Energy transfer in sodium bromide slightly doped with copper and manganese ions

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R Aceves†, M A Camacho, U G Caldiño, A F Muñoz and J O Rubio

Departamento de Física, Universidad Autonoma Metropolitana Unidad Iztapalapa, PO Box 55-534, 09340 Mexico DF, Mexico

Abstract. The optical properties (emission, excitation and lifetime data) of NaBr slightly doped with Cu^+ and Mn^{2+} ions have been studied in the present investigation. The analysis of the spectroscopic data obtained indicated that the $Cu^+ \rightarrow Mn^{2+}$ energy transfer takes place in this material even at very low impurity concentrations and after the crystals are subjected to severe quenching treatments. This fact suggested that the donor and acceptor ions are not randomly distributed in the lattice of sodium bromide but rather occur as small impurity complexes of Cu^+–Mn^{2+}. The data shown in this paper substantiate the ionic radius criterion proposed by Rubio *et al*, which predicts pairing between two impurity ions in a crystal when their average ionic radius equals the radius of the host ion they replace.

1. Introduction

Recently, Rubio and co-workers reported in a series of papers [1–3] the Eu-sensitized Mn fluorescence in single crystals of NaCl, NaBr and NaI. In all these systems, a non-radiative energy transfer process was found to occur from the donor Eu^{2+} ions to the acceptor Mn^{2+} ions even at very low impurity concentrations and after the crystals were subjected to severe quenching treatments. From this finding and other experimental observations, it was inferred that the Eu $\rightarrow$ Mn energy transfer process taking place in the doubly doped crystals of NaCl:Eu:Mn, NaBr:Eu:Mn and NaI:Eu:Mn occurs in the Eu^{2+}–Mn^{2+} close pairs which are preferentially formed in the sodium halide lattices.

From the analysis of the emission, excitation and lifetime data obtained in slightly doubly doped crystals of NaCl:Cu:Mn and NaCl:Sn:Mn, Rubio *et al* [4,5] also concluded that the observation of either copper-sensitized manganese fluorescence or tin-sensitized manganese fluorescence in the samples analysed, indicated that the donor and acceptor impurity ions were not randomly distributed in the sodium halide lattice but rather occurred as impurity clusters of either Cu–Mn or Sn–Mn.

The experimental findings mentioned above are in contrast with most impurity-sensitized luminescence situations where a random distribution of sensitizers and activators through the solid material is found. They seem to be, however, quite relevant findings since then the fluorescence efficiency of a manganese-doped phosphor material may be strongly enhanced by pumping through either Eu^{2+}, Sn^{2+} or Cu^+ ions introduced in the material simultaneously during preparation.

† Also at Instituto de Física, Universidad Autónoma de Puebla. On leave from Centro de Investigación en Física, Universidad de Sonora, Mexico.

In order to explain the strong tendency for the formation of small complexes of donor–acceptor impurity ions in the sodium halide lattices, Rubio *et al* [1] proposed a criterion which is based on the ionic radii of the impurities. If the average ionic radius of the two ions is nearly identical to that of the host cation ion for which they substitute in the lattice, then impurity-pair formation is probably favoured to reduce the strain in the lattice introduced by the presence of each impurity alone. Since this criterion may provide a reasonable basis for selecting impurity ions and host crystals which might lead to the development of efficient phosphor materials, it seems to be of interest to explore its applicability in other kinds of doubly doped crystals.

With this objective in mind, the optical properties of NaBr slightly doped with Cu^+ and Mn^{2+} ions have been analysed and the results obtained are reported in the present paper. $Cu^+ \rightarrow Mn^{2+}$ energy transfer is expected to occur in sodium bromide since the $3d^9 4s \rightarrow 3d^{10}$ ($^3E_g \rightarrow ^1A_{1g}$) emission transition of the Cu^+ ions overlaps some Mn^{2+} absorption bands in this material.

The analysis of the spectroscopic data that we obtained in two-activator crystals of NaBr:Cu^+:Mn^{2+} was carried out with the aid of the optical data previously reported [6–9] for the systems NaBr:Cu^+ and NaBr:Mn^{2+}.

2. Experimental details

Single crystals of NaBr doped with only copper ions and doubly doped with copper and manganese ions were grown in our laboratory in evacuated quartz tubes using the Bridgman technique. Some crystals were also grown using the Czochralski technique at the Crystal Growth Facility at the Institute of Physics, National University of México. The crystals showed the same optical characteristics irrespective of the growth technique employed. The concentration of copper in the quenched crystals of NaBr:Cu^+ and NaBr:Cu^+:Mn^{2+} was estimated from the D_1 absorption band of Cu^+ ions peaking at ~ 4.77 eV, using Smakula's equation with a value for the oscillator strength [7] of 0.067. The manganese concentration in the NaBr:Cu^+:Mn^{2+} was determined by atomic absorption spectrophotometry. Thermal quenching was carried out by heating the samples for the least 2 h at 870 K, in vacuum, and then cooling them, as fast as possible, into acetone.

Optical absorption measurements were performed with a Perkin–Elmer model 330 double-beam recording spectrophotometer. Continuous fluorescence spectra were obtained using the same equipment as that described previously [2–5]. All the emission and excitation spectra were corrected for lamp intensity and photomultiplier sensitivity.

For the lifetime measurements, the samples were excited at 266 nm with 10 ns pulses of a Lumonics HY-1200 quadrupled Nd:YAG laser. The sample fluorescence was detected by a cooled Hamamatsu R943-03 photomultiplier tube and processed by a Hewlett-Packard model 54201A digitizing oscilloscope.

The low-temperature measurements were taken with the crystal mounted in the cold finger of an Air Products DE-202 cryogenic refrigerator.

3. Results

Figure 1 shows the 11 K emission spectra of a quenched NaBr:Cu^+ (20 ppm): Mn^{2+} (120 ppm) crystal under excitation at (a) 266 nm and (b) 250 nm. By exciting the sample at 266 nm, an UV band peaking at 358 nm and an orange–red band peaking at ~ 620 nm are observed. Excitation at 250 nm produces an additional UV band peaking at 306 nm.

The UV emissions have the same characteristics (peak position, halfwidth and temperature dependence) as the copper emission bands observed in our quenched samples of NaBr only contaminated with Cu^+ ions. They are also similar to those previously reported by Emura and Ishiguro [8] for the Cu^+ emission in monocrystalline NaBr. Therefore, the emission bands peaking at 306 and 358 nm observed in the emission spectrum of two-activator NaBr:Cu^+:Mn^{2+}, correspond to the transitions $^1E_g \rightarrow {}^1A_{1g}$ (E_S band) and $^3E_g \rightarrow {}^1A_{1g}$ (E_L band) of Cu^+ ions, respectively [8]. The orange–red band appears only when the NaBr:Cu^+ crystal is simultaneously doped with Mn^{2+} ions. Moreover, the peak position of this band moves to shorter wavelengths when the sample temperature is increased. This behaviour is usually observed for Mn^{2+} emission in crystalline matrices. The orange–red band was, therefore, attributed to the $^4T_{1g}$ (G) $\rightarrow {}^6A_{1g}$ (S) transition of Mn^{2+} in NaBr.
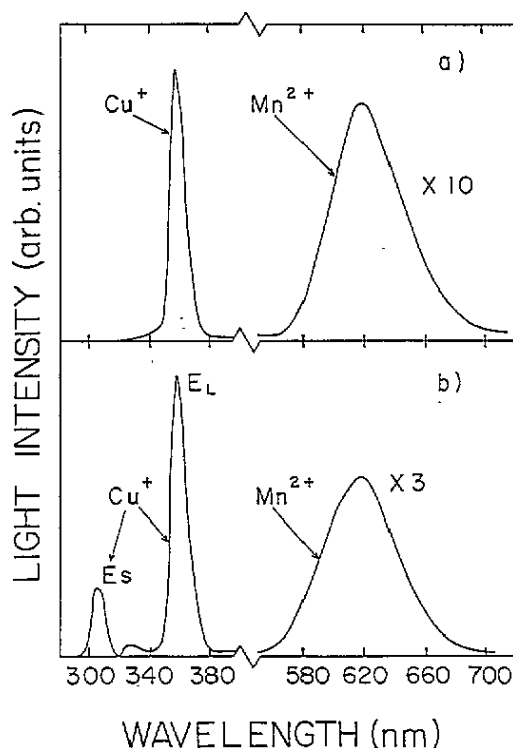

Figure 1. The 11 K emission spectra for an acetone-quenched doubly doped crystal of NaBr:Cu (20 ppm):Mn (120 ppm) excited at (a) 266 nm and (b) 250 nm.

The 11 K excitation spectra for the Cu^+ (E_S and E_L) and Mn^{2+} emissions observed in the NaBr:Cu (20 ppm):Mn (120 nm) quenched crystal are displayed in figure 2. In all cases, the D_1 and D_2 excitation bands are typical of Cu^+ ions [8]. Manganese emission is, therefore, produced by excitation into either the D_1 or D_2 absorption bands of Cu^+. The differences which can be appreciated in the excitation spectra of the copper and manganese emissions may suggest that the nature of the complex centre in which the emissions at 306 and 358 nm are produced is different to that in which the red luminescence originates as a consequence of a non-radiative $Cu^+ \rightarrow Mn^{2+}$ energy transfer process.

Lifetime measurements performed in the quenched doubly doped crystals indicated that the Cu^+ luminescence decay consisted of a pure exponential decay, unlike the non-exponential decays usually observed in donor $\rightarrow$ acceptor energy transfer processes. The lifetime value associated with the decay was found to be 148 μs at 270 K, 429 μs at 60 K, and 3.4 ms at 11 K. These lifetime data are nearly identical to those we found for the Cu^+
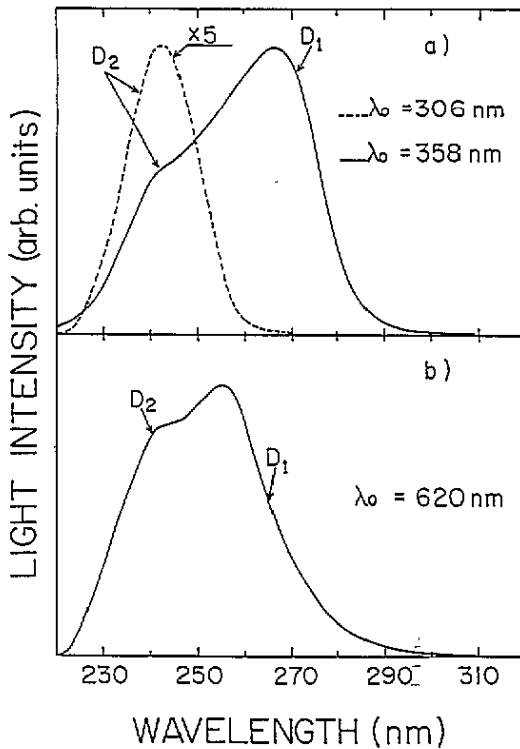
Figure 2. The 11 K excitation spectra for (a) copper E_S and E_L emissions and (b) manganese emission. These spectra were obtained from the same crystal as was employed for recording the emission spectra portrayed in figure 1.

emission in our quenched samples of NaBr only doped with Cu^+ ions (30 ppm). They are also very similar to the data previously reported for the Cu^+ emission in NaBr [10].

On the other hand, the decay scheme of the Mn^{2+} emission consisted of a pure exponential decay with no observable rise time. The lifetime value was found to be ~ 5 ms at 270 K and ~ 9 ms at 11 K.

4. Discussion

The presence of the D_1 and D_2 absorption bands of Cu^+ ions in the excitation spectrum of the Mn^{2+} luminescence indicates that the $Cu^+ \rightarrow Mn^{2+}$ energy transfer takes place in our quenched doubly doped samples of NaBr:Cu:Mn. This process is expected to occur in NaBr since the E_L emission band ($^3E_g \rightarrow {}^1A_{1g}$ transition) of Cu^+ ions overlaps the $^6A_{1g} \rightarrow {}^4T_{1g}$ (P), $^6A_{1g} \rightarrow {}^4E_g$ (D) and $^6A_1 \rightarrow {}^4T_{2g}$ (D) absorption transitions of Mn^{2+} in this host crystal [6] as can be appreciated from the data portrayed in figure 3.

If we assume that the Cu and Mn ions were randomly distributed in the crystals employed, the interaction distance between them is so large (~ 70 Å) that energy transfer over such distances is expected to be less efficient. On the other hand, it is well recognized that, regardless of the non-radiative energy transfer process between donor and acceptor ions in solids, the decay pattern of the donors should be affected by the presence of the acceptor ions. Our experimentally determined spectroscopic data revealed, however, that in our slightly doped NaBr:Cu:Mn crystals this is not the case.

This latter fact and the observation of a Cu $\rightarrow$ Mn energy transfer at very low concentrations of copper and manganese ions may suggest that these rather occur as small impurity complexes of Cu^+-Mn^{2+} in the lattice of sodium bromide. In these complexes, the
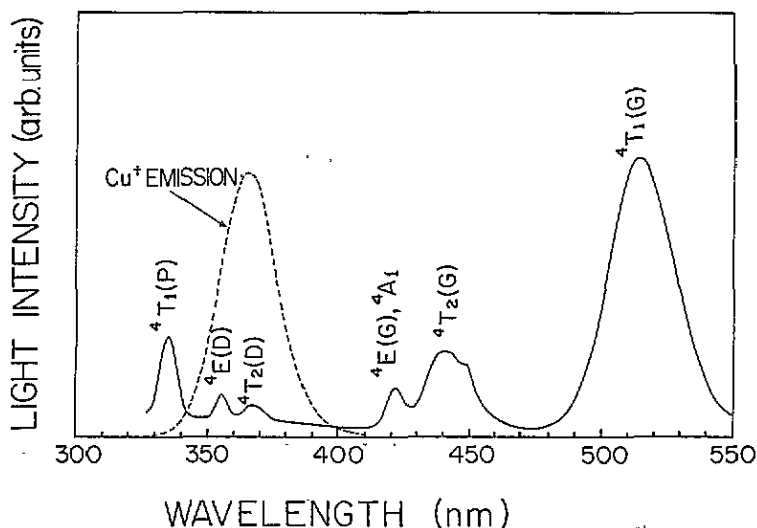
Figure 3. Room-temperature Cu^+ emission (– – –) and Mn^{2+} absorption (——) spectra in sodium bromide.

energy transfer from Cu^+ to Mn^{2+} may proceed at a rapid rate which quenches the donor luminescence completely. This conclusion is supported by our lifetime data which show that the Cu^+ lifetimes in NaBr:Cu (20 ppm):Mn (120 ppm) and in NaBr:Cu (30 ppm) are the same within experimental error ($\pm 3\%$). On the other hand, the unassociated copper ions are, on average, at such a distance from the manganese ions that no energy transfer can take place, therefore leaving the lifetime of the Cu^+ ions unchanged. According to this scenario, the Cu^+ ions which are forming the Cu–Mn complexes do not exhibit any fluorescence and the observed copper emission in our slightly doubly doped crystals of NaBr:Cu:Mn originate exclusively from the Cu^+ ions which are not interacting with the Mn^{2+}.

According to the ionic radius criterion, the preferential formation of Cu–Mn pairs is expected to occur in the lattice of sodium bromide since the average ionic radius of the Cu^+ and Mn^{2+} ions is similar to that of the Na^+ ions for which they substitute. The ratio of the number of Cu^+ ions associated with Mn^{2+} ions (N_{Cu-Mn}) to the total concentration of copper (N_T) in our quenched doubly doped crystals was estimated using a simple model, in which both the sensitizer and activator impurity ions are treated as two-energy-level systems [4]. This model is only applicable at very low temperatures where the Cu^+ ion can be described by two energy levels, i.e., the $^1A_{1g}$ ground state and the metastable $^3T_{1g}$ (^3E_g) excited level from which the E_L emission originates. The basic assumptions of this model have been described elsewhere [4]. According to them, the ratio N_{Cu-Mn}/N_T in the limit of weak pumping is given by

$$\frac{N_{Cu-Mn}}{N_T} = \frac{(I_{Mn}/I_{Cu})(\beta^r_{Cu}/\beta_{Cu})}{\beta^r_{Mn}/\beta_{Mn} + [(I_{Mn}/I_{Cu})(\beta^r_{Cu}/\beta_{Cu})]} \tag{1}$$

where β^r and β are the radiative and fluorescence decay rates, respectively, and I_{Cu} and I_{Mn} are the integrated intensities of the copper and manganese emissions observed in the acetone quenched doubly doped samples under excitation into the D_I absorption band (266 nm) of the copper ions. If our 11 K data ($I_{Mn}/I_{Cu} \simeq 0.15$, $\beta^r_{Cu} \simeq \beta_{Cu} \simeq 294$ s^{-1} and $\beta^r_{Mn} \simeq \beta_{Mn} \simeq 111$ s^{-1}) are employed in equation (1), then N_{Cu-Mn}/N_T is found to be
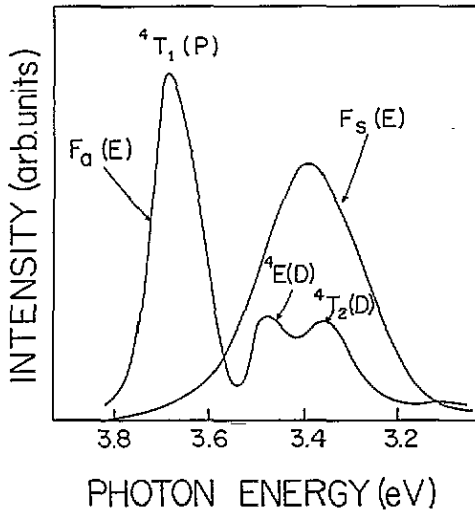
Figure 4. The normalized line-shape functions for the Cu^+ emission ($F_s(E)$) and Mn^{2+} absorption ($F_a(E)$) in the overlap region at room temperature.

~ 0.13. Thus, about 13% of the total concentration of Cu^+ ions in two-activator NaBr:Cu (20 ppm):Mn (120 ppm) crystals are associated with Mn^{2+} ions.

From the same two-energy-level model and the rise time (t_{max}) of the manganese emission, which was determined to be shorter than 25 ns, the rate of $Cu^+ \to Mn^{2+}$ energy transfer (W_{sa}^{exp}) was roughly estimated from the expression derived by Muñoz and Rubio [4]:

$$W_{sa}^{exp} > \frac{1}{t_{max}} \ln\left(\frac{\beta_{Cu}}{\beta_{Mn}}\right) + \beta_{Mn} \tag{2}$$

the result being $W_{SA} > 1.4 \times 10^8$ s^{-1} at 300 K

Taking into account that Cu^+ absorption transitions can be partially allowed in crystals while those of the Mn^{2+} ions are forbidden, it is reasonable to assume that the $Cu^+ \to Mn^{2+}$ energy transfer mechanism occurring in NaBr is of the electric quadrupole–quadrupole type. According to Dexter's theory, the transfer rate for such interaction is given by [10]:

$$W_{sa}^{QQ} = \frac{3\hbar^4 c^4 f_q^2 \lambda_s^4 Q_a \Omega(F_s, F_a)}{4\pi n^4 \tau_s^0 f_d^2 R_{sa}^{10}} \tag{3}$$

where $\Omega(F_s, F_a) = \int F_s(E) F_a(E) E^{-4}\, dE$ represents the spectral overlap integral between the normalized shapes of the Cu^+ emission, $F_s(E)$, and Mn^{2+} absorption, $F_a(E)$, in the overlap region (figure 4). The meaning of the remaining symbols in equation (3) has been described elsewhere [10]. Using the room-temperature absorption spectrum of Mn^{2+} in NaBr reported by Marco et al [6], $\Omega(F_s, F_a)$ was found to be $\sim 1 \times 10^{-2}$ eV^{-5}. Using this value in equation (3) with $Q_a \simeq 4.8 \times 10^{-23}$ eV cm^2, $f_d \sim 10^{-7}$ and $f_q \sim 10^{-10}$, the critical interaction distance for energy transfer was found to be about 14 Å at 300 K. This value is quite a bit smaller than that (~ 70 Å) estimated assuming a random distribution of Cu^+ and Mn^{2+} ions in our crystals. Therefore, the observation of a $Cu^+ \to Mn^{2+}$ energy transfer in our quenched doubly doped samples suggests that this process occurs in small Cu–Mn complexes which are preferentially formed in the lattice of sodium bromide instead from Cu^+ and Mn^{2+} ions randomly distributed.
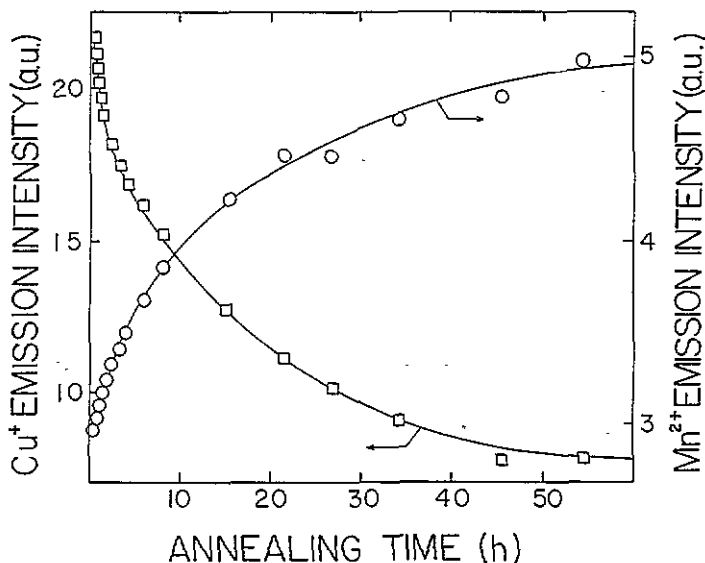
Figure 5. The evolution of the intensities of the Cu^+ and Mn^{2+} emissions observed in our quenched double-doped crystals of NaBr:Cu (20 ppm):Mn (120 ppm) as a function of the annealing time at room temperature.

It is also found from equation (3) that in order to account for the estimated rate of Cu → Mn energy transfer (> 1.8×10^8 s^{-1}), the interaction distance between Cu^+ and Mn^{2+} ions in our quenched crystals of NaBr:Cu:Mn must be shorter than 4 Å. Taking into account the lattice parameter of sodium bromide, the shortest interaction distance between Cu^+ and Mn^{2+} ions in this host occurs in a Cu^+–Mn^{2+} dimer complex along a ⟨110⟩ direction. This interaction distance is ∼ 4.2 Å if one does not consider any lattice distortion caused by the introduction of the two impurities in the crystal; this distance being larger than that estimated from equation (3). However, it is well known that the Mn^{2+} ions enter the lattice of NaBr substitutionally for the sodium ions [6], whereas the Cu^+ ions are not located at normal sodium lattice points: rather they are displaced [7] along the ⟨110⟩ or ⟨111⟩ directions by about 0.5 Å. Therefore, it is reasonable to expect that in a Cu^+–Mn^{2+} dimer complex along a ⟨110⟩ direction, the interaction distance between these two ions will be shorter than 4 Å, and that the efficient process of energy transfer observed in our crystals takes place in this kind of complex. Other small-aggregate complexes in which a copper ion is surrounded by several manganese ions occupying the positions of first neighbours could be also appropriate in accounting for the estimated rate of Cu → Mn energy transfer.

At this point, it should be mentioned that an exchange interaction mechanism might be also responsible for the Cu → Mn energy transfer taking place in the small impurity aggregates. However, a calculation of the energy transfer rate using this interaction mechanism was not attempted since only a very rough estimate can be obtained. In fact, the calculation is strongly dependent on the wave-function overlap integral of the donor and acceptor electrons involved in the exchange interaction. This makes it important to use accurate expressions for the wave functions which are not known at the present time.

As a last remark, it is important to mention that the Cu^+ → Mn^{2+} energy transfer in the as-grown crystals was found to be more efficient than in the quenched ones. The intensity of the Mn^{2+} emission under Cu^+ excitation was found to decrease drastically when the

as-grown crystal was quenched into acetone. However, annealing of the quenched crystals at room temperature produced the growth in intensity of the Mn^{2+} emission at the expense of that of Cu^+ as can be appreciated from the data portrayed in figure 5; this behaviour being a consequence of the fact that Cu–Mn clusters are formed when the quenched crystals are stored at 300 K.

5. Conclusions

NaBr single crystals slightly doped with Cu^+ and Mn^{2+} ions were investigated using the photoluminescence technique. The spectroscopic data obtained indicate that the $Cu^+ \rightarrow Mn^{2+}$ energy transfer process which takes place in this system occurs in small complexes of copper–manganese (dimers, trimers, etc) which are preferentially formed in the lattice of sodium bromide. This preferential impurity clustering, which has been considered to be infrequent in most studies of energy transfer between impurities in solids, appears to be a quite relevant finding which may help us to design more efficient phosphor systems. The results obtained substantiate the ionic-radius criterion proposed by Rubio and co-workers to predict impurity pairing in a solid material.

Acknowledgments

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