Fluorescence line narrowing study of Cr^{3+} ions in cordierite glass nucleating $MgAl_2O_4$ nanocrystals

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Abstract

The luminescence of Cr^{3+} ions in cordierite glass nucleating $MgAl_2O_4$ nanocrystallites has been investigated. The time resolved fluorescence line narrowing measurements and the temperature dependence of the homogeneous line width show that most Cr^{3+} ions are inside the nanocrystallites. Cr^{3+} ions occupy non-equivalent crystal sites, due to the Mg^{2+}–Al^{3+} inversion effect. The values of the homogeneous line width compare well with those of previous studies in crystals. No surface effect has been observed due to the large size of the crystals. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The interest in growing nanocrystallites doped with optically active ions, dispersed in a glassy host, derives from the expectation of enhanced optical properties in this class of materials. The change in chemical and physical properties of optical glasses due to the nucleation and growth of crystalline particles has been extensively investigated [1–11]. Particular attention has been devoted to the study of the vibrational dynamics of the particles and to their interaction with the bulk dynamics [12–16]. It has been found that the addition of small quantities of transition metal or rare earth ions can strongly influence the nucleation process [17,18], and that nanoscale size restriction may enhance the homogeneous line broadening of the optical transitions [15,16].

The local environment around the optically active ion can be very different depending on the glass composition, the nucleating agent, the method used to induce nucleation and the size of the crystallites. Different sites are available for the luminescent ion in a glassy ceramic: (i) the sites of the glassy phase, (ii) the sites inside the nanocrystallites, (iii) the sites at the crystal–glass interface. For application in the field of solid state laser, it is important to know precisely where the optically

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active ion is located. In fact, the spectral characteristics of the luminescent ions (especially in the case of transition metal ions) are strongly dependent on the local environment [19,20]. The site-selective laser excitation allows one to obtain luminescence spectra which are very different for luminescent ions located at different environments [21]. Cordierite glass doped with Cr^{3+} is an attractive system for studying in detail the dependence of the luminescence on the local environment. The Cr^{3+} ions act at the same time as efficient nucleating agents and as structural fluorescent probes [1,3,7,22,23]. In cordierite glass, the formation of nanocrystallites of $MgAl_2O_3$ spinel after heat treatment above 800°C is well known, and the presence of Cr^{3+} ions in the nanocrystallites has been ascertained [1–4,6,7,23]. In the work of Duval et al. [12] very low-frequency Raman-scattering bands were observed, due to the acoustic vibrations of the nanocrystallites. By considering the vibrational modes of a free, homogeneous elastic body of spherical shape, the size of the nanocrystals (between 20 and 35 nm depending on heat treatment) was deduced. The results were in good agreement with small-angle neutron scattering data.

In this work we report on the site selective luminescence of Cr^{3+} ions in one of the samples investigated in previous works [1,3,23], in order to determine the distribution of the Cr^{3+} local environments.

2. Experimental

The glass of composition $52SiO_2$–$34.7Al_2O_3$–$12.5MgO$–$0.8Cr_2O_3$ was heated at 950°C in air for 10 min in order to induce nucleation. Nanocrystallites in $MgAl_2O_3$ spinel form, with a diameter of 35 nm, were obtained in previous works [1,3,23]. The luminescence spectra were obtained by exciting with either an Ar^+ or a HeNe laser. A dye laser pumped by an Ar^+-ion laser (line width 0.1 cm^{-1}), or by another pulsed dye laser (line width 0.2 cm^{-1}) pumped in turn by an excimer laser, was used for site-selective excitation experiments. Time-resolved spectra were obtained either with the pulsed source or by using a chopper to gate the

exciting continuous wave (CW) laser beam. Rayleigh scattering of the laser light was eliminated by means of a rotating chopper placed in front of the entrance slit of the monochromator, which was synchronised in antiphase with the laser pulse, so as to intercept the scattered radiation during the excitation pulse. The luminescence was analysed with a double monochromator (resolution 0.15 cm^{-1}) and detected using a photon counting system. For low temperature measurements the sample was mounted in a helium continuous-flow cryostat, whose temperature was controlled to within 1 K.

3. Results and discussion

3.1. Luminescence spectra

In a simplified energy level diagram of the Cr^{3+} ion in an octahedral crystal field (CF), the two lowest excited levels are ^2E and $^4T_2$. For low values of the CF, the $^4T_2$ state is at lower energy than the ^2E state; for high CF the opposite is true. The characteristics of luminescence from ^2E and $^4T_2$ are quite different. The $^2E \rightarrow {}^4A_2$ transition is characterised by the presence of one or two zero-phonon lines (ZPLs), with a one-phonon sideband (SB). Since this transition is spin-forbidden the radiative decay time is usually measured in milliseconds. On the contrary, the transition $^4T_2 \rightarrow {}^4A_2$ shows a very broad sideband connected to very weak ZPLs. Moreover, its characteristic radiative decay time is of the order of 100 microseconds because the transition is spin-allowed [24]. In a crystal the local CFs acting on different dopant ions are very similar: the energies of the levels are close and a small inhomogeneous broadening is observed in the ZPLs. In a glass, the dopant ions experience a wide range of CF. Therefore, the luminescence from such systems may contain emission from the ^2E level of Cr^{3+} ions at sites with high CF, as well as emission from the $^4T_2$ level of Cr^{3+} ions at low CF sites. Another consequence is the large inhomogeneous broadening of the ZPLs. On the basis of these general considerations we can expect that in our system the luminescence will be rather complex. In fact we are in the presence of

several contributions to the luminescence from the different sites available for the Cr^{3+} in the system: (i) the sites of the glassy phase (ii) the sites inside the nanocrystals of $MgAl_2O_4$ spinel (iii) the sites localized at the interface between the crystal particles and the glassy phase.

Fig. 1 shows the spectra obtained under CW excitation at 514.5 and 623.8 nm. For excitation at 514.5 nm at room temperature (Fig. 1(a)), the spectrum shows a broad structured band centred at 14540 cm^{-1} with a full width at half maximum (FWHM) of about 150 cm^{-1} and a smooth vibronic SB. At 4.2 K (Fig. 1(b)) the band appears more structured, revealing the presence of almost four distinct peaks. The spectrum is very similar to that of Cr^{3+} doped spinel crystals [25,26]. Non-exponential decays are observed at all frequencies and temperatures in lifetime measurements. At least two different decay times of about 9 and 3 ms are present in the luminescence of Fig. 1(a). At low temperature these two main contributions have lifetimes of the order of 15 and 5 ms, respectively. Moreover, the lifetime of the long-living sites is not the same for the different peaks in the spectrum of Fig. 1(b). In fact, we measured a decay
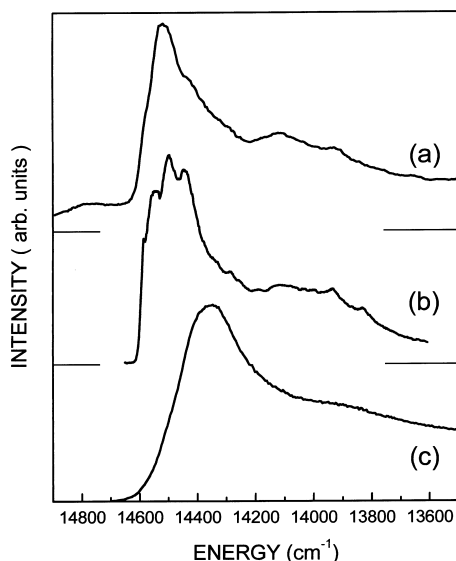
time of 18 ms at 14575 cm^{-1} and one of 12 ms at 14430 cm^{-1}.

The time resolved spectra, recorded at different delays under pulsed excitation of the 514.5 nm line, are reported in Fig. 2. The spectrum with the longest delay (Fig. 2(b)) provides better evidence for the presence of the four peaks, while the spectrum relative to shortest delay (Fig. 2(a)) shows broader bands in the ZPLs range. Mikenda et al. [26] explained the luminescence features of $MgAl_2O_4$:Cr^{3+} spinel in terms of a cations inversion effect. In the ideal crystal structure, as in natural crystals, Al^{3+} ions occupy octahedral sites and Mg^{2+} ions occupy tetrahedral sites. Cr^{3+} ions substitute for Al^{3+} ions at octahedral sites. Cation inversion produces a variety of Cr^{3+} local environments, but the relevant effects will be due to inversion in the first few coordination spheres. There are six first-neighbour cation sites around a Cr^{3+} ion, which should be occupied by Mg^{2+} ions in the ideal crystal and six second-neighbour cation sites, which should be occupied by Al^{3+} ions. For a low degree of inversion, the most probable configuration different from the ideal one is given by the presence of one Al^{3+} ion in one of the six Mg^{2+} tetrahedral sites, or of one Mg^{2+} ion in one of the six Al^{3+} octahedral sites [26]. The occurrence of the different local configuration can be

Fig. 1. Luminescence spectra of Cr^{3+} ions obtained under continuous excitation by the 514.5 nm line at 300 K (a) and at 4.2 K (b) and by the 632.8 nm line at 4.2 K (c).
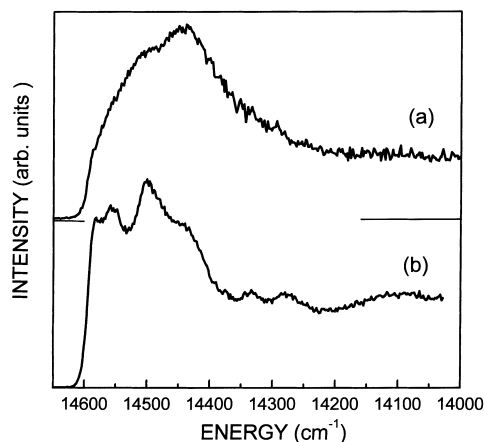

Fig. 2. Time-resolved luminescence spectra of Cr^{3+} ions obtained at 4.2 K under pulsed excitation at 514.5 nm. Pulse duration 35 ms, with simultaneous detection (a) and detection from 30 to 50 ms after laser switch-off (b).

estimated at a given degree of inversion by statistical arguments [26]. The degree of inversion depends on the thermal history of the sample. In natural crystals, which present normal order, high temperature annealing produces marked irreversible inversion [27]. In this framework, a well defined line is expected for each local configuration; the long-range disordered distribution of the cations together with the presence of local defects is responsible for the broadening of the lines [26,28]. By comparison with the results of Ref. [26] we can assume for the peak at the highest energy (14575 cm^{-1}) a nearly ideal configuration (no inversion) around the Cr^{3+} ion, but it is not possible to identify the different Al^{3+}–Mg^{2+} configurations which produce the broad peaks at lower energies in Fig. 2(b). Site selection in the large number of sites available for the Cr^{3+} ion in this system can be achieved by exciting at different energies in the $^4A_2 \rightarrow {}^4T_2$ absorption bands [29].

In Fig. 1(c) we report the spectrum obtained by CW excitation at 632.8 nm at LHe temperature. The spectrum shows a large peak centred at 14380 cm^{-1} with a long tail towards the infrared region. Fluorescence decay measurements, performed at several energies, show that a relevant contribution is characterised by time constants in the range of hundreds of microseconds. Time resolved spectra, obtained at room temperature under pulsed excitation of the 632.8 nm line, are reported in Fig 3. The spectrum detected at short delay (Fig. 3(a)) is dominated by a large band whose maximum lies in the near-infrared spectral region. At long delays (Fig. 3(b), (c)) the intensity of the broad band strongly decreases, and the peak in the 14300–14600 cm^{-1} range becomes the dominant feature. It sharpens and shifts to higher energies by increasing the detection delay. The broad band of Fig. 3(a) is assigned to $^4T_2 \rightarrow {}^4A_2$ luminescence from Cr^{3+} ions in low CF sites of the glass [1]. These centres are efficiently excited by the red light of the He–Ne laser. On the contrary, the high CF Cr^{3+} sites are more efficiently excited by the green light of the Ar^+ laser, since at 623.8 nm they can only weakly absorb in the $^2T_1$ state and its SB. The bands in the frequency range 14200–14600 cm^{-1} are assigned to high CF Cr^{3+} sites having the ^2E as the first excited level. The actual spectral lineshape
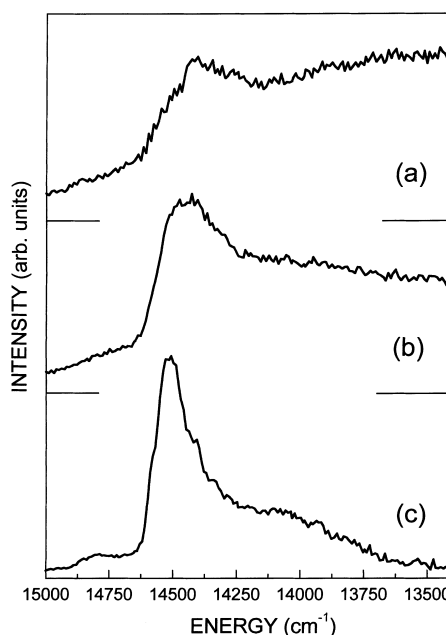

Fig. 3. Time-resolved luminescence spectra of Cr^{3+} ions obtained at 300 K under pulsed excitation by the 632.8 nm line; (a) pulse duration 0.4 ms and simultaneous detection, pulse duration 25 ms with detection from 1 to 5 ms (b) and from 15 to 30 ms (c) after laser switch-off.

depends on the excitation energy and on the detection delay. The luminescence of Figs. 2(b) and 3(c), detected at long delays, should be mainly due to $^2E \rightarrow {}^4A_2$ ZPLs and SBs of crystalline sites. The luminescence with a lifetime of the order of few milliseconds, evidenced by the broad peak centred at about 14350 cm^{-1} in Fig. 1(c), is probably due to Cr^{3+} ions in the glassy phase having relatively low CF, but with the ^2E state at lower energy than $^4T_2$.

3.2. Time resolved resonant fluorescence line narrowing spectra

In order to get more detailed information on the luminescence of the different centres, we performed some time resolved resonant fluorescence line narrowing (TRRFLN) measurements. In a CF of symmetry lower than octahedral, the ground state $^4A_2$ is split into two doublets ($m_s = \pm 3/2$, $m_s = \pm 1/2$).

The spectra in Fig. 4 show the ground-state splitting (GSS) relative to the long-living centres. They were obtained at different detection energies in the inhomogeneous profile with high resolution in the range across the excitation laser line. The width of the resonant sharp central line is due to the instrumental resolution. The satellite lines which appear to be broader than the central line, reflect an energy spread in the GSS. In Fig. 4(c)–(f) a large distribution of splittings from about 0.4 to 1.7 cm^1 is observed. The mean splitting increases by increasing the energy of the resonant line. In the high-energy range of the inhomogeneous profile (Fig. 4(a),(b)) the GSS is quite well defined with values of 1.8 and 1.5 cm^{-1}, respectively. For the short-living centres a broad distribution of splittings from about 0.6 to 1.5 cm^{-1} is observed in the whole inhomogeneous profile, reflecting once more
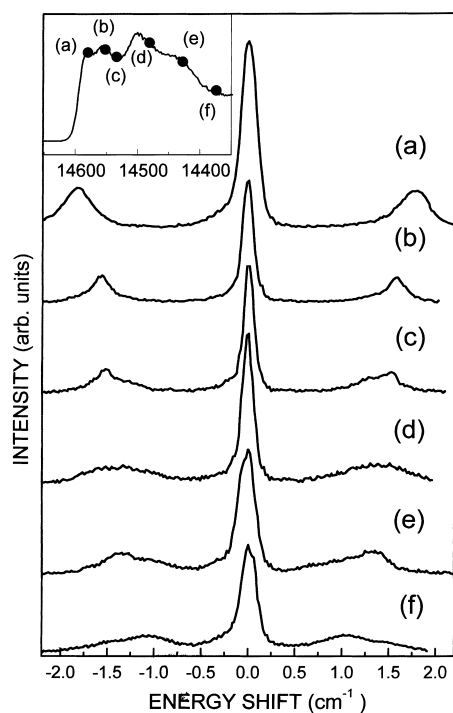
the large distribution of sites with low CF. We unsuccessfully tried to measure the ^2E splittings. In all cases, even for excitation in the high energy tail of the $^4A_2 \rightarrow {}^2E$ band, a very broad distribution of splittings was found and a detailed analysis in terms of different sites was not possible. We can conclude that only the luminescence occurring at the high energy tail of the spectrum, and having long lifetimes, originates from well defined crystalline sites, which can be selected by resonant excitation. The luminescence at energies lower than about 14550 cm^{-1} is due to Cr^{3+} ions occupying a large distribution of sites in the nanocrystals, in the glassy phase, and probably at the interface. Their different contributions to the luminescence cannot be well isolated.

The presence of different crystalline and glassy sites, not easily distinguished, demands caution in taking TRRFLN measurements to study the temperature dependence of the homogeneous line width (Γ_h). Many measurements were performed by exciting at different energies by a pulsed or a chopped CW laser and detecting at different delays. The results of some of these measurements are reported in Fig. 5. Γ_h at temperature T is obtained from a fit of the TRRFLN spectrum with a curve given by the convolution of the low temperature spectrum with a Lorentzian curve of line width $2\Gamma_h$, and taking into account the temperature dependence of the relative populations of the $m_s = \pm3/2$ and $m_s = \pm1/2$ doublets of the $^4A_2$ ground state [30]. Γ_h increases with decreasing excitation frequency, while the temperature dependence is similar. The set of measurements with the smallest $\Gamma_h(T)$ corresponds to Cr^{3+} ions excited in the highest energy peak of the $^4A_2 \rightarrow {}^2E$ absorption profile. These centers have well defined GSS and long lifetimes. As shown in Fig. 5, $\Gamma_h(T)$ of the Cr^{3+} ions excited at 14575 cm^{-1} is very close in value to that of ruby (full circle) [31,32]. It presents a T^2 behavior at high T with a crossing to a higher T power dependence at low temperature. In the range 70–170 K, the homogeneous line width is fitted by a power law $\Gamma_h(T) \propto T^\alpha$ with $\alpha = 4.0 \pm 0.2$. The data of ruby have been interpreted in terms of two phonon Raman processes, that should result in a T^7 dependence at low T, and in a T^2 dependence at high T [31,33]. For comparison,
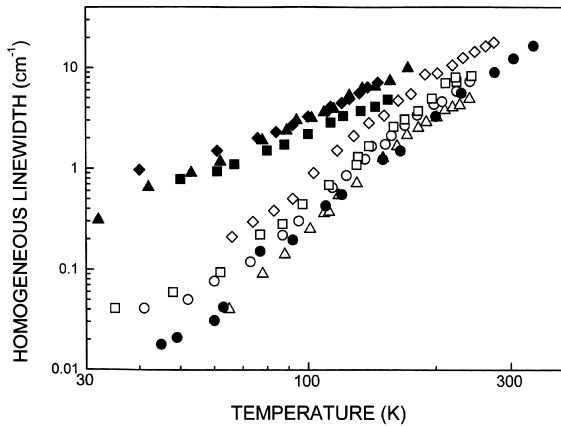

Fig. 4. TRRFLN spectra of the $^2E \rightarrow {}^4A_2$ transition at 4.2 K for six different excitation energies within the inhomogeneous profile as shown in the inset: (a) 14580 cm^{-1}; (b) 14552 cm^{-1}; (c) 14534 cm^{-1}; (d) 14481 cm^{-1}; (e) 14428 cm^{-1}; (f) 14374 cm^{-1}. Pulse width 35 ms and detection from 20 to 50 ms after laser switch-off.

Fig. 5. Temperature dependence of the $^2E \rightarrow {}^4A_2$ homogeneous line width. Excitation at $14\,575$ cm^{-1} (open triangles), $14\,502$ cm^{-1} (open circles), $14\,438$ cm^{-1} (open squares) by a pulse width of 35 ms and detection from 20 to 50 ms after laser switch-off. Excitation at $14\,300$ cm^{-1} (open diamond) with a pulsed dye laser and detection for 0.8 ms after the laser pulse. The full symbols show the homogeneous line widths of the $^2E \rightarrow {}^4A_2$ transition of Cr^{3+} ions in other systems: ruby (circle) [31], mullite glass (diamond) [34], ED-2 silicate glass (square) [35], zinco-borate glass (triangle) [35].

we also report in Fig. 5 the data of Γ_h for Cr^{3+} in mullite (full diamond) [34], ED-2 silicate (full square) [35] and zincoborate glasses (full triangle) [36]. In the investigated glasses, the measured values of Γ_h are larger than those observed in crystals, with a temperature behavior crossing from T^2 at high T, to a nearly linear T dependence at low T. On the basis of this comparison with ruby, we can assign these Cr^{3+} centers to crystalline $MgAl_2O_4$ sites. Recently, low temperature hole burning measurements have shown that the limited size of the nanocrystals causes increase of Γ_h [15,16]. In the present case, this effect seems not to be present, probably because of the larger size of the crystals and the higher temperature of measurement.

The increase of Γ_h with decreasing luminescence frequency can be attributed to stronger coupling with phonons for Cr^{3+} ions in distorted sites, with shorter lifetimes. We recall that the distortion is attributed to Mg^{2+}–Al^{3+} ion exchange in the ideal structure of the spinel. Cation neighbors in inverted position distort the Cr^{3+} site from the trigonal symmetry, causing an increase in the radiative

transition rates and coupling with the crystal vibrations. However, we cannot exclude that the observed increase of Γ_h with decreasing energy is partially due to a contribution of ions in the glass or in crystalline sites near the interface, strongly interacting with the glass dynamics. The high-power T dependence, observed in the 50–150 K range at all excitation energies, when compared to the nearly linear T dependence of Γ_h observed in different glasses in the same range of temperatures, strongly indicates that at least the major part of the excited Cr^{3+} ions are in the crystalline phase.

We tried unsuccessfully to isolate a set of Cr^{3+} ions having a $\Gamma_h(T)$ value typical of the glassy phase. The luminescence excited at $14\,300$ cm^{-1} by a pulsed dye laser and detected in the first 0.8 ms (Fig. 5, diamonds), is certainly due in part to Cr^{3+} in the glassy phase, but the contribution from crystalline sites is the dominant one in determining the behavior of $\Gamma_h(T)$. It should be noted that in this case a very critical situation occurs: we are exciting at the same time Cr^{3+} ions in sites of very different nature, with very different Γ_h. At each temperature we can measure an average Γ_h, but the weights of the different sites can change with T. In fact, many important parameters which identify a site, such as the transition rate and frequency, change with T. Therefore, in a set of measurements taken with fixed laser frequency and detection delay, the contribution to the luminescence of different Cr^{3+} ions can change as T changes, strongly reducing the relevance of the Γ_h results. Anyway, we observe that Cr^{3+} ions in the glassy phase, cannot be isolated even at the most favourable excitation frequencies and delay times. We can conclude that most of the Cr^{3+} ions, after the nucleation of $MgAl_2O_4$ nanocrystals, have entered the crystal structure.

Acknowledgements

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