GEs contribution to Cd RoHS exemption request for Display applications

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Introduction

GE would like to take this opportunity to provide input to Oeko-Institue and the European Commission on the status of a widely used phosphor alternative to both Cd-containing and non-Cd quantum dots (QDs). This phosphor is Potassium Fluorosilicate and is commonly referred to as KSF or PFS. We will use KSF for the remainder of this document. All commentary in this response is intended to apply only to the display portion of the exemption. It is not our intent to comment on applications relating to lighting. This contribution is split into three sections for clarity

Section 1 will provide a summary of KSF technology as it is not clear that any of the prior submissions did an adequate job of describing this technology. As a company that invested in the development of this technology, and therefore a company that holds a large patent portfolio in this technology space, GE is in a uniquely suited position to educate on the topic of KSF phosphor development and technical status as an alternative material to Cd-containing QDs.

In **Section 2** we will point directly to incorrect or misleading statements about KSF and phosphors in prior submissions to correct the inaccuracies so that Oeko and the European Commission can make an educated decision on the future status of Cd restrictions. It is vital that your understanding of the competitive technology is accurate and complete.

In **Section 3** we have included direct answers to your list of questions where appropriate guiding this solicitation for feedback and provide evidence supporting our recommendation that all exemptions for Cd QDs in displays be rejected.

We appreciate your consideration of our input and would be happy to answer any questions that are not adequately addressed in this document.

Section 1: KSF background information

Since 2014 KSF red phosphor has been used in >50 billion (1 billion=10^9) LED packages for use in displays. It is widely considered the go-to option for wide color gamut LCDs. Figure 1 shows the unique optical signature of KSF emission, providing 5 extremely narrow peaks in the red region which is part of what makes this phosphor an excellent match for display technology.

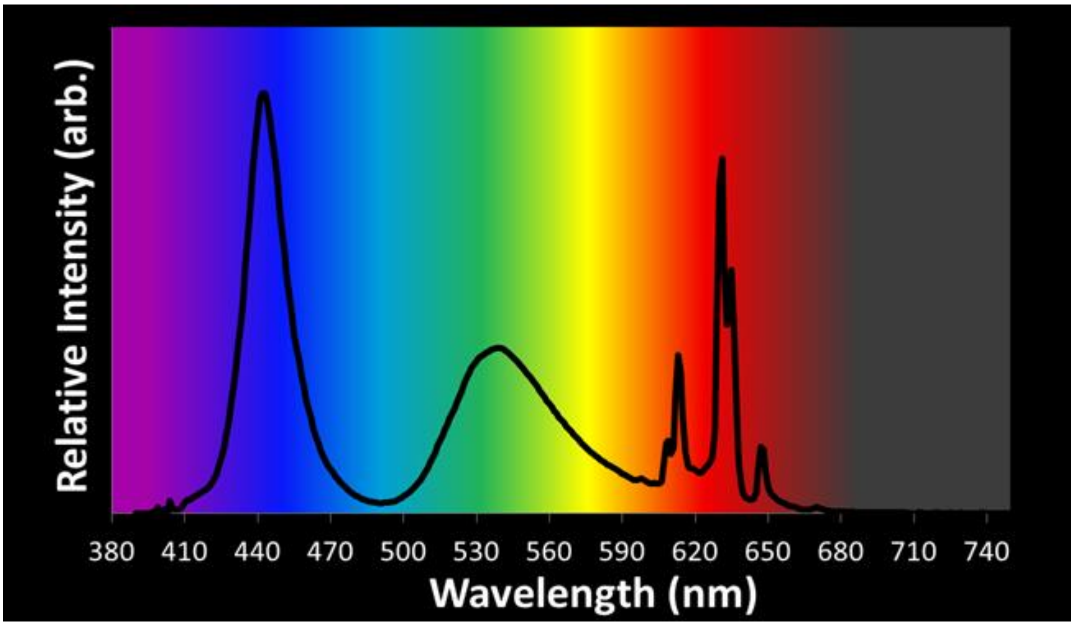


Figure 1. A typical spectrum produced from a blue LED with green phosphor and GE's red KSF phosphor. Virtually no light is lost to the infrared and the ultra-narrow peaks provide excellent color gamut.

KSF phosphor is typically packaged directly on top of the LED chip without an additional encapsulation layer for protection from atmosphere and meets or exceeds all reliability requirements for modern displays. It has been designed to withstand 10s of thousands of hours under the extreme conditions on chip without degrading and without encapsulation layer. It is also possible to use KSF in remote parts, as demonstrated in commercial displays from major electronics manufacturers. GE has developed multiple size options of KSF to meet market needs. All these products use the same fundamental material, potassium fluorosilicate with manganese, $K_2(SiF_6):Mn^{4+}$, and all have quantum efficiencies well above 90%, approaching unity.[1] This means that nearly every single blue photon that is absorbed will be re-emitted as a red photon.

As an additional attachment (pdf) we have included GEs presentation from the Society for Information Display's "Display Week 2022" conference where we summarize the performance advantages of KSF phosphor. GE has presented similar information at public conferences for the past 5 years, and we are happy to provide this additional information upon request.

Section 2. Corrections to statements in Pack 15

Here we will point to multiple locations in Pack 15 submissions where inaccurate or misleading statements were made about KSF. It is vital that Oeko and the European Commission have an up-to-date and accurate understand of that status of KSF phosphor to make an informed decision about current and future exemptions to RoHS regulations.

2.1 In the November 2019 Submission from Nanosys (Figure 2) there exist inaccurate descriptions relating to the properties and performance of KSF.

https://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_15/4th_Consultation/Contributions/contribution_Nanosys_RoHS15_InP_Stakeholder_Response_20191106.pdf

[1] J.E. Murphy et al., SID Symposium Digest of Technical Papers **46**, 927-930 (2015); DOI: 10.1002/sdtp.10406

> **Review of impact of potential new RoHS substance restrictions for Indium-Phosphide** nanosys
>
> Phosphors
>
> Another alternative to consider is phosphor materials such as Potassium Fluorosilicate (KSF) phosphor. However, KSF suffers from other performance limitations and toxicity concerns.
>
> KSF phosphor cannot meet the higher color gamut requirements of the BT.2020 standard adopted in 2015. This color standard will drive the display market to use a deeper red emission which KSF cannot reach. Additionally, KSF has a slow response time on the order of milliseconds that precludes its use in high refresh rate displays demanded by the market.
>
> Finally, it appears that the natural decomposition of a KSF:Mn^{+4} microscopic material in acidic or alkaline conditions, like the potential conditions found in landfills, could result in both acute and chronic toxicity if the host matrix is compromised. Solutions of potassium fluorosilicate once compromised may form hydrofluoric acid, which is a weak base, and readily reacts with compounds containing calcium and magnesium including living tissue. [25] The US Government's National Oceanic and Atmospheric Administration (NOAA)'s CAMEO chemical database characterizes potassium fluorosilicate as, "highly toxic, may be fatal if inhaled, swallowed or absorbed through skin."[26] Long term studies are needed to determine if decomposing microscopic phosphor has the potential to release metal ions, including potassium fluorosilicate (KSF), into the environment.

Figure 2. Excerpt from Nanosys submission November 2019.

<u>On the topic of color gamut:</u>

KSF is used in displays that reach 100% DCI-P3 color gamut, which is the current standard for wide color gamut displays. In addition, it provides an excellent match for Rec2020 red color point: the color point of KSF is very close to the requirements of Rec2020 (Figure 3) and beyond the requirements of DCI-P3. It is inaccurate to say that KSF cannot meet the wide color gamut requirements of future displays beyond DCI-P3.

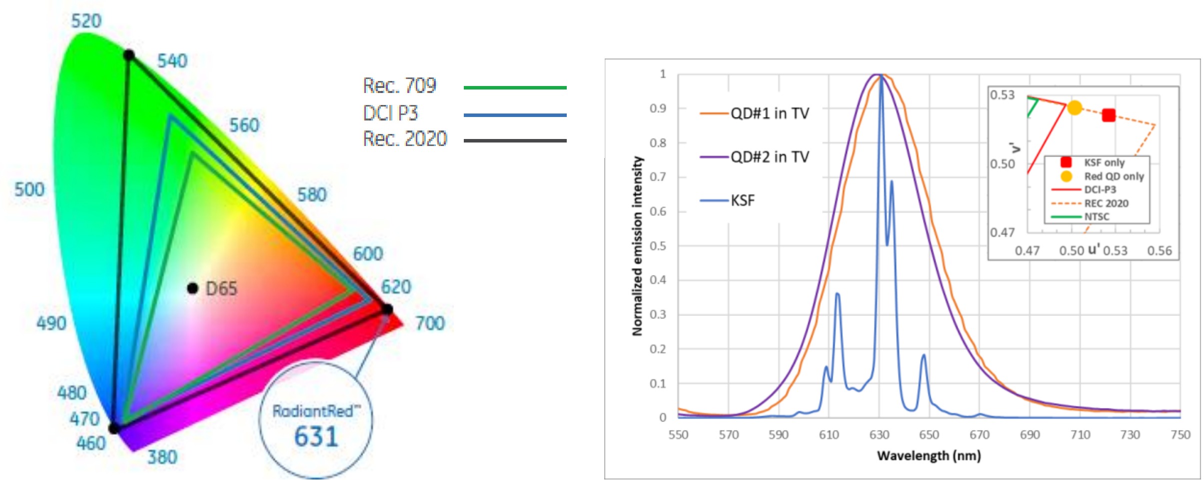


Figure 3. KSF can reach beyond the current standard of DCI-P3 and approach Rec 2020 color gamut depending on system design.

Property	KSF phosphor	Red InP QD	Red Cd-based QD
Color gamut	**5 peaks <2nm each**	FWHM >40nm commercially	FWHM 25-30nm commercially
Max % EQE	**IQE > 90%, EQE >70%**	EQE <40%	EQE>50%
Reliability to air	**No encapsulation necessary in commercial products**	Encapsulation required	Encapsulation required
Reliability to moisture	**No encapsulation necessary in commercial products**	Encapsulation required	Encapsulation required
high temperature quenching	**no loss at 100 °C**	>20% loss at 100 °C	>5% loss at 100 °C
High temp. curing degradation	**<2% at 150 °C for 30 min.**	>20% at 80 °C for 20 min.	Unknown
Reliability to high blue flux	**Commercialized on chip**	Not commercial on chip	Commercialized for lighting
Passivation film required (O_2/H_2O)	**no**	Yes	Yes
Self-absorption	**no**	Yes, all QD colors	Yes, but less than InP QD
Scatterance	RI = 1.4 so provides some scattering at typical sizes	Must add scattering agent	Must add scattering agent
Photoluminescence decay time	LCD like response time	Faster in microLED with no LCD	Faster in microLED with no LCD
Absorption	Requires >2x QD thickness	**Higher abs. coefficient**	**Higher abs. coefficient**

Table 1. Comparison of properties relevant to displays for KSF and QDs.

On the topic of response time:

KSF has a response time on the order of milliseconds, and this has not prevented adoption in display technology. Liquid crystal switching speeds are typically the slowest component of a display which are on the order of ~10 ms, which is slower than the response time of KSF[1]. In fact, KSF is implemented in some of the fastest response time displays such as gaming laptops and monitors with refresh rates of up to 300 Hz (3.3 ms). In these configurations display makers have developed LED driving methods for handling the slower response time of KSF such that it does not degrade image quality while also maintaining the efficiency, brightness, and color gamut required by gaming enthusiasts. It is also possible to leverage phosphor mixtures including KSF with another faster response time phosphor to reduce the average response time.

Some examples of gaming laptops with 300 or greater Hz refresh rate containing KSF include the Dell G7 laptop, Alienware m17 laptop, and HP OMEN 15 laptop (Figure 4). Again, the commercial implementation of KSF-containing LEDs in these products clearly demonstrates that they are readily used in high refresh-rate displays versus hypothetical arguments based on a single materials characteristic.

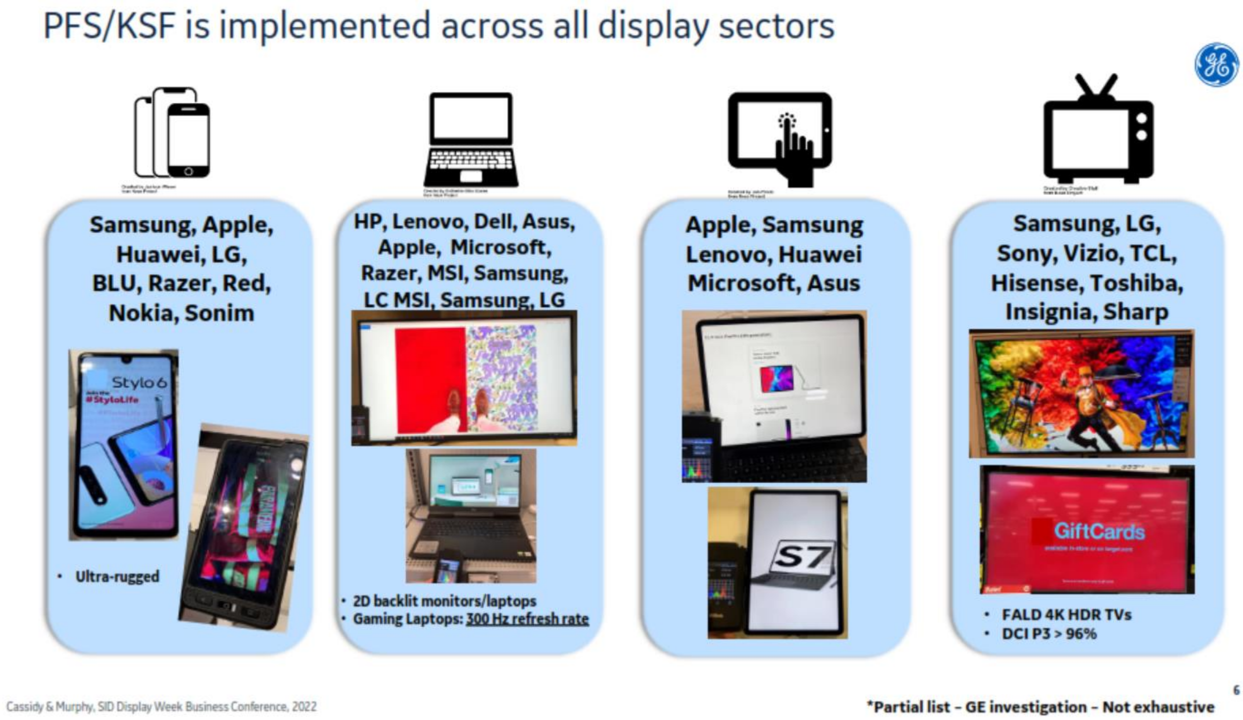


Figure 4. Commercial products using KSF phosphor as surveyed in U.S. electronics stores in 2021-2022.

<u>On the topic of toxicity:</u>

KSF phosphor does not contain any RoHS restricted elements or compounds, and the composition is potassium fluorosilicate with manganese. The base compound has a sister compound, sodium hexafluorosilicate, that is widely used as a fluoridation compound in water treatment[2]. The two compounds have similar hazard profiles according to their SDS[3].

2.2 In Nanosys' 2019 response to the questionnaire for Cd exemption they stated that *"Various red and green-emitting LED phosphor technologies are available today such as KSF. These technologies have poor efficiency for BT.2020 color gamut."*

Link to Nanosys response:

https://rohs.exemptions.oeko.info/fileadmin/user_upload/RoHS_Pack_15/3rd_Consultation/contribution_Nanosys_RoHS15_Ex_Joint_Cd_QD_20190512.pdf

It is inaccurate to say that KSF has poor efficiency. GE's internal testing of components in commercial displays shows that KSF-containing parts have higher external quantum efficiency (EQE) than QD-containing parts (Table 1). KSF is already broadly adopted across all display categories (mobile, tablet, laptop, monitors, TVs) in wide color gamut displays reaching DCI-P3 gamut, an industry standard that is relevant for today's display and out towards the next five years. Rec2020 is an aspirational goal that will be challenging to achieve for all down-converting technology, phosphor or QD. Part of the issues with potential Rec2020 display products are that

[2] https://www.cdc.gov/fluoridation/engineering/wfadditives.htm
[3] Gelest website [https://www.gelest.com/]

they will have higher energy consumption[4] and may have additional artifacts such as viewer metamerism. The arguments for enabling Rec2020 displays are based on extremely low volume display products and aspirational standards versus commercial realities.

2.3 Due to these inaccurate statements, Oeko stated in their own questionnaire that *"for alternative non-cadmium materials, the quantum efficiency and reliability under on-chip operating conditions had not been resolved yet."* As KSF is an alternative material for Cd-based QDs that has been used in over 50 billion LEDs, this statement is inaccurate. As described above, the efficiency, color gamut, and reliability of KSF can meet current and future needs for displays in all markets. It is important that Oeko and the European Commission understand accurately the status of alternative materials to make an educated decision on RoHS restrictions.

Section 3. Answers to Questionnaire

Here you will find GE's responses to several of the questions posed by Oeko. All responses are intended to address only displays applications. GE chooses not to comment on lighting applications.

1. *Can you confirm that such development took place, meaning that Cd-free quantum dot alternatives, providing a comparable performance level to that of* ***on-surface*** *CD QDs, are available on the market and therefore an exemption is no longer required for Cd-QD in on-surface display applications? If not,*
    a. *please specify for which applications you regard an exemption as necessary: lamps/ displays, consumer/ laboratory, mobile/ stationary, and*
    b. *please explain why you consider an exemption to still be justified, providing technical data and evidence to support your views.*
       No comment from GE at this time.
2. *Are Cd-QD used in* ***on-chip*** *configurations in lighting and or displays on the market? If so,*
    a. *how do they compare with alternative lighting/display technologies with respect to technical performance, reliability and environmental, health and consumer safety impacts?*
       As far as we know there are no example of Cd-QDs on chip being used in displays. LEDs containing KSF red phosphor on-chip have been commercially available and widely used in displays since 2014. They have equal or better color performance than most commercially available QD types and have superior efficiency due to high EQE as well as no overlap between absorption and emission (see Fig. 5) – a common drawback of QD technologies. Additionally, they can be used in any existing form factor – on chip or film (on surface).
    b. *Please explain if an exemption for such applications is justified in your view, providing technical data and evidence to support your views.*
       GE recommends that no exemption be granted for Cd in displays as RoHS compliant alternatives already exist and are widely used, namely, KSF. See discussion in section 2 about the performance of KSF.

    c. *How high are the mass and concentration (ppm, mg/mm^2 screen or LED area) of Cd in such applications?*

[4] https://lcd.creol.ucf.edu/Publications/2015/oe-23-18-23680.pdf

No comment from GE at this time.

i. *How is the amount expected to change in the next 5 years?*

ii. *How do the mass and concentration of Cd relate to each other in terms of: Cd per mm^2 screen area/LED, concentration by weight in homogeneous materials, ppm, weight per screen/lighting application?*

iii. *Which part of Cd-QD/ LEDs/ screens/ solid state lighting is regarded as the homogeneous material?*

d. *How developed is the market of displays for RoHS compliant Cd-QD and for Cd-free QD for consumer/ professional, stationary/ mobile displays?*

No comment from GE at this time.

e. *How developed is the market of solid-state lighting for RoHS compliant Cd-QD and for Cd-free QD for consumer/ professional, stationary/ mobile displays?*

No comment from GE at this time.

3. *Should an exemption be granted,*
    a. *are there additional applications where Cd-QD could be used and where it provides benefits to the environment, health and/or to consumer safety?*
    b. *what is the expected amount of Cd entering the EU market annually? Please specify clearly to which application area and for which configuration type your answer refers.*

No comment from GE at this time.

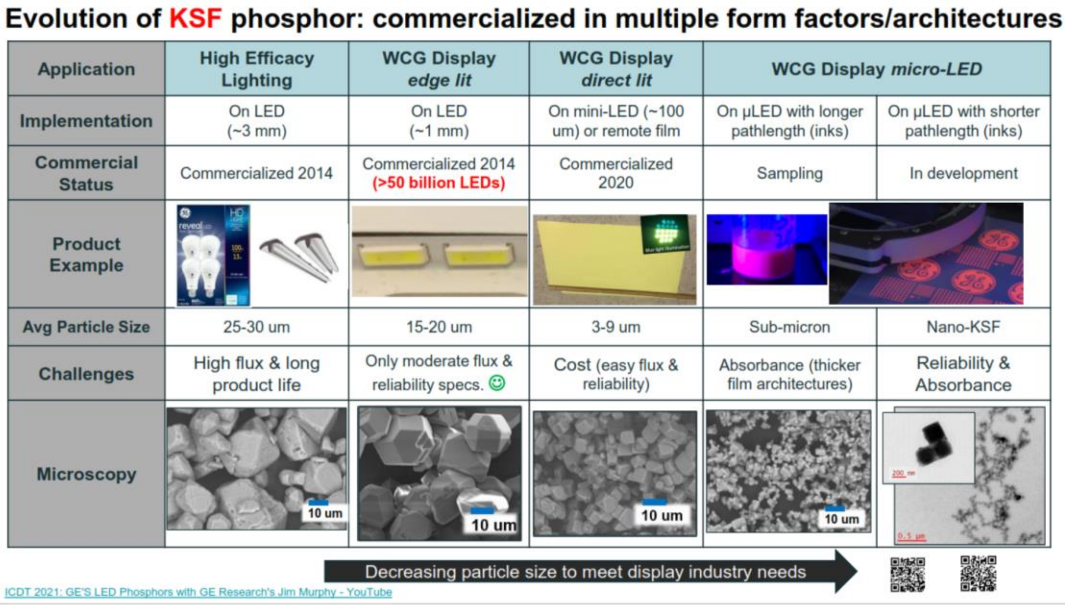
4. *What **substitutes** are of relevance on the **substance level** (i.e., QD that do not include Cd such as InP and InGaN)?*

    a. *What is their status of development and in what applications on the market are they already applied?*

GE has patented, commercialized, and licensed KSF red phosphor and is developing a narrow band green phosphor. Both contain no elements or compounds restricted under RoHS. Red KSF is especially relevant in your consideration of an exemption for Cd for displays as KSF is a highly relevant substitute to Cd-containing QDs.

KSF red phosphor has been optimized for display applications by modifications to the phosphor size, composition, and surface to achieve excellent reliability on-chip or in film forms without additional encapsulation. Figure 5 below summarizes the advancements that have been made related to phosphor size to meet the demands of the display industry. This slide and associated video voiceover from ICDC 2021 conference can be found here:

https://www.youtube.com/watch?v=6UC27vf4Vew



Evolution of KSF phosphor: commercialized in multiple form factors/architectures

Application	High Efficacy Lighting	WCG Display *edge lit*	WCG Display *direct lit*	WCG Display *micro-LED*	
Implementation	On LED (~3 mm)	On LED (~1 mm)	On mini-LED (~100 um) or remote film	On µLED with longer pathlength (inks)	On µLED with shorter pathlength (inks)
Commercial Status	Commercialized 2014	Commercialized 2014 **(>50 billion LEDs)**	Commercialized 2020	Sampling	In development
Product Example					
Avg Particle Size	25-30 um	15-20 um	3-9 um	Sub-micron	Nano-KSF
Challenges	High flux & long product life	Only moderate flux & reliability specs. ☺	Cost (easy flux & reliability)	Absorbance (thicker film architectures)	Reliability & Absorbance
Microscopy	10 um	10 um	10 um	10 um	

Decreasing particle size to meet display industry needs

ICDT 2021: GE'S LED Phosphors with GE Research's Jim Murphy - YouTube

Figure 5. Summary of multiple PFS phosphor types versus their application and commercial implementation.

b. *How developed are dye-doped rather than quantum dot-doped nanoparticles?*

No comment from GE at this time.

c. *How do the substitutes compare to Cd-QD with respect to energy-efficiency, light quality (CRI or colour gamut) and lifetime?*

In terms of efficiency, it has been found[4] that "*The on edge and film approaches for QD are not as efficient as white LED with 2 phosphors.*" Importantly, this paper did not consider KSF-containing LEDs as it was a new material at the time of publication, so the gap in efficiency has only widened with KSF leading the way.

LCD backlights are very complex optical systems and numerous loss mechanisms are possible. The major advantages that KSF has over QD is the high quantum efficiency (>90% of absorbed blue photons are re-emitted as red), virtually no re-absorption (Figure 6), and high reliability without any encapsulation layers. Re-absorption is important because it lowers the overall efficiency of the display. Since QD efficiency is <100%, every absorbed photon has a non-zero probability of being converted to heat. In a back light unit of an LCD where blue, green, and red photons are bouncing around with multiple passes through the optical films (including QD film) additional absorption events results in lower light output. Our own internal testing found the EQE (external quantum efficiency) of all QD films tested by GE was significantly less than those using KSF (Table 1). The absence of additional encapsulation layers can also aid in system efficiency since any additional layers in the LCD will lead to more absorption and photon recycling. While these effects from encapsulation can be minimized/reduced, they cannot be completely eliminated.

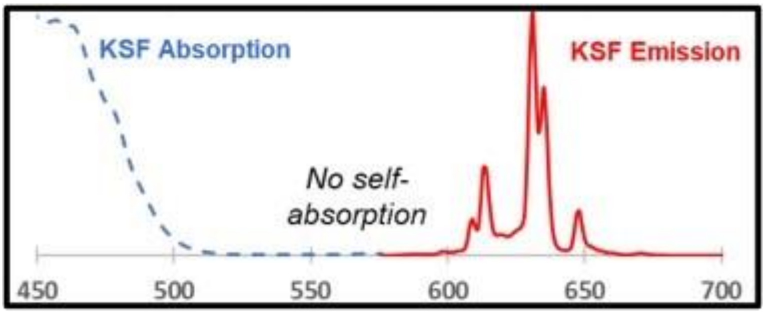


Figure 6. KSF does not show any re-absorption losses of green or red light.

d. *What are the environmental, health and consumer safety advantages and disadvantages of their use as compared to CD QD?*

KSF does not contain any the RoHS restricted elements or compounds, as the composition is Potassium Fluorosilicate with Manganese.

GE's narrow band green phosphor under development remains confidential, however it too does not contain any RoHS restricted elements or compounds.

e. *Do the substitutes contain other substances of concern? Which and in what quantities?*

No comment from GE at this time.

f. *Are obstacles to their application technical or economical?*
KSF is already a commercially available technology and is widely used in displays as a narrow band red phosphor. There are currently 19 companies who license the technology for use in display, with >50 billion LEDs sold containing KSF since 2014. The use of KSF containing LEDs continues to grow (Figure 7).

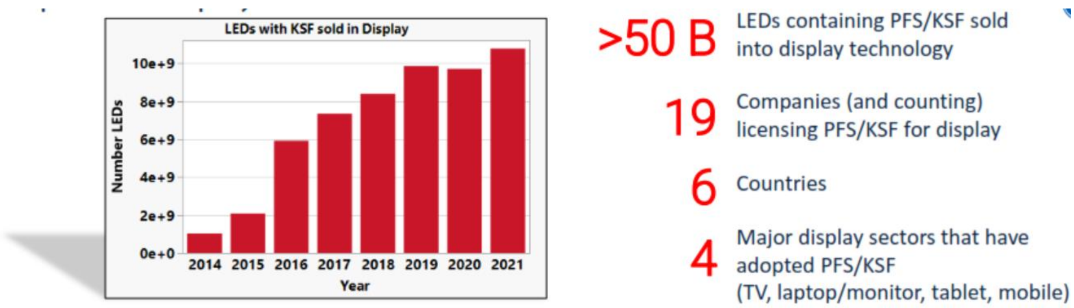


Figure 7. Growth of KSF-containing LED sales since introduction in 2014.

5. *What substitutes exist at the* ***device technology level*** *(alternative components or alternative lamp/display technologies)?* No comment from GE at this time.

   a. *As there are different display technologies on the market, some using white backlight and others not, would it be technically feasible to substitute white backlight and thus Cd-QD in all display applications?*
   b. *As there are different lighting technologies on the market, is it technically feasible to use such technologies in all relevant SSL lighting applications where Cd-QDs are applied?*

c. *What are the environmental, health and consumer safety disadvantages of their use as compared to CD QD? Do the substitutes contain other substances of concern? Which and in what quantities?*

d. *Are obstacles to their application technical or economical?*

6. *What are the main parameters of the energy usage of applications/ devices in which CD QD (and their alternatives) are used? How does energy consumption change in relation to changes in the size, quality of light, periphery settings/ technology, contrast and brightness? Please consider providing a comparison in tabular form.* No comment from GE at this time.

7. *Which are the expected treatment routes of applications containing Cd-QD at the end-of-life stage (e.g., lighting equipment and displays)?* No comment from GE at this time.
   a. *Please explain which of these applications is collected separately and which are treated with mixed WEEE, and what treatment stages are performed for each fraction.*
   b. *Within the standard treatment routes applied in the EU, are the existing installations equipped to cope with the present amount of Cd in related applications?*

Summary

Based on the data shared here demonstrating KSF phosphor as a valid alternative to Cd and non-Cd based QDs we do not support any exemptions for Cd in displays. We thank you for allowing GE to contribute to your evaluation.

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