds to a wet chemical preparation and blue emission at 440 nm and orange–red lines at 593 and 618 nm [42]. These bands correspond with the mentioned Ce3+ and Eu3+ activators, though no excitation wavelengths nor concentration dependent data are given on the provided page. Although the formula in the title is that of a phosphate, the abstract identifies the material as "sulphate-based. The excerpt fails to identify coactivators that act to transfer energy to each other. Combustion synthesis in air of the $Ca_{10}(PO_4)_6F_2:Eu^{2+}$ excerpt is reported to be blue-emissive at 432 nm when excited by 348 nm [27]. In Eu^{2+} the excitation is from $^4f_7$ to $^4f_6$ $^5d_1$ and the emission is from $^4f_6$ $^5d_1$ to $^4f_7$. The emission direction given in the provided abstract is not used! Due to the fact that only the first page is available, it is not possible to fully assess the evidence for the formation of Eu^{2+} under the stated atmosphere; valence sensitive analysis would support the interpretation. In the excerpt from the $Ca_{14}Al_{10}Zn_6O_{35}:Eu^{3+}$ it is mentioned a nominal red emitting aluminate composition [16] but the abstract and introduction are referring to unrelated borate compositions and cations. That means that this excerpt does not result in a quantitative spectral or site-symmetry claim. The new provided $NaLi_2PO_4:Eu^{3+}$ report reinforces the phosphate comparison [22]. A series with nominal x = 0.001–0.02 was produced by modified solid state diffusion; the highest reported relative intensity is for x = 0.005. The strongest listed line of the excitation spectrum, monitored at 618 nm, is at 394 nm, and emission measurements are made with the excitation at 393 nm. The red emission peak is at 618 nm with another line at 595 nm and reported CIE coordinates are (0.6872, 0.3125). These are colour coordinates NOT quantum efficiency. The paper alternates the $Na(_{1-x})Li_2PO_4$ and $NaLi(_{2-x})PO_4$ labels without offering a definitive answer to the question of substitution and charge-compensation model. The SEM particles are given as 1-5 µm, which is different from the particulates description in the methods being 100-150 µm. The emission at 593 and 620 nm has been reported for a lead-containing phosphate, $Ca_2Pb_3(PO_4)_3Cl:Eu^{3+}$, with excitation at 396 nm [32]. The highest reported intensity in the quoted range of 0.1–1 mol% is for the sample of 1 mol% and does not indicate

a quenching threshold at the top of the range. The two emission lines are consistent with Eu^{3+} $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions. The identification of the 396 nm excitation as 4f – 5d of the source is not followed: a line in the near-UV is normally identified as an intra-4f excitation to $^5L_6$. Nor does it require two emission features to be seen in order to be considered that the two are sharing a single crystallographic site. In addition, lead content needs to be evaluated on a composition-by-composition basis before being put into practice. The full $Ce3^+$ study of the same nominal $Ca_2Pb_3(PO_4)_3Cl$ host gives for it the excitation of 331 nm and a broad blue peak of 443 nm [39]. It is tabulated with relative emission intensities of 30.749, 246.784, 266.406 and 299.572 arbitrary units (a.u.) at nominal Ce^{3+} loadings of 1, 2, 5 and 10 mol%, respectively. The values are not quantum yields or brightness rankings across hosts, but are only relative to the samples within that experiment. The maximum given intensity is at the maximum loading tested and the table is not, in itself, a determination of the onset of quenching. The 5d to 4f relaxation of a 4f1 ion is described as Ce^{3+} emission; the Eu^{2+} like electronic configuration that is printed in the conclusion is not used. In the inherited report [32] the comparison with the Eu3+ emission at 593 and 620 nm in the same nominal host shows activator dependent colour. Further silicate evidence comes from the first page of Panse et al. [46]. The article reports combustion synthesis of its host named as LiSiO3:Ce3+ and a broad blue emission centered at 440 nm and excitation feature at 332 nm. A nominal formula is used as printed without silent adjustment to a lithium metasilicate stoichiometry. This is an excerpt only and the full report is not available, therefore full composition, charge compensation, phase purity and concentration dependence can not be determined. The absorption of Ce^{3+} is related to 4f to 5d excitation and its emission is related to 5d to 4f relaxation. Kokode et al. report $Ba_2Si_3O_8$:Tb^{3+} emission of green color with 352 nm excited light [47]. The scanned first page provided shows nominal additions of Tb in the range 0.1–2 mol%, and heat treatment at 350 °C for 8 h. It does not give the concentration resolved spectra, which would be required for finding an optimum or quenching threshold. It does not have a garbled printed transition label, the dominant green Tb^{3+} feature is conventionally associated with $^5D_4 \rightarrow {}^7F_5$ [1]. Persistent phosphors are mentioned in its introduction, but the provided page does not show afterglow for this composition. The complete $KBaPO_4$:Ce^{3+} paper is included in the paper concentration series [52]. According to it, it has an excitation maximum at 330 nm, a broad blue emission, which is referred to as 440 nm in the abstract and 441 nm in the body and conclusion, and the CIE coordinates (0.234, 0.035). Table 1 of that article gives relative emission intensities of 208.9125, 251.2584, 414.01 and 635.4033 arbitrary units at 1, 2, 5 and 10 mol% Ce^{3+}, respectively. The intensity rises monotonically with the measured series, with no quenching threshold being found for the highest measured intensity of 10 mol%. The numbers are kept as arbitrary intensity units (as in the source table) and not the nanometre units (as written in the prose of the source table) for intensity. The abstract discusses synthesis by combustion, while in the experimental section, a wet chemical synthesis is described, but furnace temperature is indicated ambiguously. These relative intensities and a resolved broad band, separately, provide no unique dopant site or absolute efficiency.

Table 2 Source data of concentration and relative intensity of KBaPO4 Ce3+ [52]

Ce3+ concentration mol%	Emission intensity a.u.
1	208.9125
2	251.2584
5	414.01
10	635.4033

4.3. A broad blue-emitting aluminate example is provided by $BaAl_{12}O_{19}$:Ce^{3+} [34]. One sentence in the abstract and the principal discussion report 331 nm excitation and 440 nm emission, but another sentence in the abstract has 435 nm and the conclusion changes the host label to

$CaAl_{12}O_{19}$. So I'm keeping the 331/440 nm pair as the principal result and didn't solve the identity inconsistency. These data provide some evidence for host-sensitive 5d–4f emission but no evidence for an efficiency improvement over other Ce^{3+} hosts. Another nominal aluminate host is introduced in the wet chemical $MgCuAl_{10}O_{17}:Ce^{3+}$ conference report [40]. Its abstract states that it has an excitation of ~350 nm and an emission at ~445 nm, while the detailed PL section shows a peak excitation at 355 nm and blue emission at 441 nm. The values of these sources are stored individually. In addition the report provides incompatible micro size descriptions so that no single particle-size estimation is taken. The blue maximum of this material is similar to that of $SrAl_{12}O_{19}:Ce^{3+}$ [15] though this does not mean that they have the same yield, site occupancy or thermal stability. Two separate reports, [36,37] are documented for the sulfate chloride $Na_{21}Mg(SO4)_{10}Cl_3:Ce^{3+}$. The provided 2019 opening page is for combustion preparation and 330 nm excitation and 442 nm emission [36]. The three page report from 2018 refers to modified precipitation and specifies about 350/445 nm in the abstract and 355/441 nm in the body and captions [37]. These values are not averaged, but are maintained on a source-by-source basis. This difference is not a demonstrated sulfate precursor in the written reagent list, nor are the host captions consistent. A concentration dependent oxide example is given in the complete $Y_2O_3:Er^{3+}$ report [25]. TEM is then used following combustion synthesis and a mean particle diameter of 20 ± 1.8 nm is reported. It is reported that the paper emits at 506, 522 and 711 nm when excited with 356 nm excitation, and the maximum emission occurs at 3 mol% in its 1–5 mol% series. The reported chromaticity is (0.291, 0.397). Peak positions are reported as is, but detailed Er3+ term assignments are not necessarily independent, and repeated composition labels like (Y0.99Er0.02)2O3 are not normalized site fractions. These data are representative of intensity as a function of concentration, but do not represent validated performance of these devices in white light. The located green feature at 545 nm after combustion preparation described at 550 °C [4] is now directly supported by the ZrO_2:Tb3+ opening page. Calibrated yield, a verified concentration optimum and the trap parameters are not given in sufficient detail from the excerpt. The absence of these data on the front page is not to be interpreted as lack of these in the full paper. The comparison is extended to stored excitation [35] in the case of $Sr_5(Si_2O_7)Cl_4:Eu^{2+}$. The paper indicates a primary PL peak at approximately 500 nm, with a secondary peak at approximately 410 nm, when the excitation is below 320 nm. Following 15 min exposure at approximately 254 nm, its fitted persistent-emission decay components are 32, 67.6 and 130 s.

The TL glow features are reported at around 105 °C and 175 °C at a heating rate of 5 °C s^{-1}. These time constants describe a fitted afterglow response, and not the intrinsic Eu^{2+} radiative lifetime; glow-peak temperatures are not thermal-quenching thresholds. The abstract and experiment text have synthesis at 750 °C and sintering at 900 °C for 2 h, respectively. These preparation steps have to be clarified prior to replication. The presence of two PL features and a multicomponent afterglow does not provide any information about specific crystallographic sites or trap species.

4.4 Superconductors, semiconductors, and superconductor-semiconductors hybrid devices Organic PL is a result of molecular electronic structure and its interaction with the environment. The polarity of the solvent, molecular rigidity and aggregation can modify transition energies and nonradiative losses. Limiting the motion of molecules can increase the emission in some systems, but aggregation can suppress it in other systems. The singlet and triplet pathways are controlled as in the case of the delayed fluorescence experiments of Uoyama et al. [11]. Note that its electric device performance is different from the optical quantum yield (OQY) obtained during PL characterization. A different approach to tunability is offered by semiconductor nanocrystals. When dimensions become small enough, confinement can alter the electronic energies, and composition, strain and surface passivation can also affect emission. Core and shell structures can decrease losses that are related to the surface, however, shell growth and ligand exchange can also create new interfaces. The use of nanocrystals as emitters in optical tagging has been proven early on biological labelling [10]. Biological suitability still needs to be addressed by evidence of

colloidal stability, functionalization and behaviour of the complete labelled system. A comparison is a non rare earth activator. Uke and Panse report on the solid state diffusion synthesis of BaS:Bi nanophosphor with 425 nm excitation and 575 nm emission – versus a 608 nm bulk emission feature [50]. The one page abstract indicates a nominal optimum of 0.3 mol% Bi and a Scherrer size of ~20 nm, which is "close" to the estimate from TEM. It is the 575 nm maximum, which is in the yellow region, although it is described in the source as green. This shift towards shorter wavelength, of 33 nm, is consistent with a change in the properties of the samples but cannot be separated from changes in defects, flux, local environment or activator distribution from this excerpt. No information is provided about radiative lifetime or absolute quantum yield. But the range of PL materials is extended by carbon based emitters, defect centres and metal halide semiconductors. They should be classified according to the species from which they are demonstrated to emit, and not a synthesis label. For instance, emission of a carbon containing preparation can be due to molecular fluorophores, surface states or to a carbonaceous core. Unique mechanism assignment requires purification, fractionation and correlated spectroscopy. These are conceptually included here as additional members of these larger families, but not as a complete survey. A computational comparison is shown as a boundary between optical response and luminescence. A modified Becke–Johnson potential [38] was used in the calculation of the electronic gaps, which were found to be 1.98 eV for the chloride and 0.30 eV for the iodide, as reported in the first page supplied for the Na_2InGaX_6 (X = Cl, I) study. Absorption, band gaps and thermoelectric transport properties are not experimental PL measurements. No evidence of emission maxima, quantum yield, radiative lifetime or any light-emitting device performance for these compositions is given in the excerpt. There are three previous studies that demonstrate the need for separation of absorption evidence from emission. The reported crystallite size of the solvothermal ZnO–NiO prepared at nominal 1:1 with the assistance of Aloe-vera is 13.91 nm and the direct Tauc gap is 2.52 eV [43]. For CdSe films deposited at 300 °C, a mean XRD crystallite size of 16.3 nm and an optical gap of 1.78 eV have been reported [44]. The CdO opening page states that spray deposition was performed at 300 °C and that the optical gaps were 2.24 to 2.49 eV. These measurements are for structural and absorption context, not measured PL maxima, yields of photons or radiative lifetimes. Especially, no Tauc gap should be transformed to an assumed emission wavelength. This measurement boundary is further supported by the additional thin film studies. A $CdSe_{1-x}Te_x$ alloy opening page reports x = 0.0, 0.3, 0.6 and 1.0, Scherrer sizes of 16–24 nm and optical gaps decreasing from 1.79 to 1.51 eV [48]. $CdSe_{0.3}Te_{0.7}$ thickness study was conducted separately, with a deposition temperature of 573 K, mixed hexagonal and cubic diffraction features, and additional TeO_2 peaks, and a gap of 1.51 eV at 1033 nm thickness, increasing to 1.52 eV at 1207 nm thickness [49]. The complete CdTe spray deposition report shows 474 nm – 1.64 µm SEM grain sizes and an optical gap of 1.45 eV. It incorrectly labels the EDAX prose as Se in a CdTe composition statement and this passage is therefore not used as proof of stoichiometry. None of these results includes measured PL spectra, PL quantum yield or PL lifetime of the available material; these are all descriptions of absorption, morphology and phase behavior. This means that their absorption gaps are not reported as emission peaks.

Table 3 Source reported excitation and emission features

Nominal host and activator	Excitation nm	Emission nm	Evidence and reference
BaAl12O19:Tb3+ / Mn2+	380 / 340	545 / 550	Opening abstract [26]
SrMg2Al16O27:Tb3+ / Eu3+	353 / 396	545 / 597, 614	Opening abstract [3]
Ba2Sr2Al2O7:Tb3+, Eu3+, Dy3+	Not specified	Colour tuning reported	No numerical maxima in excerpt [2]
Ca10(PO4)6F2:Eu2+	348	432	Opening abstract; valence

			evidence incomplete [27]
KCaPO4:Ce3+ / Eu3+	332 / 396	442 / 620	Full article; procedure inconsistencies [28]
KNaPO4:Ce3+ / Eu3+	330 / 396	442 / 620 monitored	Opening abstract; nominal formula [29]
Ca2PO4Cl:Tb3+ / Mn2+	380 / 405	545 / 591	Opening abstract [21]
Ca2PO4Cl:Dy3+	365	482, 573	Opening abstract [20]
Ba3Gd(BO3)3:Ce3+	343	488, 501	Full article; 3 mol% maximum reported [30]
Ba3Y(BO3)3:Ce3+	376	456, 473	Opening abstract [6]
Sr2B2O5:Tb3+	353	545	Full PL article [31]
Sr2BO3Cl:Tb3+	380	546	Opening abstract [9]
LiSr4(BO3)3:Tb3+	370	545	Opening page [19]
Sr2Mg(BO3)2:Tb3+	353	546	Opening abstract [5]
LiBO2:Tb3+	353	545	Opening abstract [18]
Sr3Gd(BO3)3:Tb3+ / Eu3+	352 / 364 in abstract	543 / 613	Full article; body values differ [7]
Sr3Gd(BO3)3:Ce3+	260 in body	314	Full article; transfer tests use 252 nm [7]
Ca2Pb3(PO4)3Cl:Eu3+	396	593, 620	Partial article; 1 mol% maximum in stated range [32]
NaLi2PO4:Eu3+	393 used; 394 peak	595, 618	Multi-page article; nominal x = 0.005 intensity maximum [22]
Ca12Al14O32F2:Eu3+	396	593, 620	Opening page; method wording differs [24]
MgPbAl10O17:Eu3+ / Dy3+	396 / 350	592, 618 / 484, 574	Opening abstract [33]
BaAl12O19:Ce3+	331	440 principal; 435 also stated	Multi-page article; host label inconsistent [34]
Y2O3:Er3+	356	506, 522, 711	As reported; term assignments need checking [25]
ZrO2:Tb3+	379	545	Opening page [4]
$Sr5(Si2O7)Cl4:Eu^{2+}$	320	500; weaker 410	Multi-page article; prompt PL [35]
$Na21Mg(SO4)10Cl3:Ce^{3+}$	330	442	2019 opening page [36]
$Na21Mg(SO4)10Cl3:Ce^{3+}$	350 abstract; 355 body	445 abstract; 441 body	2018 article; host captions differ [37]
$Li2Mg1-xZrO4:xTb^{3+}$	380	543 dominant; 488, 583, 625	Full article [23]; nominal 2 mol% maximum
$SrAl12O19:Ce^{3+}$	331	442	Full article [15]; CIE (0.228, 0.040)
$Ca2Pb3(PO4)3Cl:Ce^{3+}$	331	443	Full article [39]; relative-

			intensity series in text
MgCuAl10O17:Ce^{3+}	350 abstract; 355 body	445 abstract; 441 body	Three-page report [40]; discrepant values
Sr2Mg(BO3)2:Tm^{3+}	UV; not specified	Approximately 450	Opening page [41]
KSrPO4:Ce^{3+} / Eu^{3+}	Not specified	440 / 593, 618	Opening page [42]; host wording inconsistent
LiSiO3:Ce^{3+} nominal label	332	440	Opening page [46]; composition unresolved
Ba2Si3O8:Tb^{3+}	352	545	Opening page [47]
BaS:Bi	425	575 nano; 608 bulk	Opening page [50]; source colour label corrected
KBaPO4:Ce^{3+}	330	440 abstract; 441 body	Full article [52]; 10 mol% highest tested intensity

The values are only the spectral features that were reported, not independently validated optima. Features of one activator are separated by a comma and activators are separated by a slash in the same order as in the first column. The values of excitation and emission are not directly comparable measures of brightness, yield or device performance. Qualitatively, $MgSrAl_{10}O_{17}$ [8] and $Ca_{14}Al_{10}Zn_6O_{35}:Eu^{3+}$ [16] are mentioned here.

5 Synthesizing new materials and synthesizing in a different way Phase formation, dopant distribution, particle morphology and defect chemistry is determined by synthesis. The precursors are simply mixed and reacted at high temperatures and ground in conventional solid state processing. It can generate powders with crystals, but it might take a lot of energy and many times to do so, and it might make large particles. Volatilization, agglomeration and changes in oxidation state of the activator must be considered with respect to the optical advantage of increased crystallinity. One of the selected studies is the solution combustion technique that is well known among the studies [2, 5, 6]. Dissolved precursors and fuel can enhance mixing and allow for rapid reaction. The powder obtained may be porous, and may need further annealing. Reproducibility is affected by fuel balance, solution composition, ignition conditions and cooling. The transient local environment of a combustion process can not be described as a nominal furnace temperature only. Claims of inherent "greenness" of combustion must be evaluated in terms of the reagents, gas release, processing yield, and energy usage. It is also specifically mentioned that the Eu3+ activated Ca12Al14O32F2 phosphor is obtained by combustion synthesis [24]. Some alternatives for control of mixing, morphology and particle size are sol–gel and hydrothermal and precipitation routes. This does not necessarily imply a total reduction of the environmental impact by lowering the synthesis temperature, if purification or subsequent crystallization is extensive. Surface chemistry is particularly significant for nanocrystals as a high percentage of atoms reside on the surface that are in contact with ligands or solvent. Smaller particles may be more dispersible and have more surface related quenching pathways. The structural compatibility and charge balance must be fulfilled in dopant substitution. The introduction of a compensating vacancy, interstitial or other substituent may be needed when a divalent host cation is replaced by a trivalent activator. These changes can affect the luminescence without depending on the concentration of the activator. Actual site occupancy or oxidation state are not therefore defined by nominal precursor composition. This can be complemented with structural refinement, elemental analysis and, if applicable, valence sensitive spectroscopy. [1]

6 Characterization and reliable interpretation

6.1 Structural and chemical measurements

Structural measurements, as well as absolute chemical measurements, can be made. Powder X ray diffraction can be used to determine the crystalline phases present and to determine if the principal host structure is formed after processing. Weak impurity phases can not be detected. Occupation of a particular crystallographic site can not be verified by a match to a reference pattern. When appropriate for the quality of the data and the model, refined lattice parameters and phase fractions are useful. The crystallite sizes determined by line broadening should not be confused with the particle sizes found by microscopy, since a particle may consist of a number of coherent domains. The morphology of particles, particle aggregation and size distribution are determined by electron microscopy. Energy dispersive X ray analysis could be used to confirm the presence of elements and spatial mapping, but will generally only give limited information on trace amounts of dopants or oxidation state. The infrared and Raman measurements are used as tools to characterize the vibrational groups and local bonding. These methods are more powerful when they are applied to test a hypothesis, and not combined as random instances of characterization images.

6.2 Steady state spectra and calibration

An emission spectrum is plotted as intensity versus the emitted wavelength for a fixed excitation wavelength. The excitation dependence of the selected emission channel is recorded in an excitation spectrum. The latter is a representation of absorption channels that feed that channel, weighted by subsequent relaxation and detection. Does not have to be a complete absorption spectrum. Sites, impurities or competing mechanisms can be distinguished by using multiple excitation or emission settings. [1] Spectra are dependent on the output of the source, band width of the monochromator, detector response, geometry and sample preparation. There is a need for correction and consistent settings in comparisons. Packing density is an issue in powders, as is scattering and reabsorption of the collected signal. High absorbance in solutions can result in inner filter effects. Thus, an in change in the intensity may be detected without a change in intrinsic quantum yield. Background spectra, blank substrates, and instrument response correction and appropriate filters should be recorded. [1]

6.3 Quantum yield time resolution and temperature

Integrating sphere approaches enable emitted photons and absorbed excitation to be related more directly, including for samples that scatter light [12]. They are still dependent on calibration, blank correction, excitation rejection and reabsorption treatment in order to be reliable. If the absorption is weak the difference between the reference signal and the sample signal may be small, which introduces uncertainty into the denominator. Report should be done with identifying the operational definition of yield and the optical geometry instead of using internal and external efficiency interchangeably. Time resolved PL will be able to separate processes that overlap in a steady state spectrum. This decrease in donor lifetime upon introduction of an acceptor is in agreement with the presence of an additional channel of donor decay, but a control is required to see whether this decay channel is useful transfer or nonradiative decay. Measurements as a function of temperature will distinguish between stable radiative behaviour and thermally activated losses, and can also show the presence of phase changes or trap release. Reversible quenching and irreversible degradation are separated by heating and cooling cycles. [1]

Table 4 Measurements needed to support common interpretations

Proposed interpretation	Required evidence	Main alternative to exclude
High luminescence efficiency	Calibrated photon yield with uncertainty	Absorption or collection geometry changes
Donor to acceptor transfer	Spectral overlap, donor kinetics and acceptor response	Direct acceptor excitation or reabsorption
Activator incorporation	Phase and composition analysis with site sensitive support	Separate dopant rich impurity phase
Thermal robustness	Temperature dependent output and recovery cycles	Irreversible chemical or structural change
Lighting suitability	Pump matching, device spectrum, efficacy and durability	Attractive powder colour without useful device output

7 Energy transfer and quenching mechanisms

Redistribution of the excitation between centres or between a host and an activator. A sensitisor may absorb where the emitter absorbs weakly and pass the absorption energy to the emitter. The multipolar nonradiative transfer relies on separation and spectral overlap, whereas exchange transfer requires a larger overlap of the wavefunctions. Radiative transfer is by means of emission and reabsorption. These routes can yield similar steady state spectral changes, and kinetic and geometric controls are required to distinguish these routes [1]. The full $Sr_3Gd(BO_3)_3$ study reveals that the Ce^{3+} emission is near 314 nm when excited at 260 nm and that the coactivated ones have been studied under excitation at 252 nm [7]. The spectral overlap of its donor-emission and acceptor-excitation, along with enhanced emission of its acceptor near 613 and 543 nm, in its Ce^{3+}/Eu^{3+} and Ce^{3+}/Tb^{3+} comparisons, respectively.

In the Eu3+/Tb3+ comparison, red emission is stronger whilst green emission is suppressed. The observations can be attributed to sensitization and excitation redistribution, and the comparisons presented do not quantify the efficiency of transfer via donor lifetime shortening. They should thus be called spectral evidence for proposed transfer, as direct excitation and reabsorption still need controls. In the same article there are discrepancies between internal reporting as a constraint for quantitative use [7]. The abstract states that its Tb3+ optimum is 3 mol%, while the concentration discussion indicates that the intensity peaks at 4 mol%. There are also variations across the abstract and body between excitation values and also host labels Sr3Gd and Sr3Y are switched several times. Here the red lines at 595 nm and 613 nm are labeled with the traditional Eu3+ and 5D0 → 7F1 and 5D0 → 7F2 designations rather than the 5D1 designations given in portions of the source [1,7]. The contradictory optimum Tb3+ nor a special excitation condition is considered to be resolved. A frequently used estimate for the lifetime is $\eta ET = 1 - \tau DA/\tau D$ for a similar donor population, with τD being the donor lifetime in the absence of the acceptor, and τDA being the donor lifetime in the presence of the acceptor. Here it is assumed that the independent addition of the acceptor does not alter the donor radiative rate or its other loss channels. The assumption can be broken down by site redistribution, local structural changes and nonexponential kinetics. When two emissions are observed simultaneously and there is spectral overlap, it is therefore a beginning observation, and not full evidence of transfer. [1] Quenching of useful emission by increased[53] loading in the activator is known as concentration quenching. Migration to defects or cross relaxation is possible, but will be promoted by shorter intercentre distances. Additional explanations[54] are based on solubility limits, clustering and impurity formation. The concentration at which the measured intensity is maximum will depend on the host, the synthesis and excitation conditions.

It cannot be carried over to other compositions or used as a universal optimum for the same ion. This is illustrated[55] in the Y2O3:Er3+ series, where it increases with loading to 3 mol% and then decreases above that level in the range explored here (1–5 mol%) [25]. In contrast, the highest intensity at 1 mol% for Ca2Pb3(PO4)3Cl:Eu3+ is at the upper limit of its stated range, and does not define the beginning of concentration[56] quenching [32]. Thermal quenching occurs when an increase in temperature opens up nonradiative channels such as multiphonon relaxation, configurational crossover or ionization of an excited carrier into extended states. Sometimes for a dominant activated loss channel, the expression $I(T) = I0/[1 + C \exp(-Ea/kBT)]$ is used. Here Ea is an effective activation energy, kB is Boltzmann's constant and C is a fitted prefactor. If the fit is successful, it does not necessarily[57] mean that only the microscopic pathway is responsible for the intensity trends, because several centres, temperature dependent absorption or structural change can result in the same intensity trends. [1].

8 Applications and performance requirements

8.1 Lighting and displays

There are eight applications and performance requirements. Phosphor converted lighting consists of a pump source and a single or multiple wavelength converting materials. The phosphor needs to be able to absorb the pump efficiently and to have a useful emitted spectrum at the operating temperature. The rare earth aluminates and borates listed below are pertinent candidates [2, 3, 4, 5, 6, 7]. However, a designation as a candidate should not be confused with performance in an assembled device. The overall system can be affected by the electrical efficiency of the pump, extraction rate of the optics and losses in the conversion process[58]. The chromaticity coordinates are a summary of the perceived colour of an observer model. They are not a measure of quantum yield, colour rendering or durability. Correlated colour temperature has meaning[59] only for the appropriate near white sources, and is not suitable for highly saturated emitters. A combination[60] of narrow emission lines can look white, but is not very good at revealing object colours. Before claiming lighting advantages, device level spectra, key colour quality metrics, luminous efficacy and stability tests are necessary. For displays, one of the most critical properties is the narrowness of the emission bands, colour gamut, patternability and stability of the emission under repeated excitation. The processing and tuning of organic emitters and quantum dots are different than ceramic phosphors [10, 11]. The PL in dilute solution may differ from that in a dense film due to aggregation, charge transfer or reabsorption. The assessment should consequently be carried out in a step-wise manner, starting[61] from single emitters up to the desired optical stack.

8.2 Sensing imaging and materials diagnostics

PL sensing is based on the optical response of PL to temperature, chemical environment, pressure or the concentration of the analyte. Intensity based measurements are easy to make but are subject to illumination and concentration drift. Some of these dependencies can be overcome by using ratiometric methods and lifetime measurements[62] but bring with them calibration requirements. Analytical performance should include selectivity, detection limits (based on appropriate blanks) and response time and reproducibility in the analytical matrix of interest. [1] Spatially resolved observation of biological structures can be achieved by using fluorescent labels, which is the basis for the fundamental semiconductor nanocrystal labelling [10]. Spectral separation, photostability, targeting and compatibility to the biological system is important for useful imaging, in addition to brightness. Fluorescence alone does not provide proof of identity of a biological target.[63]

Independent recognition chemistry and controls remain as needed. PL can provide information about defects, recombination pathways and spatial heterogeneity in materials research without electrical contacts. Nonuniform regions not revealed by bulk average measurements may be detected in the mapping and time resolved measurements. Low PL intensity

however could be due to increase in nonradiative recombination or efficient transfer of carriers out of the measured region. Quenching can then be a component of a beneficial process, such as in charge extracting devices. To draw a clear distinction between these possibilities, correlated structural, electrical and optical measurements are required.

9 Critical synthesis and research priorities :-The key research and synthesis priorities are: The design patterns provided are for two complementary designs. The emission of Tb3+ is repeated around 543–546 nm and its chosen ultraviolet excitation wavelengths vary. In the case of Ce3+ hosts, larger shifts in emission position are observed, such as 442 nm in KCaPO4 and 456/473 nm in Ba3Y(BO3)3, which are in line with the increased[64] sensitivity of the hosts to 5d states [5,6,9,18–21,28,30,31]. An activator can generate a variety of colours in the same nominal host as exemplified by the aluminate and phosphate comparisons [3,21,26,28]. These observations are indicative of compositional screening and not a universal host ranking. This trend is expanded by newly added phosphate, aluminate, oxide and sulfate chlorides [22,24,25,32–37]. But there are limits to the spectral agreement between nominal hosts, and differences between reports that are internally inconsistent[65] cannot establish a causal host or synthesis effect. This trend continues for the emission at 543 nm of Tb3+ from lithium magnesium zirconate [23] and at 442–443 nm of Ce3+ from SrAl12O19 and Ca2Pb3(PO4)3Cl [15,39]. Limited evidence depth with blue and orange–red features from Tm3+ borate and KSrPO4 excerpts [41,42]. The MgCuAl10O17 report illustrates the issue of not recording the abstract and body wavelength values separately [40]. The extra added silicate and phosphate reports exhibit Ce3+ blue maximums around 440–441 nm and Tb3+ green emission around 545 nm [46,47,52]. The plots of their peak positions in the nominal hosts are similar and can be used for colour screening, but they are not necessarily a measure of comparable absorption, site occupancy or conversion efficiency. The BaS:Bi TL data indicate that the concentration optimum is process (emission process) dependent [14] and BaS:Bi extends the comparison beyond rare earth activators [50]. Thus the spectral features are recorded in Table 3, but not the inferred efficiencies.[66] One of the common misreading errors made in the case of phosphors is going from the attractive spectrum to a device claim. The evidence in between is very significant: reproducible phase formation, actual activator concentration, calibrated yield, pump compatibility, thermal cycling, moisture resistance and integration behaviour.[67]

A sum of these measurements may be more significant than the generation of a new "nominal" composition and the reporting of only "normalized" spectra. If results are negative, that is, if the recovery is poor after heating, this should be reported as well since this will set the scope for application. Mechanistic studies should involve the comparison of competing explanations. To transfer the energy, it is useful to have donor only, acceptor only and coactivated samples prepared under conditions of match together with concentration dependent kinetics and excitation resolved measurements. Trap-related measurements[68] should be avoided in the case of persistent emission, and should be separated from prompt PL. In case of surface dominated nanomaterials purification and surface modification controls are required for identification of the emitting population. Processing scalability and ecological impact should also be taken into account as a factor for future development. Practical sustainability is impacted by rare earth availability[69] solvent and fuel use, furnace energy, yield and lifetime. For lead or cadmium containing systems, composition-specific assessments are required instead of optical performance based claims. Comparable function and durability should be used to gauge promising alternatives. The selection of candidates can be made by computational screening, but experimental validation of the phase stability, defects and optical behaviour is required to make the predictions. All complete[70] composition; synthesis conditions; phase evidence; excitation and emission settings; absolute or clearly defined[71] relative yield; decay analysis; temperature response and batch variability should be included in a minimum transferable dataset. Calibrated spectra and raw decay data would allow more meaningful comparison than[72] the tables of peak intensities. Then, application-specific measurements should be taken depending on the type of intended use of

the material as lighting, sensing, imaging or diagnosis.

10 Conclusions:- The appearance of photoluminescence is a result of competition between radiative relaxation, nonradiative loss, transfer and trapping. The inorganic phosphor studies provided here show the Tb^{3+} line emission and the Eu^{3+} red emission, the Ce^{3+} host sensitive bands, and the blue–yellow Dy^{3+} emission with distinct Mn^{2+} responses. Matching excitation to the pump, as well as an emission colour is as important as is shown in the aluminate, borate and phosphate examples. The overall molecular and semiconductor context allows to relate these findings with the state character, its confinement and its surface chemistry. The example of the afterglow of chlorosilicate also illustrates the need for separation between the components with very short decay and those with TL glow peaks from prompt PL lifetime and thermal-quenching measurements [35]. The predicted absorption properties of perovskite are still a comparative study, and not a measured emission study [38].

The concentration–intensity series for Ca2Pb3(PO4)3Cl:Ce3+ is still a relative comparison to the instrument [39]. The use of examples of new absorption-gap products [43–45] enables a focus on the importance of measuring emission rather than inferring luminescent performance from electronic or optical gaps. The new evidence includes Ce3+ silicate which has the blue emission and KBaPO4 green emission, Tb3+ barium silicate green emission and Bi activated BaS emission [46,47,50,52]. The KBaPO4 intensity series is only valid in the measurement conditions used and can not be used for a cross material efficiency ranking. The thermoluminescent information of traps is provided by Er3+ activated Y2O3, and the optical gaps of CdSeTe and CdTe are contextual absorption measurements [14,48,49,51]. The outcome of this review is that selection of materials is linked to measured physical quantities, but with the uncertainty introduced from the incomplete and internally inconsistent reports.

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