Luminescence and High-Resolution Transmission Electron Microscopy Study of Cr^{3+}-Doped $LaPO_4$ and $LaMgB_5O_{10}$

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The luminescence properties of the compounds $LaPO_4$:Cr and $LaMgB_5O_{10}$:Cr at 4.2 K are reported. Furthermore, the morphology of these compounds has been studied with a high-resolution transmission electron microscope (HRTEM). The Cr^{3+} ion shows a Stokes-shifted broad-band emission in the near-infrared region which is attributed to the $^4T_2 \rightarrow {}^4A_2$ transition. In the excited state of Cr^{3+} a large relaxation takes place. The luminescence characteristics are typical for Cr^{3+} in a glass. It is concluded that the Cr^{3+} ion is not built-in into either $LaPO_4$ or $LaMgB_5O_{10}$ but is present in an amorphous surface layer. The amorphous second phase is observed in HRTEM images.

Introduction

We are involved in a project studying the influence of impurities on the luminescence quantum efficiency of lamp phosphors. The influence of Cr^{3+} on the luminescence efficiency of (La,Ce,Tb)PO_4 and (Ce,Gd,Tb)MgB_5O_{10} has been investigated.[1,2] It was determined that none of the doped transition-metal ions has any influence on the luminescence efficiency of (La,Ce,Tb)PO_4.[1] The influence of Cr^{3+} on the luminescence efficiency of (Ce,Gd,Tb)-MgB_5O_{10} is very limited.[2] In the present paper we will discuss the luminescence properties of $LaPO_4$ and $LaMgB_5O_{10}$ doped with Cr^{3+}. These investigations are aimed at a better understanding of the effect of Cr^{3+} on the luminescence efficiency of (La,Ce,Tb)PO_4 and (Ce,Gd,Tb)MgB_5O_{10}.

Furthermore, materials in which Cr^{3+} has a broad-band emission are of interest since these materials are suitable candidates for tunable solid-state laser materials[3] and solar concentrators.[4,5]

In the $^4A_2$ ground state the Cr^{3+} ($3d^3$) ion has a strong preference for octahedral coordination.[6] However, the $LaPO_4$ lattice does not offer a cation site with octahedral coordination. The La^{3+} ion in $LaPO_4$ is coordinated by nine oxygen ions: eight at a distance between 2.4 and 2.7 Å and a ninth at about 3 Å.[7-9] It is unlikely that the Cr^{3+} replaces P^{5+} due to the large difference in ionic radii[10] and the necessity of charge compensation. The Mg^{2+} ion in $LaMgB_5O_{10}$ has a distorted octahedral coordination with four oxygens at 2.07 Å and two oxygens at 2.31 Å.[11] However, charge compensation is necessary if Mg^{2+} is replaced by Cr^{3+}.

Experimental Section

The measurements were performed on powder samples with the compositions $LaPO_4$:Cr and $LaMgB_5O_{10}$:Cr. The samples were doped with either 0.1 or 1 mol % chromium. The starting materials are La_2O_3 (Rhône-Poulenc 99.99%), MgO (Philips Lighting), $(NH_4)_2HPO_4$ (Merck p.a.), H_3BO_3 (Merck p.a.), and $(NH_4)_2Cr_2O_7$ (Fluka p.a.). The $LaPO_4$:Cr samples were prepared in a similar way as described in ref 1, but they were fired in air and no flux was used. If not otherwise stated in the text, the $LaPO_4$ samples were prepared with an excess amount of $(NH_4)_2$-HPO_4 (15 mol %).

The $LaMgB_5O_{10}$:Cr samples were prepared in a similar way as described in ref 2, but all samples were fired in air. An excess amount (25 mol %) of H_3BO_3 was used. It was not possible to obtain single-phase $LaMgB_5O_{10}$ by using a stoichiometric amount of H_3BO_3.

All samples were checked by X-ray powder diffraction using Cu Kα radiation. All samples proved to be single phase. No indication of an amorphous phase was observed. All samples are white.

Diffuse reflection spectra were recorded on a Perkin-Elmer Lambda 7 UV-vis spectrophotometer using $BaSO_4$ as a reference. Emission and excitation spectra were recorded on a Spex Fluorolog spectrophotometer equipped with an Oxford flow cryostat and with a xenon lamp as an excitation source. A Melles Griot 13DAS011 silicon photodiode was used to detect the emitted light. A lock-in amplifier at 313 Hz was used to improve the signal-to-noise ratio. The excitation spectra are corrected for the lamp output. The emission spectra are corrected for the sensitivity of the silicon photodiode.

The samples investigated by high-resolution electron microscopy (HRTEM) were prepared by dipping a holey carbon-coated grid into an ultrasonically dispersed hexane suspension of the ground sample. The HRTEM images were obtained with a JEOL 2000-EX instrument equipped with a top entry specimen holder

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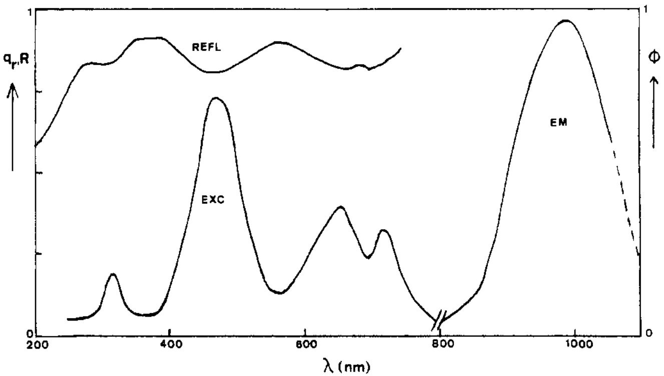

Figure 1. Diffuse reflection spectrum (REFL) at room temperature of $LaPO_4$:Cr (prepared with an excess of $(NH_4)_2HPO_4$). Emission (EM) and excitation (EXC) spectra of the Cr^{3+} luminescence at 4.2 K. Φ gives the radiant power per constant wavelength interval in arbitrary units; q_r gives the relative quantum output.

and an ion pump. The structural resolution of this microscope is 0.21 nm.

Results

$LaPO_4$:Cr. The diffuse reflection spectrum of $LaPO_4$:Cr (1%, prepared with an excess of $(NH_4)_2HPO_4$) shows absorption bands at 670, 460, and 300 nm and an intense band at wavelengths shorter than 280 nm (Figure 1). Upon excitation at 460 nm at 4.2 K the $LaPO_4$:Cr sample shows an emission in the near-infrared region. The excitation spectrum of the infrared emission at 4.2 K is shown in Figure 1. Excitation spectra recorded at different emission wavelengths are identical. The excitation spectrum is in accordance with the reflection spectrum. The luminescence properties of a sample doped with 0.1% Cr are similar.

Since Cr^{3+} is a $3d^3$ ion, the following assignment is made: the band at 670 nm is ascribed to the $^4A_2 \rightarrow {}^4T_2$ (^4F), the band at 460 nm to the $^4A_2 \rightarrow {}^4T_1$ (^4F), and the band at 300 nm to the $^4A_2 \rightarrow {}^4T_1$ (^4P) transition.[12] The absorption band in the reflection spectrum at wavelengths shorter than 280 nm is not present in the excitation spectrum. This absorption band is ascribed to a charge-transfer transition of Cr^{3+} and its oxide ligands. The excitation band at 670 nm has a dip around 685 nm. This dip is also present in the reflection spectrum. The spectral position of this dip coincides with the spectral position of the spin-forbidden excitation transition to the ^2E and $^2T_1$ levels. Therefore it is ascribed to Fano antiresonance between the $^4T_2$ and the ^2E and $^2T_1$ levels.[13] The low spectral resolution prevents a more detailed analysis.

The emission spectrum at 4.2 K consists of a broad structureless band with a maximum at about 1000 nm (Figure 1). This emission is ascribed to the $^4T_2 \rightarrow {}^4A_2$ transition. The full width at half-height is 1850 cm^{-1}. The luminescence is quenched by raising the temperature (Figure 2). At 100 K the emission intensity has dropped to 50% of its value at 4.2 K.

Upon excitation at 460 nm, samples of the compositions $GdPO_4$:Cr and $La_{0.95}Eu_{0.05}PO_4$:Cr show an emission in the infrared upon excitation at 460 nm similar to that of the $LaPO_4$:Cr sample (4.2 K). In the excitation spectrum of the infrared emission the excitation lines of Gd^{3+} or Eu^{3+} were not observed.

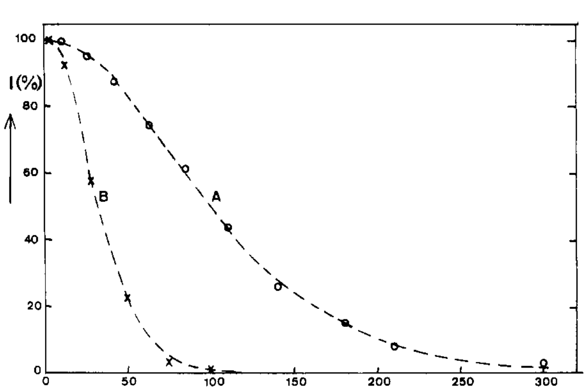

Figure 2. Integrated emission intensity of Cr^{3+} as a function of temperature. (A) $LaPO_4$:Cr (λ_{exc} = 460 nm); (B) $LaMgB_5O_{10}$:Cr (λ_{exc} = 430 nm).

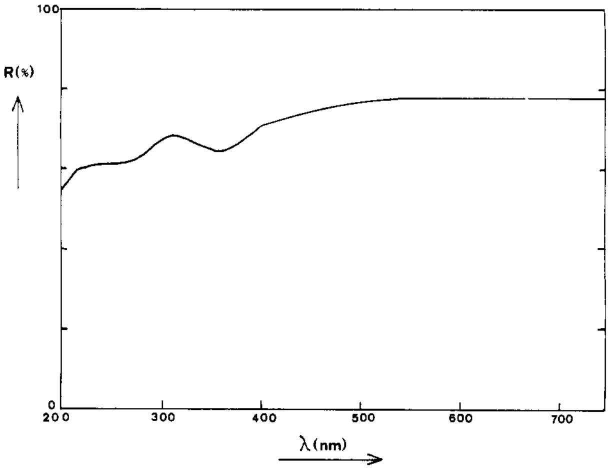

Figure 3. Diffuse reflection spectrum of $LaPO_4$:Cr (0.1%) prepared with a stoichiometric amount of $(NH_4)_2HPO_4$ at room temperature.

The reflection spectrum of $LaPO_4$:Cr (0.1%) prepared without an excess of $(NH_4)_2HPO_4$ is shown in Figure 3. The absorption bands present in this reflection spectrum cannot be ascribed to Cr^{3+}. However the reflection spectrum is similar to that of $CaCrO_4$ and K_2CrO_4.[14] Following the assignment of the chromate absorption bands, the shoulder at 450 nm is ascribed to the $^1A_1 \rightarrow {}^1T_1$ ($t_1 \rightarrow 2e$) transition, the band at 380 nm to the $^1A_1 \rightarrow {}^1T_2$ ($t_1 \rightarrow 2e$) transition, and the band at 260 nm to the $^1A_1 \rightarrow {}^1T_1$ ($4t_2 \rightarrow 2e$) transition. No luminescence is observed upon excitation into these absorption bands at 4.2 K.

Samples of compositions $LaPO_4$ and $LaPO_4$:Cr (1%) prepared with an excess of $(NH_4)_2HPO_4$ have been studied with high-resolution transmission electron microscopy. A HRTEM image representative of $LaPO_4$:Cr (1%) is presented in Figure 4A. Two different regions can be distinguished in it. On one hand, there are two well-ordered areas, the crystallographic analysis of which shows that they consist of monoclinic $LaPO_4$, space group $P2_1/n$. The zone axis was found to be [021]. Accordingly, the fringes at 0.25 nm correspond to the lattice planes (21−2), and those at 0.33 nm to the planes (200). Only the latter type of fringes are observed in the ordered region on the

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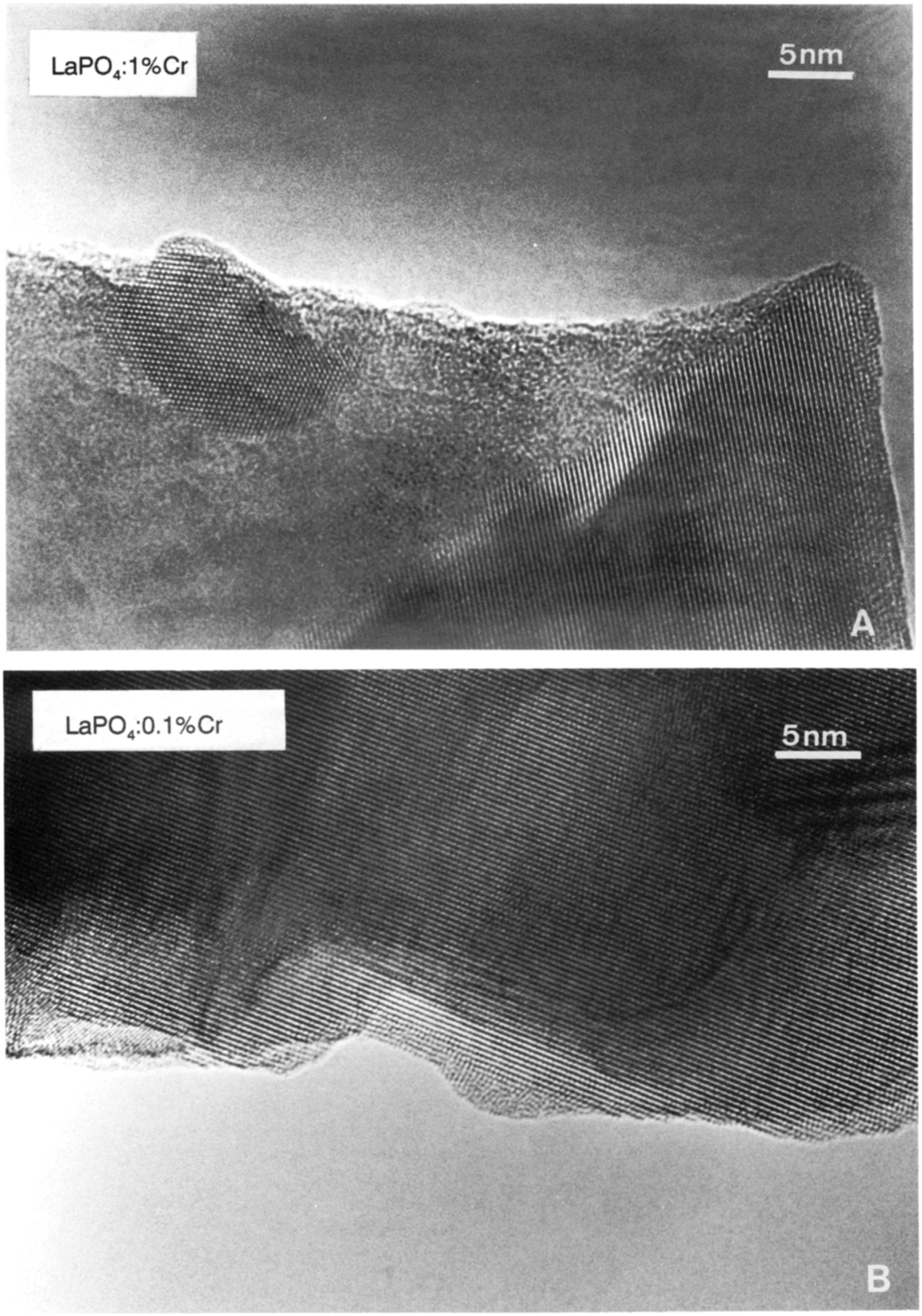

Figure 4. (A) High-resolution transmission electron microscopy image of $LaPO_4$:Cr (1%) prepared with an excess of $(NH_4)_2HPO_4$. (B) High-resolution transmission electron microscopy image of $LaPO_4$:Cr (0.1%) prepared with the stoichiometric amount of $(NH_4)_2HPO_4$.

right-hand side of Figure 4A. On the other hand, a relatively large region containing no long-range order can be observed in Figure 4A. This shows that crystalline and amorphous phases coexist in this sample. The HRTEM images of an undoped $LaPO_4$ sample are similar to those of $LaPO_4$:Cr (1%), although in the former the amount of amorphous phase appears to be smaller than in the latter.

Samples of compositions $LaPO_4$ and $LaPO_4$:Cr (0.1%) prepared without an excess of $(NH_4)_2HPO_4$ have also been studied with HRTEM. Both samples prepared without

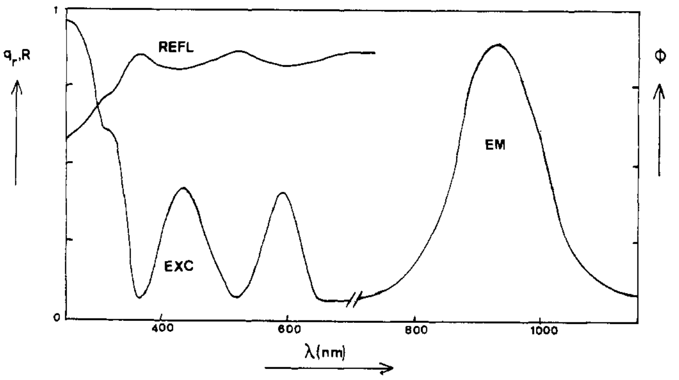

Figure 5. Diffuse reflection spectrum of $LaMgB_5O_{10}$:Cr at room temperature (REFL). Emission (EM) and excitation (EXC) spectra of the Cr^{3+} luminescence at 4.2 K.

excess of $(NH_4)_2HPO_4$ do not show the large amorphous regions observed for the samples prepared with an excess amount of $(NH_4)_2HPO_4$. However, the surface of the samples prepared without an excess of $(NH_4)_2HPO_4$ is not well defined. The particles appear to be covered with a thin amorphous layer (Figure 4B).

$LaMgB_5O_{10}$:Cr. The diffuse reflection spectrum of $LaMgB_5O_{10}$:Cr^{3+} shows two absorption bands with maxima at 600 and 430 nm (Figure 5). Furthermore, an intense broad absorption band which starts at 370 nm and continues to shorter wavelengths is observed. Upon excitation at 430 nm at 4.2 K, the $LaMgB_5O_{10}$:Cr^{3+} sample luminesces in the near-infrared region. The excitation spectrum of the infrared emission is shown in Figure 5. The excitation spectrum is in accordance with the reflection spectrum. The excitation spectra recorded at different emission wavelengths are identical. The following assignment is made: The band at 590 nm is ascribed to the $^4A_2 \rightarrow {}^4T_2$ (^4F), the band at 430 nm to the $^4A_2 \rightarrow {}^4T_1$ (^4F), and the shoulder at 325 nm to the $^4A_2 \rightarrow {}^4T_2$ (^4P) transition. The broad band at 260 nm is ascribed to a charge-transfer transition of Cr^{3+} and its oxide ligands.

The emission spectrum shows a structureless broad band. The emission is ascribed to the $^4T_2 \rightarrow {}^4A_2$ transition. The maximum of the emission band is situated at about 935 nm. The full width at half-height is 2000 cm^{-1}. Emission spectra recorded at different excitation wavelengths are identical. The luminescence is strongly quenched by raising the temperature (Figure 2). At 35 K the emission intensity has dropped to 50% of its value at 4.2 K. Above 100 K no luminescence could be observed. We have also studied the luminescence properties of $LaMgB_5O_{10}$:Cr samples co-doped with Sr^{2+} or Li^+. The luminescence properties of these samples are similar to the luminescence properties of $LaMgB_5O_{10}$:Cr. The luminescence properties of $LaMgB_5O_{10}$:Cr do not correspond with the optical data of the spinel $MgCr_2O_4$.[15]

Samples with compositions $LaMgB_5O_{10}$:Cr, $La_{1-x}Ce_xMgB_5O_{10}$:Cr, and $La_{1-x}Gd_xMgB_5O_{10}$ have been studied with high-resolution transmission electron microscopy. Representative examples of HRTEM images of $LaMgB_5O_{10}$:Cr^{3+} and $La_{0.4}Gd_{0.6}MgB_5O_{10}$ are presented in parts A and B in Figure 6, respectively. The crystal planes are clearly visible in the bulk of the particles of both samples (see bottom of parts A and B in Figure 6). This shows that the bulk of the particles is crystalline. However, on the surface of the particles there appears to be an amorphous layer. This can be observed clearly in the upper part of parts A and B of Figure 6. The thickness of the amorphous layer on the surface of the $La_{0.4}Gd_{0.6}MgB_5O_{10}$ particles is estimated to be 5 nm. The amorphous layer on the surface of the $LaMgB_5O_{10}$:Cr particle is less well defined. The thickness is between 5 and 15 nm.

Discussion

The luminescence characteristics of $LaPO_4$:Cr (prepared with an excess of $(NH_4)_2HPO_4$) and $LaMgB_5O_{10}$:Cr are similar. The absorption and excitation spectra of the infrared emission of $LaPO_4$:Cr and $LaMgB_5O_{10}$:Cr are in accordance with the Tanabe–Sugano diagram of an octahedral $3d^3$ ion.[12] The octahedral crystal field strength sensed by Cr^{3+} can be derived from the position of the maximum of the $^4A_2 \rightarrow {}^4T_2$ transition.[12] The D*q* value for $LaPO_4$:Cr is found to be 1490 cm^{-1}. This is a relatively small value.[4,12,16] The D*q* value for $LaMgB_5O_{10}$:Cr is found to be 1670 cm^{-1}.

A comparison of the excitation spectra of $LaPO_4$:Cr and $LaMgB_5O_{10}$:Cr (Figures 1 and 5, respectively) shows that the emission of the latter can be excited in the charge-transfer transition, but that of the former cannot. For d–d excitation, the former shows a more efficient emission with higher quenching temperatures. This can be explained from earlier results[17] that show that the luminescence of ions with effective charges behave oppositely for intraatomic and charge-transfer transitions.

The broad-band emission of $LaPO_4$:Cr and $LaMgB_5O_{10}$:Cr is ascribed to the $^4T_2 \rightarrow {}^4A_2$ transition of Cr^{3+}. This broad–band emission is characteristic of Cr^{3+} in a low crystal field environment.[12] The Stokes shift of the Cr^{3+} emission in $LaPO_4$:Cr is found to be 4900 cm^{-1}. The Stokes shift of the Cr^{3+} emission in $LaMgB_5O_{10}$:Cr is found to be 6000 cm^{-1}. Comparably large Stokes shifts are reported only for Cr^{3+}-doped glasses.[6] Stokes shifts reported for the Cr^{3+} emission in oxide crystals are between 2400 and 3500 cm^{-1}.[6] A large Stokes shift indicates a large relaxation in the excited state.[18]

The large relaxation in the excited state of Cr^{3+} is also clear from the temperature dependence of the Cr^{3+} luminescence in both lattices. The Cr^{3+} luminesence in $LaMgB_5O_{10}$:Cr is quenched at lower temperatures than the Cr^{3+} luminescence in $LaPO_4$:Cr. This is in accordance with the larger Stokes shift of the Cr^{3+} emission in $LaMgB_5O_{10}$:Cr compared to the Stokes shift of the Cr^{3+} emission in $LaPO_4$:Cr.

The large values of the Stokes shift and the low quenching temperature of the Cr^{3+} emission in $LaPO_4$:Cr and in $LaMgB_5O_{10}$:Cr indicate that the surroundings of the Cr^{3+} ion must have an open structure.[18]

The large relaxation in the excited state is a result of the fact that the ground state of Cr^{3+} requires octahedral coordination, whereas in the $^4T_2$ state the necessity for octahedral coordination is absent.[6,19] In crystals the coordination cannot be changed upon excitation to the $^4T_2$ state, since the coordination is fixed by the crystal

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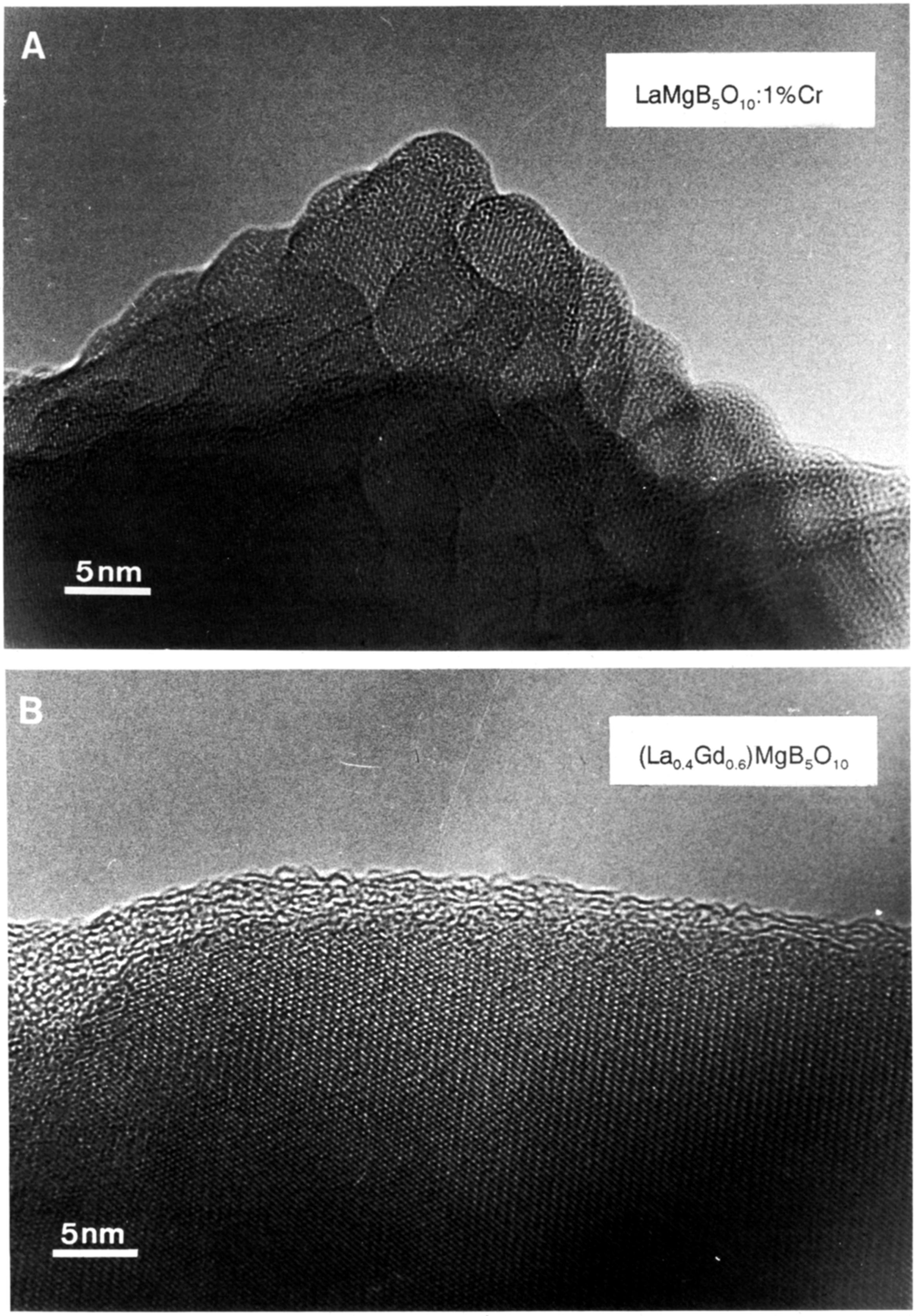

Figure 6. (A) High-resolution transmission electron microscopy image of $LaMgB_5O_{10}$:Cr (1%). (B) High-resolution transmission electron microscopy image of $La_{0.4}Gd_{0.6}MgB_5O_{10}$.

structure. In a glass, however, the surroundings are "soft" due to the loosely coordinated structure of glass. In the ground state Cr^{3+} creates its own octahedral coordination. Upon excitation to the $^4T_2$ state the preference for octahedral coordination vanishes, and the surroundings can adjust to the most favorable coordination.

No energy transfer from Gd^{3+} or from Eu^{3+} to Cr^{3+} in $GdPO_4$:Cr and $La_{0.95}Eu_{0.05}PO_4$:Cr is observed, although there is spectral overlap between the emission of Gd^{3+} and Eu^{3+} and the excitation bands of Cr^{3+}. Therefore it is concluded that Cr^{3+} is present in a second phase and is not built into the crystalline $LaPO_4$ structure. Similar results have been obtained for $La_{1-x}Ce_xMgB_5O_{10}$, $La_{1-x}Gd_xMgB_5O_{10}$, and $La_{1-x}Tb_xMgB_5O_{10}$ doped with Cr^{3+}.[2]

Summarizing, we conclude on the basis of the luminescence results that Cr^{3+} in $LaPO_4$:Cr (sample prepared with an excess of $(NH_4)_2HPO_4$) and in $LaMgB_5O_{10}$:Cr is not built into the host lattice but is present as a second phase with a glassy character. An amorphous second phase is indeed observed in the HRTEM images for both $LaPO_4$:Cr and $LaMgB_5O_{10}$:Cr. This amorphous layer is also present in undoped samples. The reflection spectra of $LaPO_4$:Cr and $LaMgB_5O_{10}$:Cr samples washed with a diluted HCl solution (1:5) are similar to those of samples which are not washed. Hence it is concluded that the amorphous surface layer does not dissolve.

The requirement of an octahedral coordination for the ground state of Cr^{3+} is apparently strict. Since the crystal lattice of $LaPO_4$ does not offer such a cation site, the Cr^{3+} ion creates its own octahedral site in the amorphous surface layer and is not built into the $LaPO_4$ lattice.

Although the Mg^{2+} site in $LaMgB_5O_{10}$ offers a distorted octahedral coordination, it apparently does not fulfill the requirements of the Cr^{3+} ion. This is probably caused by the necessity of charge compensation upon replacing Mg^{2+} by Cr^{3+}. Hence $LaMgB_5O_{10}$:Cr was co-doped with either Sr^{2+} or Li^+ as charge compensators to stimulate the replacement of Mg^{2+} by Cr^{3+}. On basis of the ionic radii of Sr^{2+} and Li^+,[10] it is expected that Sr^{2+} replaces La^{3+} and Li^+ replaces Mg^{2+}, respectively. However, co-doping with Sr^{2+} or Li^+ did not influence the Cr^{3+} luminescence. Hence, co-doping with Sr^{2+} and Li^+ did not promote the incorporation of Cr^{3+} into $LaMgB_5O_{10}$ under our experimental conditions. It is unlikely that Cr^{3+} replaces B^{3+} due to the large difference in ionic radii.[10]

It was not possible to show the presence of Cr^{3+} directly in the amorphous surface layer or to obtain a chemical analysis of the surface layer on the $LaPO_4$ and $LaMgB_5O_{10}$ particles by microanalysis due to the limited structural resolution of the equipment used (about 50 nm).

The amount of amorphous material present in $LaPO_4$ samples prepared with a stoichiometric amount of $(NH_4)_2HPO_4$ is smaller than in the sample prepared with an excess of $(NH_4)_2HPO_4$. Samples prepared without an excess of $(NH_4)_2HPO_4$ show only a very thin amorphous surface layer in the HRTEM images. To see if in the absence of amorphous phases the doped Cr^{3+} would be forced to replace La^{3+}, we doped a $LaPO_4$ sample prepared without an excess of $(NH_4)_2HPO_4$ with Cr. However, in this case the co-doped Cr is present as Cr^{6+} and not as Cr^{3+}. The amount of amorphous layer is apparently not enough to provide a stable octahedral coordination for Cr^{3+}. In view of the large charge and size difference, it is unlikely that Cr^{6+} replaces La^{3+} in the $LaPO_4$ lattice. The CrO_4^{2-} complex is probably present on the surface of the $LaPO_4$ particles. McDaniel and Martin have reported stable chromate complexes on silica surfaces.[20] Another possibility is that CrO_4^{2-} replaces a PO_4^{3-} group. In this case charge compensation is necessary.

Payne et al.[21] have reported the luminescence properties of Cr^{3+}-doped fluoride crystals with the fluorite structure (e.g., CaF_2, SrF_2). The fluorite lattice does not offer a proper octahedron. However, it is suggested by the authors that the F^- anions relax about the Cr^{3+} ion to form an octahedral site and thus creating the possibility for the incorporation of Cr^{3+}. Apparently the rigidity of oxygen anion structure of the phosphate and borate groups prevents such a relaxation in $LaPO_4$ and $LaMgB_5O_{10}$.

The results on $LaPO_4$ doped with Cr^{3+} are different from the results on $LaPO_4$ doped with Fe^{3+}. Our results on the Fe^{3+} luminescence in $LaPO_4$ are reported in ref 22. From the luminescence results it is clear that Fe^{3+} is built into the crystal lattice of $LaPO_4$. The ground state of Fe^{3+} does not require octahedral coordination so that Fe^{3+} can replace a La^{3+} ion. $LaMgB_5O_{10}$ doped with Fe did not show any luminescence in the visible or near-infrared regions at 4.2 K upon UV excitation.[2]

More generally, one should be aware that crystalline powders of borates and phosphates may easily obtain amorphous phases. This is generally missed by X-ray diffraction. Their presence may have negative consequences for the physical properties of the material.

Conclusions

We have shown that an amorphous layer is present on the surface of $LaPO_4$ and $LaMgB_5O_{10}$ samples. Doped Cr^{3+} is present in this amorphous layer and is not built into the crystal lattices of $LaPO_4$ and $LaMgB_5O_{10}$. This is caused by the strict requirement of Cr^{3+} for an octahedral coordination. Both crystal lattices do not fulfill this requirement. Therefore, the Cr^{3+} ion creates its own octahedral coordination in the amorphous surface layer. The presence of such amorphous phases may influence certain materials properties in a negative way.

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