Red Shift of CT-Band in Cubic Y$_2$O$_3$:Eu$^{3+}$ upon Increasing the Eu$^{3+}$ Concentration

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In this article we describe the redshift of the charge transfer band of nanosized cubic (Y$_{1-x}$Eu$_x$)$_2$O$_3$ upon increasing the Eu$^{3+}$ concentration. This redshift amounts to 0.43 eV (25 nm) in going from 0.1 Mol % Eu$^{3+}$ to 100 Mol % (which is pure Eu$_2$O$_3$). The charge transfer band consists of two broad sub-bands; both shift almost parallel with the Eu$^{3+}$ concentration and are related to the two symmetry sites for the cation, C$_2$ and C$_{3i}$, in the bixbyite-type lattice. The area ratio of the bands is 3:1 and is the first direct evidence for the population of the two lattice sites by the Eu$^{3+}$ cations being in accord with the crystal structure ratio. A model is presented that quantitatively describes the redshift of the charge transfer band of (Y$_{1-x}$Eu$_x$)$_2$O$_3$. This model is based on the Madelung energy of the transferred charge. Other models are briefly discussed, but are discarded.

The red luminescent phosphor Y$_2$O$_3$:Eu$^{3+}$ has been studied extensively, because of its rather high efficiency and high stability to electron bombardment, UV-irradiation and ion bombardment. These attributes led cubic Y$_2$O$_3$:Eu$^{3+}$ to be widely employed in cathode ray tubes (projection tubes) and it is still used in fluorescent lamps. Many properties of this phosphor have been studied by photoluminescence (PL) and cathodoluminescence (CL) spectrometry and have been well documented, because of its industrial applications. Notwithstanding the extensive literature on Y$_2$O$_3$:Eu$^{3+}$, voids still exist in our knowledge on this phosphor. One of these voids is related to the position of the charge transfer (CT) band in the excitation spectrum, although this subject has been widely studied. In the present study we shall of the charge transfer (CT) band in the excitation spectrum, although this subject has been widely studied. In the present study we shall

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where $\chi(O^{2-})$ is the optical electronegativity of the O$^{2-}$ ion, and $\chi(M^{3+})$ is the optical electronegativity of the central metal ion, Y$^{3+}$ or Eu$^{3+}$ in our case. The constant 3.72 in Eq. 1 adapts electronegativity to the eV-scale. When we set $\chi(O^{2-}) = 3.44$ (Pauling’s electronegativity), we find for $\chi(M^{3+}) = 2.12$, which is larger than 1.2 in Pauling’s scale. In spite of this discrepancy, it is possible to represent the E$_{CT}$ of various classes of phosphors with Eq. 1.13,15–17 Dorenbos17 pointed out that Eq. 1 necessarily has a limited scope, because it does not account for the site size and the binding strength of the valence band electrons. Krupp et al.18 have proposed a correction to Eq. 1 that accounts for size variations of the site, where the Eu$^{3+}$ dopant is located. This enabled the comparison between the E$_{CT}$ values of similar phosphors doped with Eu$^{3+}$ in terms of electronegativity.

The E$_{CT}$ and the bandgap Eg of phosphors like Y$_2$O$_3$:Eu$^{3+}$ are related by the photo-ionization (or photoconductivity) threshold E$_{PI}$ according:19

$$E_g = E_{CT} + E_{PI}. \quad [2]$$

If E$_{PI}$ is not being affected strongly by changing the dopant concentration, then a plot of Eg versus Eu-concentration would give information on the E$_{CT}$. The bandgap of Y$_2$O$_3$:Eu$^{3+}$ with Eu$^{3+}$ concentrations between 1 and 11 Mol % has recently been evaluated by Prasanna kumar et al.20 They found that the Eg decreased from 5.3 eV at 1% Eu$^{3+}$ to 4.1 eV at 11 Mol % Eu$^{3+}$, which is a big change over a limited concentration range. It is unknown whether the E$_{CT}$ is also changing over this concentration range; hence, it is impossible to relate this bandgap information to E$_{CT}$.

Apart from the position of the CT-band of Y$_2$O$_3$:Eu$^{3+}$, one may also consider its composition in terms of C$_2$ and C$_{3i}$ contributions, in a similar way as we have done in our treatment of the F$_{9/2}$ → gD$_{7/2}$ excitation band in Y$_2$O$_3$:Tb$^{3+}$.21 By deconvolution two separate bands have been found: a C$_2$-related band at 282 nm and a C$_{3i}$-related band at 305 nm. Jia et al.7 found that the CT-band in Y$_2$O$_3$:Eu$^{3+}$ has contributions from Eu$^{3+}$ at a C$_2$-site and a C$_{3i}$-site. They concluded that Eu$^{3+}$ in C$_2$ sites contributed most to the CT-band and that this C$_2$ contribution is mainly at the VUV-side of the CT-band.

The theories mentioned above on the change of the E$_{CT}$ in Y$_2$O$_3$:Eu$^{3+}$ are based on the following observations:

1. Redshift of the E$_{CT}$ when the Eu$^{3+}$ concentration is increased in Y$_2$O$_3$:Eu$^{3+}$;
2. Redshift of the E$_{CT}$ when the diameter of Y$_2$O$_3$:Eu$^{3+}$ nanoparticles is decreased;
3. Variation of the E$_{CT}$ in similar phosphors doped with Eu$^{3+}$. 
Since the studies of Pelova et al.,\textsuperscript{2} Chang et al.,\textsuperscript{3} and Hang et al.,\textsuperscript{4} refer to a limited range of Eu\textsuperscript{3+} concentrations, we thought it worthwhile to extend the range between 0.001 and 1 of x in (Y\textsubscript{1-x}Eu\textsubscript{x})\textsubscript{2}O\textsubscript{3}. In this systematic study of (Y\textsubscript{1-x}Eu\textsubscript{x})\textsubscript{2}O\textsubscript{3} we measured and analyzed beside the E\textsuperscript{CT} also the intensity ratios of some peaks in the excitation and emission spectra.

**Experimental**

Synthesis of (Y\textsubscript{1-x}Eu\textsubscript{x})\textsubscript{2}O\textsubscript{3} - Synthesis of (Y\textsubscript{1-x}Eu\textsubscript{x})\textsubscript{2}O\textsubscript{3} – The following chemicals were used in this work, yttrium oxide (99.99%) and europium oxide (99.99%) (Ampere Industrie, France); urea, nitric acid and isopropanol (IPA) (Fisher Scientific, UK); all chemicals were used as received. The synthesis of Y\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+} nanoparticles by the homogeneous hydrothermal decomposition of urea method which has been extensively described in our earlier work.\textsuperscript{21–25} The ageing of the turbid suspensions after the onset of precipitation was continued for one hour at a temperature above 85°C (this is the temperature at which urea slowly decomposes in aqueous media at a rate that is sufficient to supply the reactants in a controlled manner by a single nucleation event followed by uniform particle growth of the desired precipitate). After this ageing period the precipitate was filtered, washed three times with de-ionized water and dried in an oven at 80°C. The phosphor precursor particles were then annealed at 980°C in a furnace in air for four hours to yield cubic nanosized Y\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+} phosphor particles. This annealing temperature favors the creation of cubic crystallites that yielded optimum luminescence characteristics.\textsuperscript{23} The crystal structure of the (Y\textsubscript{1-x}Eu\textsubscript{x})\textsubscript{2}O\textsubscript{3} samples after annealing was bixbyite, which is cubic with some O\textsuperscript{2-} vacancies.\textsuperscript{20–23} The (Y\textsubscript{1-x}Eu\textsubscript{x})\textsubscript{2}O\textsubscript{3} samples that were synthesized had Eu\textsuperscript{3+} concentrations of 0.1, 0.3, 1, 2, 4, 5, 6, 8, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90 and 100 Mol %.

**Equipment and methods.** – Photoluminescence (PL) spectra (both excitation and emission) of the samples were collected using a Bentham phosphor spectrometer system (Bentham Instruments Ltd., Reading, UK.), configured with M300 excitation and emission monochromators and 0.2 mm slits. High resolution spectra and various excitation spectra at wavelengths in the range between 220 and 500 nm were recorded with a Horiba Jobin Yvon Fluorolog-3 spectrophotometer (Edison, USA). The absolute wavelength calibration of the monochromators could be off by maximally 1 nm; however, relative wavelength values were accurate within 0.05 nm.

The morphology and particle size assessment of the phosphor powders were conducted in a FESEM, Supra 35 VP, Carl Zeiss, Germany.

**Results and Discussion**

Figs. 1a–1c show FESEM images of annealed (Y\textsubscript{1-x}Eu\textsubscript{x})\textsubscript{2}O\textsubscript{3} spherical phosphor particles on a carbon substrate. From Figs. 1a to 1c it can be derived that the average diameter of the particles varied between 200 and 250 nm, which did not depend on the concentration of Eu\textsuperscript{3+}; it was virtually equal for all concentrations. All the samples of (Y\textsubscript{1-x}Eu\textsubscript{x})\textsubscript{2}O\textsubscript{3} spherical phosphor particles were observed to be comprised of tessellated crystallites 40 nm to 100 nm; some particles indicate that there are small voids within.

Fig. 2 shows the excitation spectra of (Y\textsubscript{1-x}Eu\textsubscript{x})\textsubscript{2}O\textsubscript{3} with x = 0.02, 0.04, 0.05, 0.06, 0.15, 0.2, 0.4, 0.6, 0.7 and 1.0 between 250 and 500 nm, monitored at 611.8 nm. This 611.8 nm line in the emission spectrum of Y\textsubscript{2}O\textsubscript{3}:Eu\textsuperscript{3+} determines the red fluorescence of the phosphor; it has been assigned to the \textsuperscript{5}D\textsubscript{0} - \textsuperscript{7}F\textsubscript{2} (C\textsubscript{2}) transition of Eu\textsuperscript{3+} at a C\textsubscript{2} lattice site.\textsuperscript{1,26}

Fig. 2 shows that the E\textsuperscript{CT} exhibits a substantial redshift of 22 nm in going from 2% to 100% Eu\textsuperscript{3+}, while the 4f\textrightarrow{}4f transitions at 305 nm (\textsuperscript{7}F\textsubscript{2} - \textsuperscript{5}D\textsubscript{0}), 467 nm (\textsuperscript{7}F\textsubscript{2} - \textsuperscript{5}D\textsubscript{2}) and the other transitions in between are not changing. The spectrum of Eu\textsubscript{2}O\textsubscript{3} (100% spectrum) is apart from a shift of the CT-band not essentially different from the spectra of (Y\textsubscript{1-x}Eu\textsubscript{x})\textsubscript{2}O\textsubscript{3} with x < 1. This result is different from the excitation spectrum of Eu\textsubscript{2}O\textsubscript{3} published by Ozawa in 1966.\textsuperscript{23} In Fig. 2 the intensity of the \textsuperscript{7}F\textsubscript{0} - \textsuperscript{5}L\textsubscript{6} transition for pure Eu\textsubscript{2}O\textsubscript{3} is a little bit smaller than the intensity of the CT-band at 285 nm, whereas Ozawa found that the intensity of the \textsuperscript{7}F\textsubscript{0} - \textsuperscript{7}L\textsubscript{4} transition is almost 3 times larger.

The CT-bands in Fig. 2 are rather broad and show a tail at the low wavelength side although this cannot be observed easily in all the spectra presented in Fig. 2. This asymmetry could indicate the presence of more absorption bands. Therefore, the structure of the CT-band was analyzed with a deconvolution technique using four symmetric Gaussian profiles in the wavelength range between 250 and 315 nm: this allows the small peak at 289 nm and the \textsuperscript{7}F\textsubscript{0} - \textsuperscript{5}F\textsubscript{2} transition at 302 nm to be included, because at high Eu\textsuperscript{3+} concentration the CT-band is engulfing the small peak at 289 nm. The main advantage of this procedure was that the E\textsuperscript{CT} could be determined in a consistent way, instead of deriving it from a curve fitting procedure around the maximum that did not account for the small peak at 289 nm. In
our previous work the deconvolution method with Gaussian profiles has been reported,\textsuperscript{21–23} therefore, we may suffice by showing the results. In Fig. 3 deconvolutions are represented at low and high Eu\textsuperscript{3+} concentrations using an eV (energy) scale.

The four Gaussian profiles shown in Figs. 3a and 3b were fitted to the experimental spectrum using a least squares algorithm with Microsoft’s Excel solver. It is important to realize that Fig. 3 shows the CT band plotted on an energy scale so the high energy side corresponds to the low wavelength side of Fig. 2. Thus in Fig. 3 the tail (seen at low wavelength in Fig. 2) is apparent at high energy in Figure 3. Fig. 3a shows that CT-1 for \((Y_{0.9}Eu_{0.1})_2O_3\), has its maximum height at \(E > 4.96\) eV (or \(\lambda < 250\) nm), being beyond the limit of the Bentham spectrometer. At low Eu\textsuperscript{3+} concentrations some spectra were also recorded with the Fluorolog-3 to verify the trend between 235 nm and 250 nm: at 235 nm the absorption of the CT-band was low. Nevertheless, for the low concentrations of Eu\textsuperscript{3+} the determination of the CT-1 band was less reliable; however, at Eu\textsuperscript{3+} concentrations larger than 15 Mol % Eu\textsuperscript{3+}, deconvolution yielded satisfactory results, because of the large number of data points: 642 points for the represented energy range in Figs 3a and 3b. These Figs. also show that CT-2 is 2 to 3 times larger than CT-1 while their band widths are almost identical. Although the vertical scales in Figs. 3a and 3b are in arbitrary units, the signal for the sample with 80% Eu\textsuperscript{3+} was much weaker due to concentration quenching. This is reflected in the increased noisiness of the spectrum in Fig. 3b.

Fig. 4 shows a plot of the E\textsuperscript{CT} versus the concentration of Eu\textsuperscript{3+} in \(Y_2O_3:Eu^{3+}\). The curves for CT-1 and CT-2 in Fig. 4, which have been fitted to the experimental points, are more or less parallel between 20 and 100 Mol % Eu\textsuperscript{3+}. From the CT-2 curves it can be derived that the redshift from 0.1 to 100 Mol % Eu\textsuperscript{3+} is \(-0.43\) eV or 25 nm. The curves also indicate that at high Eu\textsuperscript{3+} concentrations the redshift is levelling off.

Chang et al.\textsuperscript{3} showed that the E\textsuperscript{CT} for 40 nm \(Y_2O_3:Eu^{3+}\) crystallites increased from about 254 nm to about 259 nm upon increasing the Eu\textsuperscript{3+} concentration from 3 to 14 Mol %; their E\textsuperscript{CT} are slightly lower than the E\textsuperscript{CT-2} in Figure 4 at those Eu\textsuperscript{3+} concentrations. It should be mentioned that the data of Chang et al.\textsuperscript{3} refer to non-deconvoluted spectra: the E\textsuperscript{CT} was extracted from the graph in their publication. By deconvolution, the values of E\textsuperscript{CT-2} shift by 2–3 nm to larger wavelengths compared to the (non-deconvoluted) over-all maximum of the CT-band, as can be derived from Figs. 3a and 3b. The E\textsuperscript{CT}-data of Pelova et al.,\textsuperscript{2} which refer to \(Y_2O_3:Eu^{3+}\) (1 and 3 Mol % Eu\textsuperscript{3+}) with non-defined particle and crystallite size, are about 10 nm lower than the values of Chang et al.\textsuperscript{3} Hang et al.\textsuperscript{4} have recently reported a redshift of 7 nm from 248 nm at 1 Mol % Eu\textsuperscript{3+} to 255 nm at 15 Mol %. Although they also found a second Gaussian profile at the high energy side of the CT-band, the absorption of this second band is low and deconvolution has almost no effect on the E\textsuperscript{CT}. As already mentioned in the introduction, Kang et al.\textsuperscript{5} did not find a change of the E\textsuperscript{CT} upon increasing the Eu\textsuperscript{3+} concentration from 2 to 10 Mol %. From the excitation spectrum of pure \(Eu_2O_3\) published by Ozawa\textsuperscript{26} it is impossible to derive a value for E\textsuperscript{CT}. The published E\textsuperscript{CT} for \(Y_2O_3:Eu^{3+}\) particles in the range between 40 nm and 2–5 \(\mu\)m having Eu\textsuperscript{3+} dopes \(\leq 3\) Mol % vary between 239 nm and 262 nm.\textsuperscript{27–30} This variation is surprisingly large. Since these measurements of the excitation spectra were carried out by different groups on \(Y_2O_3:Eu^{3+}\) that was synthesized by different technologies, we assume that the synthesis methods and annealing technologies are responsible for this large spread of the E\textsuperscript{CT}.
Figure 5. Part of PL spectrum. \( ^{5}\text{D}_0 \rightarrow ^{7}\text{F}_3 (C_3) \) transition at 580.6 nm is indicated by \( P_1 \), the \( ^{5}\text{D}_0 \rightarrow ^{7}\text{F}_1 (C_3) \) transition at 582.4 nm is indicated by \( P_2 \). (a) \((Y_{0.99}\text{Eu}_{0.01})_2\text{O}_3\) excited at 260 nm. (b) Deconvolution example with two Gaussian profiles and background correction (BG) for \((Y_{0.99}\text{Eu}_{0.01})_2\text{O}_3\) excited at 260.5 nm.

a much smaller spread; this spread is assumed to be mainly caused by small calibration errors of the spectrometers of about 1 nm. Since we have synthesized and annealed all samples in exactly the same way leading to identical particle size and surface morphology as shown in Figure 1, it is assumed that we have ruled out the afore mentioned source of spread: in other words, the observed redshift of the ECT is an intrinsic property of \((Y_{1-x}\text{Eu}_x)\text{O}_3\) upon increasing \( x \).

Fig. 5a shows the PL-spectrum of \((Y_{0.99}\text{Eu}_{0.01})_2\text{O}_3\) between 575 nm and 605 nm. The \( ^{5}\text{D}_0 \rightarrow ^{7}\text{F}_1 (C_3) \) transition at 582.4 nm is one of the few well-separated \( C_3 \) transitions in the emission spectrum of \( Y_2\text{O}_3:\text{Eu}^{3+} \): it is therefore a hallmark for detailed studies on the energy flow in this phosphor.\(^{4,22,28-30}\) As an indicator for the energy flow we take the ratio of the radiances of \( P_1 \) and \( P_2 \), being the \( ^{5}\text{D}_0 \rightarrow ^{7}\text{F}_0 \) (\( C_2 \)) transition at 580.6 nm and the \( ^{5}\text{D}_0 \rightarrow ^{7}\text{F}_1 (C_3) \) transition at 582.4 nm respectively. Radiance is a better criterion in the case of a difference between the full widths at half maximum (FWHM). Figs. 5a and 5b show a clear difference between the FWHM of \( P_1 \) and \( P_2 \). This difference cannot be observed at low temperatures of 4 K\(^{20}\) and 77 K.\(^{30}\) Since there are no other interfering transitions in the wavelength range between 579 and 584 nm,\(^{29}\) we assume that the \( C_3 \) peak at 582.4 nm experiences more vibronic broadening at room temperature than the neighboring \( C_2 \) at 580.6 nm.

The determination of the radiances requires a profile representation of the peaks; we took Gaussian profiles and applied also a background correction as indicated in Fig. 5b. The radiances of \( P_1 \) and \( P_2 \) were calculated with a formula that was presented in our earlier work.\(^{31}\) The result is represented in Fig. 6, in which the ratio of the radiances of \( P_1 \) and \( P_2 \) has been plotted versus the \( \text{Eu}^{3+} \) concentration. Fig. 6 does not show the whole concentration range of our experiments. The reason is that at \( \text{Eu}^{3+} \) concentrations larger than 20 Mol % the noisiness of the spectra increased and the determination of the radiance of \( P_2 \) became less accurate. Nevertheless, the trend at low \( \text{Eu}^{3+} \) concentration agrees with the CL results described in our publication.\(^{22}\) It indicates that energy from \( \text{Eu}^{3+} \) at a \( C_3 \) site is being transported to \( \text{Eu}^{3+} \) at a \( C_2 \) site when the distance between the \( \text{Eu}^{3+} \) in the lattice decreases.

Jia et al.\(^7\) claimed that the CT-band in \( Y_2\text{O}_3:\text{Eu}^{3+} \) consists of two separate bands, which they assigned to the \( C_2 \) and \( C_3 \) lattice sites of \( \text{Eu}^{3+} \) ions in the \( Y_2\text{O}_3 \) host; however, the shape and position of their bands differ substantially from the results presented in Figs. 3a and 3b. We have also analyzed our data in more detail and the results are shown in Fig. 7, which is a plot of the ratio of the radiances of CT-2 and CT-1 versus the \( \text{Eu}^{3+} \) concentration (in Mol %). The radiances of CT-2 and CT-1, having Gaussian profiles, are calculated from the fitted amplitude and width parameter. It can be seen that the CT-1 and CT-2 bands are in a ratio of 1:3, which coincides with the ratio of the \( C_3 \) and \( C_2 \) lattice sites: so we could infer that what we see in the deconvolution of the CT band is evidence for the fact that both \( \text{Eu}^{3+} \) sites make different contributions to the CT band as might be expected. The fact that we assign the bands in the opposite sense to Jia et al.\(^7\) may be because their nanoparticles are very small and though they claim they also show bulk, their spectra do not prove this and their annealed nanoparticles may not have coalesced: they may only have partially sintered. Indeed we have previously shown that annealing nanoparticles does not lead to rapid growth even in time periods of 24 hours or more (unfortunately, Jia et al.\(^7\) do not give
For pure cubic Y2O3 in the range of 0 to 100 Mol% Eu3+
1087 pm.32,33 The shortest distance dLn-O between Ln3+
atomic mixing, and is to our knowledge the best evidence to date for
in micrometer sized Y2O3:Eu3+.44 In calculating dLN-O with Eq. 3 the small differences between the
excitation wavelength. Similar results were obtained for Y2O3:Eu3+
that the ratio between these peaks does not change by varying the
nm, 255 nm, 260 nm, 265 nm, 270 nm and 275 nm. It can be seen
and P2 is a C3i-transition.

In the light of this assignment we have investigated the nature of
the CT-1 and CT-2 bands by recording PL spectra in the range between
570 nm and 590 nm as a function of the excitation wavelength. If CT-1
would be related to Eu3+ at a C3i-lattice site and CT-2 to the Eu3+
at a C2-lattice site, then it might be expected that the ratio between the
peaks P1 and P2 in Fig. 5 would vary, because P1 is a C2-transition
and P2 is a C3i-transition.

Fig. 8 is an overlay of spectra of 4% Y2O3:Eu3+ excited at 250 nm, 255 nm, 260 nm, 265 nm, 270 nm and 275 nm. It can be seen
that the ratio between these peaks does not change by varying the
excitation wavelength. Similar results were obtained for Y2O3:Eu3+
with other concentrations and also for Eu2O3 an overlay-graph was
obtained that was essentially identical to Fig.8. From these results it
might be concluded that CT-1 and CT-2 do not have symmetry-related
characteristics, however it is possible that putting energy into the CT
band at any wavelength could lead to a redistribution of this energy
over the entire lattice as this is a band that is lattice dependent: hence, it
would then not lead to symmetry related emission. Of course then, this
negative finding does not contradict the assignment we have made for
the nature of CT-1 and CT-2. We already noticed the parallel behavior of
the CT-1 and CT-2 curves in Fig. 4. Dorenbos16 mentioned that the
FWHM of the CT-band of Eu3+ in many host lattices is between
0.6 and 1.2 eV: CT-2 and CT-1 together yield an FWHM of about
0.7 eV. These arguments in favor of our assignment of the two bands
illustrate, we believe, further understanding of the complex nature of
Eu3+
the distribution of the Eu3+
influences of atomic mixing, and
spectra is suspect.

Figure 8. Overlay of spectra of 4% Y2O3:Eu3+, excited at 250 nm, 255 nm, 260 nm, 265 nm, 270 nm and 275 nm. Normalized to unity at 580.6 nm.

In calculating dLN-O with Eq. 3 the small differences between the
C2 and C3i sites in bixbyite (Y1+xEu)xO3,24,35 are neglected. It was
found that an Y3+ ion at a C2 site is not located at the ideal fluorite
position, but rather 3.2 pm off-center,34 whereas Y3+ at a C3i site is
in the center of the slightly distorted cube consisting of six O2− ions and
two diagonally opposed vacancies. If these small perturbations are
neglected, dY3O is found to be 229.5 pm and dEu3O is 235.3 pm; the
difference is 5.8 pm. The crystal ionic radii of Y3+ and Eu3+ are 104 pm
and 108.7 pm ("crystal" radii, based on a radius of 126 pm for
O2−) respectively,36 the difference amounts 4.7 pm. In other words
the actual dilation of the lattice upon inserting more and more Eu3+
is a little bit larger than one would expect using the tabulated radii of
the Eu3+ and Y3+ ions.

In the following text we shall, beside a purely electrostatic model,
also briefly discuss Jørgensen’s model of optical electronegativity,
Kronig-Penney’s model of the bandgap and an alternative bandgap-
narrowing mechanism.

Electrostatic model.—Dorenbos17 has tabulated the ECT for var-
dious cubic Ln2O3:Eu3+ (where Ln = La, Gd, Y, Lu and Sc). For
Y2O3:Eu3+ and Gd2O3:Eu3+, he mentioned 5.12 eV and 4.77 eV re-
spectively. The ionic radii of Gd3+ and Eu3+ are 107.8 pm and 108.7 pm respectively. From the chemical kinship and the size similarity
between Gd3+ and Eu3+ one expects that ΔECT between Y2O3:Eu3+
and Gd2O3:Eu3+ on the one hand and between Y2O3:Eu3+ and Eu2O3
on the other hand are almost equal. For the first pair Dorenbos indicated
that ΔECT = 0.35 eV and for the second pair, Y2O3:Eu3+ and Eu2O3,
we found 0.41 eV (1% Y2O3: Eu3+), which is indeed quite close.
Dorenbos17 and Blasse before him, based on other phosphor data,12
assumed that the differences between ECT of the cubic Ln2O3:Eu3+
with the large Ln3+ ionic radii may be explained by the Madelung
energy. Let’s investigate this hypothesis in somewhat more detail.
The Madelung energy EMa of an ionic lanthanide oxide Ln2O3 can be
written as:35

\[
EMa = -1.44 \frac{M_{Ln2O3}}{d_{Ln-O}},
\]

where MLn2O3 is the Madelung constant for the molecule Ln2O3 in the
cubic bixbyite lattice and dLn-O has been defined earlier. When dLn-O is
expressed in nm, EMa is given in eV. The Madelung constant for cubic
bixbyite-like Ln2O3 is 25.118.34,38 In Fig. 9 we have represented EMa
for the cubic Ln2O3 series together with data of Morss37 and Jenkins
and Roobottom36 for the lattice (cohesion) energy and dLn-O.36 The
lattice energies will be discussed hereafter.

Fig. 9 shows that ΔEMa between Y2O3 and Eu2O3 is 3.74 eV and
ΔEMa between Y2O3 and Gd2O3 is 3.06 eV: these differences are
about a factor of 10 larger than the corresponding values for ΔECT

Figure 9. Lattice energy and Madelung energy of cubic (bixbyite) Ln2O3.
Ma: Madelung energy. dLn-O is shortest Ln-O distance in the lattice (right hand
vertical axis), Mo: lattice energy according to Morss,37 JR-1 and JR-l: lattice
energy according to Jenkins and Roobottom.36
mentioned above; in other words, the total Madelung energy of the compound is obviously not the right quantity to compare with the ECT.

Let us consider what happens during charge transfer: during the charge rearrangement a small amount of charge $\varepsilon$ (in units of the electron charge) located at an O$^{2-}$ anion is transferred to an Ln$^{3+}$ cation according to:

$$3O^{2-} \rightarrow 3O^{-2(1-\varepsilon/2)} - 3\varepsilon \quad [5a]$$

$$2Ln^{3+} - 3\varepsilon \rightarrow 2Ln^{3+3(1-\varepsilon/2)}. \quad [5b]$$

The charge transfer during excitation of a photon can thus be represented by the following reaction:

$$Ln_2O_3 + h\nu \rightarrow 3O^{-2(1-\varepsilon/2)} + 2Ln^{3+3(1-\varepsilon/2)} + 3\varepsilon (h + \varepsilon), \quad [6]$$

where the symbols $\varepsilon$ and $h$ refer to an electron and hole respectively. According to Eq. 6 the charge transfer can be represented by the insertion of 3$\varepsilon$ electron-hole (eh) pairs. Since $\varepsilon$ is a small number, only a fraction of an eh-pair is inserted upon charge transfer. Eq. 6 implies that the Madelung energy of the insertion of 3$\varepsilon$ eh-pairs needs to be evaluated, in which a fraction of the electron is positioned at the Ln$^{3+}$ site and a (smaller) fraction of the hole at the O$^{2-}$ site. The Madelung constant $M_{LnO}$ represented in Eq. 4 is composed of two terms:

$$M_{LnO} = 2z_LM_{Ln} + 3z_OM_O. \quad [7]$$

where $z_L$ and $z_O$ are the ionic charges of the Ln$^{3+}$ and O$^{2-}$ ions, $M_{Ln}$ and $M_O$ are the Madelung constants for the cation and anion respectively and the numbers 2 and 3 represent the stoichiometric composition of Ln$_2$O$_3$. When 3$\varepsilon$ eh-pairs per molecule Ln$_2$O$_3$ are introduced, then the Madelung constant $M_{eh}$ of this insertion can be written as:

$$M_{eh} = z_LM_{Ln} + z_OM_O - \frac{3}{2} \epsilon M_{LnO} = -25.118 \epsilon. \quad [8]$$

Fig. 10a shows the experimental ECT and calculated $\Delta EM_{eh}$ curves as a function of Eu$^{3+}$ concentration for (Y$_{1-x}$Eu$_x$)$_2$O$_3$ in (a) $\Delta EM_{eh}$ and ECT for Lu$_2$O$_3$:Eu$^{3+}$, Y$_2$O$_3$:Eu$^{3+}$, Gd$_2$O$_3$:Eu$^{3+}$, Eu$_2$O$_3$ and La$_2$O$_3$:Eu$^{3+}$ versus Ln$^{3+}$ radius in (b) ECT-D data are from Dorenbos, ECT-2 data are from Figure 4.

In recent papers Dorenbos has introduced the concept of chemical shift, which is the coulomb interaction between a 4f electron near the Eu nucleus and the total charge of Eu$^{3+}$ that is located at a distance $R_Q$ from that nucleus. This chemical shift E(shift) can be written as:

$$E(\text{shift}) = -1.44 \frac{Q}{R_Q}. \quad [9]$$

where $Q = 3$, represents the total charge of the trivalent Eu ion. The distance $R_Q$, called the screening distance, expressed in nm when E(shift) is expressed in eV, is a parameter that varies from compound to compound. The similarity between Eq. 4 and Eq. 9 is striking: when the E(shift) is applied to ECT-data, it indicates that the ratios $3/R_Q$ (in Eq. 9) and $eM_{LnO}/vd_{LnO}$ (after combining Eqs. 4 and 8) represent the same behavior. The difference is that the charge $\varepsilon$ in Eq. 8 needs to be fitted to the experimental data, whereas $R_Q$ in Eq. 9 is the parameter to be fitted. Table I shows a comparison between the Madelung and chemical shift methods for the data presented here. This comparison is based on the value of $\Delta EM_{eh}$ calculated with the Madelung energy method shown in Fig. 10a, which slightly overestimates the experimental value of $\Delta EM_{eh}$.

When $R_Q$ of 100% Eu$_2$O$_3$ is chosen to be 0.193 nm, as suggested by Dorenbos, a value of $R_Q$ for Y$_2$O$_3$:Eu$^{3+}$ with 1% Mol Eu$^{3+}$ of

<p>| Table I. Comparison Madelung and Chemical Shift Methods for ECT of (Y$_{1-x}$Eu$_x$)$_2$O$_3$. |
|----------------------------------|---------------|---------------|---------------|---------------|</p>
<table>
<thead>
<tr>
<th>$\Delta EM_{eh}$ (eV)</th>
<th>$d_{Eu}$ (nm)</th>
<th>$d_{Y}$ (nm)</th>
<th>$R_Q$(Eu) (nm)</th>
<th>$R_Q$(Y) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta EM_{eh}$</td>
<td>0.62*</td>
<td>0.2351</td>
<td>0.2295</td>
<td>0.193</td>
</tr>
<tr>
<td>$E(\text{shift})$</td>
<td>0.62</td>
<td></td>
<td></td>
<td>0.1878</td>
</tr>
</tbody>
</table>

* $\Delta EM_{eh}$ refers to the Madelung constant of Eq. 8 with $\varepsilon = 0.33$. 

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[Note: The table and equation numbers are cited for reference, but the actual data and calculations are not transcribed here.]
0.1878 nm yields $\Delta E(\text{shift}) = \Delta E^\text{CT} = 0.62$ eV. The difference between $R_0$ for Eu$_2$O$_3$ and 1% Y$_2$O$_3$:Eu$^{3+}$ is 5.2 nm, which is almost equal to the difference between the radii of Eu$^{3+}$ and Y$^{3+}$, indicating that $R_0$ varies with $r_{r}$.

It is tempting to speculate about the (small) differences between the experimental $E^\text{CT}$ and the $\Delta E_{\text{M}}$ curves in Fig. 10a. For this speculation we shall make use of Fig. 9, in which both lattice energies and Madelung energies of the cubic Ln$_2$O$_3$ (including Y$_2$O$_3$ and Sc$_2$O$_3$) crystals have been plotted. Four lines are represented in Fig. 9: Ma stands for the Madelung energies of the Ln$_2$O$_3$ crystals, M0 stands for the lattice energies as tabulated by Mooss, the lines JR-1 and JR-2 are based on the lattice energies from Jenkins and Roobottom, tabulated in the Handbook of Chemistry and Physics.\(^\text{36}\) The lattice energies represented in Fig. 9 were calculated with the Born-Haber cycle from thermodynamic data or were estimated with Born-Landé’s equation. Fig. 9 shows that the Madelung energy of the Ln$_2$O$_3$ series overestimates (the absolute value of) the lattice energy by about 8%. The difference between lattice energy and Madelung energy is usually ascribed to the effect of polarizability of the ions. If we would have based the calculation of $\Delta E_{\text{M}}$ in Fig. 10a on lattice energy instead of Madelung energy, the slope of the $\Delta E_{\text{M}}$ line would be 8% less steep. However, the increasing effect of the polarizability of the cation by inserting more and more Eu$^{3+}$ in the lattice might well lead to a deviation from linearity as shown by the $E^\text{CT}$-curve. The JR-2 line in Fig 9 suggests that polarizability effects in Y$_2$O$_3$ and Sc$_2$O$_3$ are larger than in the Ln$_2$O$_3$ series, which is gainsaying the reasoning given above. However, beside the difference in polarizability between the Y$^{3+}$ and Eu$^{3+}$ ions, another effect has to be taken into account: compressibility as known from Born-Landé’s equation. Both Y$^{3+}$ and Sc$^{3+}$ are rather small ions, these may create, even after adjustment of the lattice constant, slightly more space for compression leading to a smaller Born exponent. This argument largely eliminates the contradiction mentioned here.

**Non-electrostatic models.**—In this section some non-electrostatic models will briefly be considered that could explain the behavior of the $E^\text{CT}$ shown in Figs. 2 and 4. First Jorgensen’s model of optical electronegativity will be discussed. As suggested by Krumpel et al.\(^\text{18}\) the optical electronegativity of Eu$^{3+}$, in Eu$^{3+}$-doped phosphors may be represented by a function of $(d_{\text{C-O}})^{-\chi}$, where the subscript C represents the central ion in the lattice that may be replaced by Eu$^{3+}$. In view of the small difference between the values $d_{\text{Y-O}}$ in Y$_2$O$_3$ and $d_{\text{Eu-O}}$ in Eu$_2$O$_3$, the optical electronegativity of Eu$^{3+}$ may also be described by a linear function of the $d_{\text{C-O}}$ distance in (Y$_{1-x}$Eu$_x$)$_2$O$_3$. In doing so, the experimental $E^\text{CT}$ curve can be fitted with a straight line, which is determined by two parameters $p$ and $q$ in the relation $\chi(Eu) = p + qd_{\text{C-O}}$. Since the physical interpretation of these parameters is not straightforward, we do not consider this treatment as appropriate for explaining the redshift of the CT-band in Y$_2$O$_3$:Eu$^{3+}$.

The second model to be discussed is the Kronig-Penney model\(^\text{19}\) of the bandgap of a semiconductor, which has been applied to Y$_2$O$_3$:Eu$^{3+}$ nanocrystals by Shang et al.\(^\text{20}\) According to these authors the change of the bandgap energy $\Delta E_g$ can be written as:

$$\Delta E_g = \frac{2}{3} E_v \frac{\Delta v}{v}. \quad [10]$$

where $E_g$ is the bandgap of Y$_2$O$_3$ (or Y$_2$O$_3$:Eu$^{3+}$ with a very small Eu$^{3+}$ concentration), $\Delta v$ is the change of volume of a unit cell upon Eu$^{3+}$ doping and $v$ is the volume of the cell for non-doped Y$_2$O$_3$. Shang et al. dealt with dilution of the lattice upon reducing the particle size, whereas we dealt with lattice dilution upon increasing the dopant concentration, which is different.

In going from Y$_2$O$_3$ to Eu$_2$O$_3$ the cell constant changes by 2.52% and the cell volume by 7.78%. When inserting this value for $\Delta v/v$ in Eq. 10 and taking a value of 5.6 eV for the bandgap of 1% Y$_2$O$_3$:Eu$^{3+}$, we get $\Delta E_g = 0.29$ eV, which is lower than $\Delta E^\text{CT}$, being 0.41 eV in going from 1% Y$_2$O$_3$:Eu$^{3+}$ to 100% Eu$_2$O$_3$. When plotting $\Delta E_g$ versus Eu$^{3+}$ concentration one gets a straight line, because the small change of the lattice constant leads to a linear change of $\Delta v$ versus Eu$^{3+}$ concentration. Notwithstanding the 67% agreement between the Kronig-Penney model for $\Delta E_g$ and the $E^\text{CT}$, which is surprisingly good, we discard the Kronig-Penney model because apart from the lattice constant a, the wave functions of the Ln$^{3+}$ ion are also changing upon doping. Furthermore, one should keep in mind that, because of the effect of the photo-ionization (or photo-conductivity) threshold defined in Eq. 2, a good agreement between $\Delta E_g$ and $\Delta v/v$ does not guarantee a good correlation between the $\Delta E^\text{CT}$ and $\Delta v/v$.

As a third possibility we now consider a bandgap-narrowing model that was developed in the 1970s for heavily doped Si and Ge. This model was applied to the semi-insulator GaAs by Hrivnak.\(^\text{43}\) The equation describing this type of bandgap-narrowing can be written as:

$$\Delta E_g(N) = -17.55 \sqrt{\frac{N}{10^{18} \text{cm}^{-3}}}. \quad [11]$$

where $\Delta E_g$ is the bandgap-narrowing (in eV) and $N$ is the dopant concentration in atoms/cm$^3$. For the calculation of the constant 17.55 we used a dielectric constant of 15 for Y$_2$O$_3$. By inserting the Eu$^{3+}$ concentrations in Eq. 11 as used in our experiments, $\Delta E_g$ is about one order of magnitude larger than $\Delta E^\text{CT}$. For this reason this model can be discarded as well.

Finally we must consider spin-spin interaction between the Eu$^{3+}$ ions in the lattice. Eu$^{3+}$ is a high spin ion, because the six 4f electrons are parallel oriented. The cubic lanthanide sesquioxides including Eu$_2$O$_3$ are antiferromagnetic at low temperatures. The reported Néel temperatures for all Ln$_2$O$_3$ are <10 K,\(^\text{44}\) which means that the energy for magnetic ordering is <0.9 meV. In other words, spin-spin interactions between Eu$^{3+}$ ions at neighboring sites in (Y$_{1-x}$Eu$_x$)$_2$O$_3$ have a very small effect on the energy levels and may be neglected here.

**Conclusions**

We have found that the CT-band in (Y$_{1-x}$Eu$_x$)$_2$O$_3$ has a substantial redshift upon increasing the Eu$^{3+}$ concentration. The redshift amounts 0.43 eV in going from 0.1 Mol % Eu$^{3+}$ to 100%. We have established herein that the CT-band consists of two sub-bands, both of which show equal redshift. Evidence is presented herein that these two bands are directly related to the two symmetry sites for the Ln$^{3+}$ ion in the cubic bixbyite type lattice of (Y$_{1-x}$Eu$_x$)$_2$O$_3$. The redshift of this CT-band can quantitatively be described in terms of the Madelung energy of one inserted eh-pair. The $E^\text{CT}$ of some Ln$_2$O$_3$:Eu$^{3+}$ phosphors with radii of the Ln$^{3+}$ cation that do not deviate much from those of Y$^{3+}$ and Eu$^{3+}$ (Gd$^{3+}$ and Lu$^{3+}$) can be described with this electrostatic model.

We suggest that the electrostatic analysis presented in our study could help to improve the understanding of the variation of the $E^\text{CT}$ in some of the phosphors studied and classified by Dorenbos\(^\text{39}\) by unifying his chemical shift model with the Madelung energy model. In addition as we have shown that the CT band is made up of contributions from both lattice sites it may be possible to make more detailed inferences to further the understanding of the CT bands of lattices containing more than two different lattice sites.

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**References**
