

A SEARCH FOR LUMINESCENCE OF THE TRIVALENT MANGANESE ION
IN SOLID ALUMINATES

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ABSTRACT As an alternative way of examining the prospects of the trivalent manganese ion as a luminescent centre in glasses, $\text{Al}_2\text{O}_3:\text{Mn}$, $\text{ZnAl}_2\text{O}_4:\text{Mn}$ and $\text{LaAlO}_3:\text{Mn}$ were investigated by means of spectrofluorometry. The luminescent species identified were divalent and tetravalent manganese and impurities (chromium), whereas trivalent manganese did not show luminescence at wavelengths < 800 nm in $\text{LaAlO}_3:\text{Mn}$ and $\text{ZnAl}_2\text{O}_4:\text{Mn}$ and < 1000 nm in $\text{Al}_2\text{O}_3:\text{Mn}$ for T down to liquid helium temperature. It is argued that both a strong crystal field and a large Jahn-Teller splitting quench the luminescence of trivalent manganese and these results lower the benefits for using this ion in glasses.

MATERIALS INDEX: aluminates, sodium, manganese, zinc, lanthanum

Introduction

Recently the luminescence of manganese ions in oxide glasses was reported (1). The spectral characteristics of Mn^{3+} -doped glasses are favorable for luminescent solar concentrators: a strong, broad absorption band in the visible spectrum (400 - 550 nm) (2), and an emission band around 750 nm, ascribed to the ${}^3\text{T}_1 \rightarrow {}^5\text{E}$ transition in, for example, a potassium borate glass (1).

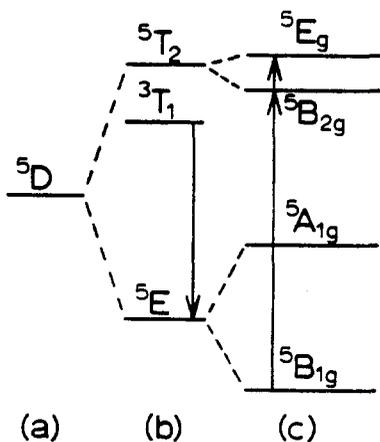
The quantum efficiency of the Mn^{3+} luminescence in such glasses is low. Hence further experiments are necessary for a general statement concerning the suitability of Mn^{3+} -doped glasses as solar concentrators. Instead of scanning different glass compositions, we choose to incorporate manganese in crystalline hosts. Luminescence properties can thus be monitored at distinct values of host parameters. Moreover, quantum efficiencies are usually higher in crystalline solids than in glasses.

The compound Al_2O_3 is an excellent host lattice for efficient luminescence, not only for Cr^{3+} (ruby) but for other ions as well (3). The rigid lattice provides a strong crystal field for dopant ions in octahedral coordination with trigonal distortion. The Al-O distance amounts to 1.86 Å. The

Mn_2O_3 structure is of a different kind (4), so that the solubility of Mn_2O_3 in the Al_2O_3 lattice will be restricted. The structure adopted by $ZnAl_2O_4$ is the cubic spinel structure, with an Al-O distance of about 2.01 Å. The Mn^{3+} ions are expected to be easily incorporated into the octahedral Al sites, since $ZnMn_2O_4$ is isostructural with $ZnAl_2O_4$, apart from a tetragonal distortion due to the Jahn-Teller effect on the Mn^{3+} ions (5). The compound $LaAlO_3$ has a slightly distorted perovskite structure (4,5). The Al^{3+} ions occupy octahedral sites with Al-O distance ≈ 1.89 Å. $LaMnO_3$ has also a perovskite structure, but with a stronger distortion which is again due to the Jahn-Teller effect. However, it seems reasonable to assume that part of the Al^{3+} ions in $LaAlO_3$ can be replaced by Mn^{3+} ions.

Concerning the optical transitions of d^4 ions, such as Cr^{2+} and Mn^{3+} , Jahn-Teller effects modify the energy level scheme from the Tanabe-Sugano description. These effects are schematically represented in fig 1. For Mn^{3+} the splitting of the ground state 5E level may run into 10.000 cm^{-1} , and of the excited 3T_2 state several thousands. This holds for coordination by six halogen or oxygen ligands, as reviewed by Lever (6).

FIG. 1
Jahn-Teller splitting of the 5E ground state and 5T_2 excited state of Mn^{3+} : a: free ion, b: octahedral crystal field and c: Jahn-Teller interaction. The arrows indicate the absorption and emission transitions observed.



From our experiments, it turns out that the Jahn-Teller effect is mainly responsible for the absence of Mn^{3+} luminescence. The observed emissions are ascribed to manganese ions in different valencies.

Preparation and spectroscopic equipment

$LaAlO_3:Mn$ and $ZnAl_2O_4:Mn$ were prepared using the oxides Al_2O_3 (Ventron), La_2O_3 (Highways Int., 99.999%), ZnO (Merck, p.a.) and MnO_2 (Baker). Dopant levels were of the order of half an atomic percent. The appropriate ratio of the powders was ball-milled and fired twice in a N_2 atmosphere; the first time at $1250^\circ C$ and the second time at $1425^\circ C$ for $LaAlO_3:Mn$ and for $ZnAl_2O_4:Mn$ both times at $1250^\circ C$.

Mn -doped Al_2O_3 was prepared by solving $MnCl_2$ and $Al(NO_3)_3 \cdot 9H_2O$ in nitric

acid. Subsequently the solution was evaporated. The remaining solid was fired twice at 1250 °C, followed by a final heat treatment at 1000 °C in a H₂/N₂ mixture (25 % H₂).

X-ray powder diffraction was used for intermediate and final checks.

Diffuse reflection spectra were measured using a Perkin-Elmer Lambda 7 UV/VIS Spectrophotometer, with BaSO₄ in the reference beam. Excitation and emission spectra were recorded on a Perkin-Elmer MPF-3L Fluorescence Spectrophotometer, equipped with an Oxford CF100 He-flow cryostat. In order to investigate the 800 - 1000 nm region an IR extended version (MPF 44) was used. All recordings were corrected for the spectral dependence of the Xe light source, the monochromators and the photomultipliers.

Luminescence lifetimes were measured using excitation either by a Moletron Pulsed N₂ Laser UV14 (337 nm) or by a Moletron pumped dye laser (DL100; 575 nm). The emission, detected through a monochromator (Spex) by an EMI 9659 QA photomultiplier was discriminated, amplified and stored in an EG&G 7100 Multichannel Analyser.

Results

The visible absorption spectrum of Mn³⁺ in glasses consists of a broad band around 470 nm, assigned to the ⁵E + ⁵T₂ transition (1,2). In order to establish the presence of Mn³⁺ in the powder samples, reflection spectra were recorded at room temperature. An absorbance representation is displayed in fig. 2.

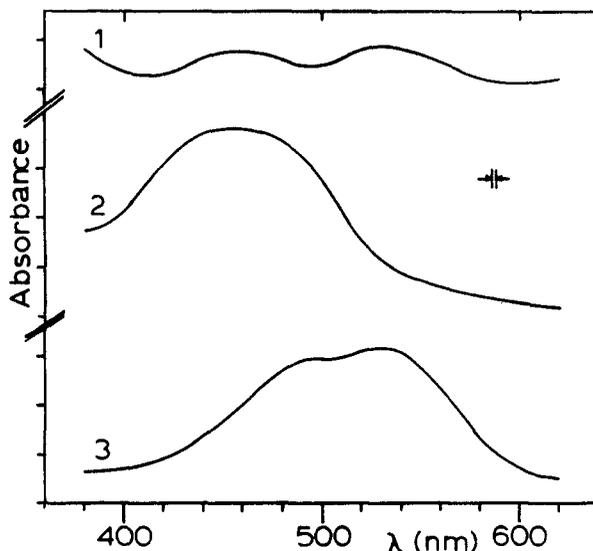


FIG. 2

Diffuse reflection spectra of the samples under study. 1: LaAlO₃:Mn, 2: ZnAl₂O₄:Mn and 3: Al₂O₃:Mn. Vertically $-\log I/I_0$ is plotted, where I_0 is the reference beam intensity.

A band around 460 nm is clearly observable for ZnAl₂O₄:Mn. In the spectrum for LaAlO₃:Mn a similar band is visible, accompanied by a band of comparable intensity around 530 nm. The spectrum, which is observed for Al₂O₃:Mn contains two bands, with maxima around 490 nm and at 540 nm. The assignment of these bands will be given in the discussion.

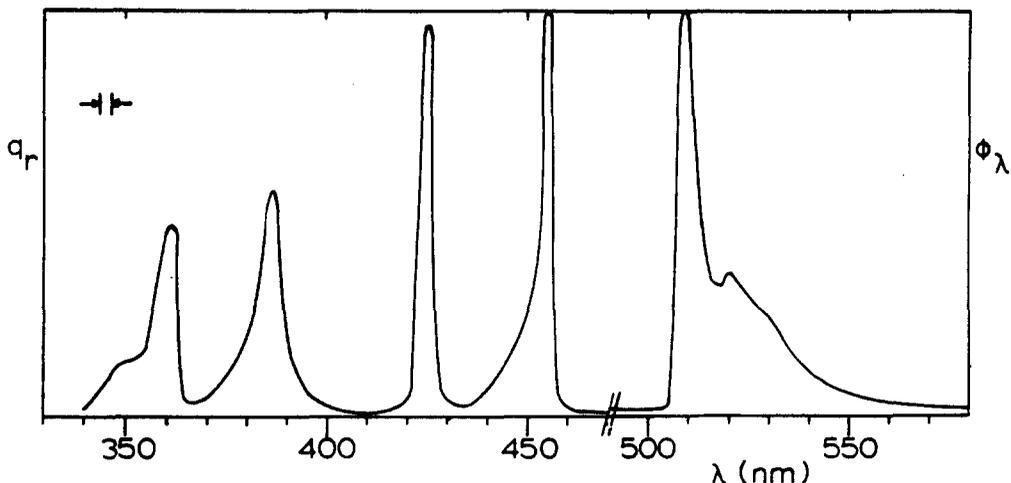


FIG. 3

Emission (exc. 456 nm) and excitation (em. 509 nm) spectra of the luminescence of $\text{ZnAl}_2\text{O}_4:\text{Mn}^{2+}$ at 4.2 K. The symbol q_r denotes the relative quantum output and ϕ_λ denotes the photon flux density.

All emission and excitation spectra have been recorded at liquid helium temperature (4.2 K). In each sample several luminescent species have been found. As in the case of glasses, most of the emissions and their corresponding excitation spectra are attributable to different oxidation states of manganese (1).

Mn^{2+} luminescence is found for each of the host lattices. Fig. 3 shows the luminescence spectra for ZnAl_2O_4 . The relatively sharp excitation bands are located at 361, 386, 425 and 455 nm. The emission peaks at 509 nm with vibronic sidebands at 520 and 530 nm. Undoubtedly this corresponds to Mn^{2+} luminescence as has been found earlier by Palumbo *et al.* (7). Mn^{2+} is situated at tetrahedrally coordinated Zn sites with a low crystal field strength, leading to emission with relatively short wavelength. Mikenda (8) has considered IR, Raman and vibronic spectra of Cr^{3+} doped spinels, with $\text{ZnAl}_2\text{O}_4:\text{Cr}$ among them. Most of the vibronic frequencies are too low to be observed in our case. The Raman spectrum contains a peak at 421 cm^{-1} . The agreement with our phonon side band at 520 nm ($\Delta\nu = 420\text{ cm}^{-1}$) is good.

In LaAlO_3 a similar luminescence is observed. The excitation spectrum is practically the same as for $\text{ZnAl}_2\text{O}_4:\text{Mn}$. The emission band is slightly red shifted (518 nm) and broader so that the vibronic structure has vanished. This emission must therefore also be due to Mn^{2+} . However, octahedrally coordinated Mn^{2+} emits in the red, so that we have to assume that this luminescence is due to Mn^{2+} ions on La^{3+} sites. The low value of the crystal field on the Mn^{2+} ion is partly due to the 12-fold coordination of the La^{3+} ions in perovskite and partly due to the effectively negative charge of the Mn^{2+} ion. Also $\text{GdF}_3:\text{Mn}^{2+}$ shows a green emission (9).

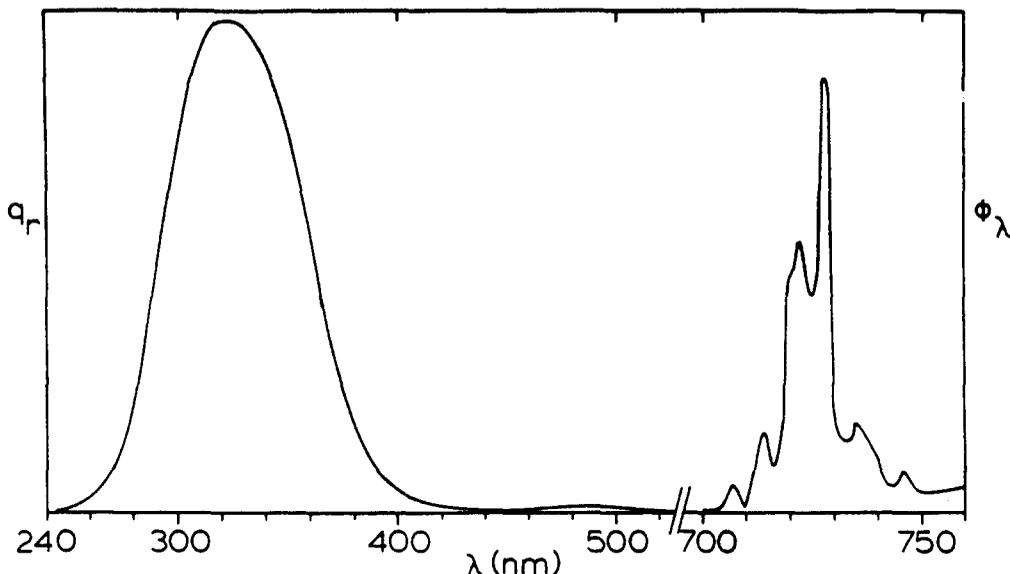


FIG. 4

Emission (exc. 340 nm) and excitation (em. 728 nm) spectra of the luminescence of $\text{LaAlO}_3:\text{Mn}^{4+}$ at 4.2 K. The symbols are explained in caption 3.

Due to a considerably stronger crystal field, the Mn^{2+} emission in Al_2O_3 is located at 600 nm. Here the excitation spectrum is dominated by a band at 282 nm, although the above mentioned structure is observed as well. The strong band is ascribed to a charge-transfer transition.

Mn^{4+} luminescence is found in Al_2O_3 , LaAlO_3 and probably ZnAl_2O_4 . The emission spectrum of LaAlO_3 (fig. 4) is in excellent agreement with earlier reports (10). The excitation spectrum contains two bands: a stronger one centered at about 330 nm and a weaker one around 490 nm. In view of the intensity differences the former is a charge-transfer band (ligand to metal), whereas the latter corresponds to a crystal-field transition (*viz.* ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$).

The emission spectrum of Mn^{4+} in Al_2O_3 (fig. 5) consists of a sharp line at 676 nm with weak vibronic structure. Excitation bands are centered around 320 nm and 470 nm. Due to the presence of Cr^{3+} , the Mn^{4+} luminescence in ZnAl_2O_4 could not be positively demonstrated.

Cr^{3+} luminescence is found in Al_2O_3 and ZnAl_2O_4 . Its appearance must be due to the presence of trace amounts (≈ 25 ppm) of chromium in the starting aluminum compounds. A reflection spectrum of undoped Al_2O_3 (made from $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) actually demonstrated two weak bands at 560 nm and 410 nm. The luminescence spectra of Cr^{3+} in ZnAl_2O_4 could be identified referring to the literature (11). In Al_2O_3 the Cr^{3+} ion exhibits a similar emission spectrum as compared to Mn^{4+} : a sharp line at 695 nm. Confusion between the two ions could be eliminated by decay measurements. Both emission lines decay nearly exponentially at 4.2 K, with decaytime 1.02 ms for the 676 nm emission which is in

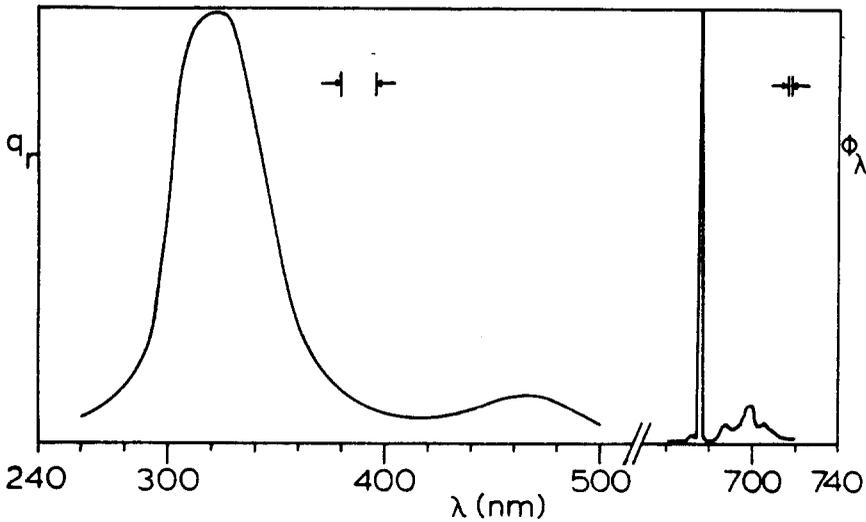


FIG. 5

Emission (exc. 325 nm) and excitation (em. 676 nm) spectra of the luminescence of $\text{Al}_2\text{O}_3:\text{Mn}^{4+}$ at 4.2 K. The symbols are explained in caption 3.

reasonable agreement with data found for Mn^{4+} in $\text{Y}_3\text{Al}_5\text{O}_{12}$ (12), and 4.30 ms for the 695 nm emission, which agrees with the value for ruby (13).

No other luminescences were found in any of the samples. For $\text{Al}_2\text{O}_3:\text{Mn}$ the spectral range up to 1000 nm was investigated, but no emission could be detected. Therefore we conclude, that the samples do not show Mn^{3+} luminescence.

Discussion

It is now possible to assign the reflection spectra. In view of the strongly forbidden character of the crystal-field transitions within the Mn^{2+} ion ($3d^5$), it seems not realistic to assume that this ion accounts for any of the features in the reflection spectra.

In $\text{ZnAl}_2\text{O}_4:\text{Mn}$ the absorption band with a maximum at 460 nm must be due to the Mn^{3+} ion: the spectral position is in agreement with the Mn^{3+} absorption band in glasses and excitation in this band does not yield Mn^{4+} luminescence. So our $\text{ZnAl}_2\text{O}_4:\text{Mn}$ sample contains Mn^{3+} and Mn^{2+} ions.

In $\text{LaAlO}_3:\text{Mn}$ neither of the absorption bands coincide with Mn^{4+} absorption, which peaks at 490 nm. Therefore, both absorption bands are ascribed to the Mn^{3+} ion. This implies that the manganese in LaAlO_3 is present as Mn^{2+} (on La^{3+} sites) and Mn^{3+} and Mn^{4+} (most probably on Al^{3+} sites).

The situation in $\text{Al}_2\text{O}_3:\text{Mn}$ is less clear. Impurities such as Mn^{4+} and Cr^{3+} can account for the bands in the reflection spectrum of Al_2O_3 . The ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ absorptions of Mn^{4+} at 470 nm and of Cr^{3+} (weaker) at 570 nm contribute to

this spectrum; this is plausible, since a superposition shifts the peaks towards each other. However, a comparison between the reflection spectra of $\text{Al}_2\text{O}_3:\text{Mn}$ and undoped Al_2O_3 shows that it cannot be excluded that Mn^{3+} is absorbing in this spectral area as well.

Unfortunately these data do not give clear information on the relative concentration of the different valencies. Yet, in view of the low total concentration of manganese, we assume that quenching due to ion-ion interaction can be neglected. Consequently, the conclusion must be that nonradiative transitions within the Mn^{3+} ion in the present host lattices are definitely the source of deexcitation.

The Mn^{3+} absorption band is ${}^5\text{E} + {}^5\text{T}_2$ in character. In LaAlO_3 a clear splitting ($\approx 3000 \text{ cm}^{-1}$) is observed. Since the site for Mn^{3+} in this lattice is not far from cubic, this effect may well be caused by a Jahn-Teller splitting of the ${}^5\text{T}_2$ level (${}^5\text{B}_{2g}$ and ${}^5\text{E}_g$, see fig. 1). This splitting could not be observed for ZnAl_2O_4 , whereas for Al_2O_3 the situation is obscured by other absorbing ions.

The question remains why the Mn^{3+} ion does not show any luminescence in the compounds under study. It will be clear that a strong Jahn-Teller effect introduces various channels for non-radiative relaxation. The energy difference between the ${}^3\text{T}_1$ level, from which the emission takes place, and the ${}^5\text{A}_{1g}$ level becomes small, as can be seen in fig. 1. This will be even more outspoken in a configurational coordinate diagram. Additionally, a strong crystal field will reduce the ${}^3\text{T}_1 - {}^5\text{E}$ distance, because an increase of the crystal field strength implies that the system approaches the high spin - low spin crossing ${}^5\text{E} - {}^3\text{T}_1$. Qualitatively it is expected that a strong crystal field and/or a strong Jahn-Teller effect will quench the Mn^{3+} luminescence.

In this respect it is interesting to note that in $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) the Mn^{3+} ion does show luminescence at room temperature (12). We have found no other reports on Mn^{3+} luminescence in crystalline solids, so this appears to be an exceptional case. The emission bands can roughly be divided into two groups, one around 700 nm (14.000 cm^{-1}) and the other around 1100 nm (9000 cm^{-1}). A possible explanation might be that this is related to the Jahn-Teller splitting of the ground state, which has then the relatively low value of 5000 cm^{-1} . This value seems to be low enough for luminescence.

Our spectral data do not allow to derive the strength of the crystal field from them. It can be noticed though, that the Cr^{3+} ion shows broad band ${}^4\text{T}_2$ emission in garnets (12) and in the glasses in which Mn^{3+} emits (for such borate glasses see ref. 14), whereas it shows narrow line ${}^2\text{E}$ emission in the three aluminate lattices under study. This means that the crystal field strength in the garnet and the glasses is relatively low, which is a favorable condition for Mn^{3+} luminescence, as we deduced above.

A weak Jahn-Teller splitting is also expected for $\text{ZnAl}_2\text{O}_4:\text{Mn}$, because the reflection spectrum (fig. 1) shows only one band for the ${}^5\text{T}_2$ level. The crystal field strength, on the contrary, must be large in view of the high spectral position of the ${}^5\text{E} + {}^5\text{T}_2$ band. Also $\text{ZnAl}_2\text{O}_4:\text{Cr}$ shows line emission. These results again confirm the qualitative assertion that weak Jahn-Teller effects and weak crystal fields are requirements to observe Mn^{3+} luminescence.

In conclusion we can state, that the Mn^{3+} ion gives rise to luminescence in very special environments only, in crystalline solids as well as in glasses. The physical background for this phenomenon is not understood in

detail at the moment. It is however stated, that both a strong crystal field and a strong Jahn-Teller effect decrease the luminescence efficiency. In the case of glasses, the subset of Mn^{3+} ions shows luminescence with a too low quenching temperature to make applications involving room temperature luminescence feasible.

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