Mn⁴⁺ MULTISITES AND Mn⁴⁺ → Tm³⁺ ENERGY TRANSFERS IN Gd₃Ga₅O₁₂ GARNETA. BRENIER, C. PEDRINI, C. MADEJ, G. BOULON and A. SUCHOCKI⁽¹⁾*Laboratoire de Physico-Chimie des Matériaux Luminescents, URA 442, Université Lyon I,
43 Boulevard du 11 novembre 1918, F-69622 Villeurbanne cedex, France*

Abstract: We report the crystal growth in our laboratory and the luminescence study of Ca²⁺-Mn⁴⁺ and Ca²⁺-Mn⁴⁺/Tm³⁺ doped Gd₃Ga₅O₁₂ garnets. Multisites of Mn⁴⁺ ions are revealed at liquid helium temperature by laser excitation and emission spectra and by decay time analysis.

1. Introduction

Cr³⁺ multisites in Gd₃Ga₅O₁₂ (GGG) single crystals have been studied previously in our laboratory¹. The effect of disorder on Cr³⁺ luminescence has been pointed out². Mn⁴⁺ ion has the same electronic configuration than Cr³⁺ (3d³) and because a charge compensation is needed (with Ca²⁺ or Mg²⁺ ion for example) to incorporate it in the crystal, this effect was expected to be increased: 3 main Mn⁴⁺ sites have been found. The luminescence of Mn⁴⁺ ion looks like the Cr³⁺ one in high crystal field systems such as Y₃Al₅O₁₂:Cr³⁺. In this latter case Cr³⁺ ions have been used as sensitizer for Tm³⁺ luminescence³. In the same way we have found a good overlap between Mn⁴⁺ emission and Tm³⁺ absorption in our crystals so Mn⁴⁺ → Tm³⁺ energy transfers have been observed.

2. Crystal growth

The crystals have been grown by the Czochralski technique under a gas flow of nitrogen (480 l/h) and oxygen (4.8 l/h) in order to decrease gallium oxide decomposition⁴. The pull rate was 0.4 cm/h and the rotation rate varied according to the crystal length from 6 to 15 rpm. The crystal size was 3 cm diameter and 10 cm length. The crystal was pulled along the <111> axis. Manganese was added in the form of MnO₂. Equal quantity of charge compensating Ca²⁺ ions were added to the melt in the form of CaCO₃. The starting composition of the melt

⁽¹⁾Permanent address: Institute of Physics, Polish Academy of Sciences, Warszawa, Poland

was: $\{Gd_{3-x} Ca_x\} [Ga_{4.95-x} Mn_x Gd_{0.5}] (Ga_3)_2 O_{12}$ with $x = 4.95 \cdot 10^{-3}$. The symbols $\{ \} , [\] , ()$ stands respectively for dodecahedral, octahedral and tetrahedral sites. The Mn/Tm-doped crystal was obtained by replacing Gd by $Gd_{1-y} Tm_y$ with $y = 0.02$.

3. Spectra

3-1. Mn^{4+} ion in octahedral site

The room-temperature absorption spectrum of GGG:Mn:Ca has in the visible region a broad band peaking at 510.4 nm and attributed to ${}^4A_2 \rightarrow {}^4T_2$ transition of Mn^{4+} ions in octahedral sites. The ${}^4A_2 \rightarrow {}^4T_1$ transition is hardly seen because it is hidden by a strong charge transfer band⁶ in the uv region but it is clearly seen in the low-temperature excitation spectrum.

By pulsed excitation in the broad band (532 nm) we obtain a liquid helium emission spectrum from 660 to 750 nm. Its main features are 2 peaks at 663.5 and 668 nm and a broad structure peaking at 681 nm. Because they have two different lifetimes, 1.138 ms and 397 μ s respectively, both peaks are assigned to ${}^2E \rightarrow {}^4A_2$ transition of two kinds of Mn^{4+} ions in octahedral sites called "A kind" and "B kind" in the following. The crystal field parameter is $Dq = 1960 \text{ cm}^{-1}$ and the Racah parameter is $B = 722 \text{ cm}^{-1}$ (these are average values for the two kinds of ions).

3-2. Three main kinds of Mn^{4+} ions in octahedral sites

Liquid helium temperature excitation spectra of 663.5 (A kind) and 668 nm (B kind) emissions can be seen figure 1-a. Each of them has two peaks corresponding to a splitting of the 2E level.

By selective excitation in the absorption lines of each kind of Mn^{4+} ion, that is to say at the maximum of the lines of the figure 1-a, we obtain the emission spectra of the two kinds of Mn^{4+} ions: figure 1-b. It can be seen that the broad structure peaking at 681 nm is mainly emitted by A kind ions. It is interpreted as a vibronic sideband of the ${}^2E \rightarrow {}^4A_2$ transition. Its excitation spectrum is the sum of the A and B kind spectra, the more important in the sum being the A kind spectrum.

By recording the excitation spectra at different emission wavelengths we have found that the 671 nm emission had a different excitation spectrum than the A and B kind ions. By selective excitation at the maximum of the line of this new spectrum (670 nm) we have obtained the emission spectrum of a third kind of Mn^{4+} ions called "C kind". Its vibronic sideband is weak like in the B case.

We believe that in the B and C case a Ca^{2+} ion is a first closest

neighbour of the Mn^{4+} ion so it removes the inversion symmetry of the crystal field :the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ electronic transition is now electric-dipole allowed and is stronger (1226 s^{-1}). In the A case the charge compensating Ca^{2+} ion takes place as the second neighbour of the Mn ion or farer so that the axial perturbation is negligible:the electronic transition is only magnetic dipole allowed, is weaker (149 s^{-1}) and its vibronic sideband (an electric dipole transition induced by odd-parity vibrations) appears comparatively stronger (730 s^{-1}).

Figure 1 (a) excitation spectra of 663.5 (A) and 668 nm (B) emissions
(b) emission spectra after 660.5 (A) and 667 nm (B) excitation

4. $\text{Mn}^{4+} \rightarrow \text{Tm}^{3+}$ energy transfers

The Tm^{3+} ion has a strong absorption at 683 nm (${}^3\text{H}_6 \rightarrow {}^3\text{F}_3$ transition) which can be seen directly on the Mn^{4+} emission spectrum of a GGG:Mn:Tm crystal (figure 2) : a radiative transfer occurs between the

two ions. We then expect that a non radiative transfer also occurs, the quantum yield of which will be higher for the Mn^{4+} ion whose emission has the best overlap with the Tm^{3+} absorption, that is to say the A kind ions. The fluorescence decay of A and B kind Mn^{4+} ions has been fitted with Yokota and Tanimoto equation⁷. It has been found that the quantum yield energy transfer is 36 % for B kind ions and 64.5 % for A kind ions at liquid helium temperature.

Figure 2: Tm^{3+} absorption and Mn^{4+} emission spectra in GGG:Mn:Ca:TM

5. Conclusion

Different kinds of Mn^{4+} ions have been pointed out in GGG:Mn:Ca single crystal. They are related to the position in the lattice of the charge compensating Ca ion. This point will be confirm in a further work on GGG:Mn:Mg and temperature dependence of non-radiative processes will be studied.

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