Spectroscopic properties of $\text{KZnF}_3: \text{Cr}^{3+}$

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The optical properties of Cr^{3+} in KZnF_3 have been investigated in the 4.2-625K temperature range by using steady-state and time-resolved laser spectroscopy. The luminescence shows a strong thermal quenching above 400K which can be analyzed on the basis of the quantum-mechanical single-configurational-coordinate model by using the Struck and Fonger method. Emission lifetime measurements and time resolved spectra show the existence of different Cr^{3+} centers in this host.

INTRODUCTION

The Cr^{3+} ion has generated a great interest in the development of new solid-state-laser materials, because of its favorable absorption and emission properties when introduced into octahedral sites of a host material. It is especially interesting to consider Cr^{3+} ions in hosts with a weak crystal-field environment because a large vibronically broadened emission occurs, and laser with a wide tuning range may be constructed. Potential applications to tunable lasers make it imperative to achieve a fundamental understanding of the spectroscopic properties of these materials. The system under investigation in this work is the cubic-fluorine perovskite $\text{KZnF}_3: \text{Cr}^{3+}$ which is a very interesting material from a technological point of view since true cw-laser operation has been achieved at room temperature (1). The Cr^{3+} ion substitutes Zn^{2+} (cubic site), thus requiring charge-compensating vacancies. As a result, in addition to cubic centres, Cr^{3+} ions with a lower symmetry, namely tetragonal or trigonal, can exist (2). In order to complete the present knowledge of the optical properties of the Cr^{3+} ion in this host we report, together with steady-state spectroscopy, time resolved measurements as a function of temperature.

EXPERIMENTAL

The sample studied in this work was grown at the Condensed State Physics Laboratory of Le Mans (France) and was doped with 1 at % of Cr^{3+} . The sample temperature was varied between 4.2 and 625K with a continuous flow cryostat. The emission measurements were made using the 633nm emission line of a 15mW He-Ne laser as exciting light. The fluorescence was analyzed with a 0.22m SPEX monochromator and the signal was detected by a Hamamatsu R7102 extended IR photomultiplier and finally amplified by a standard lock-in technique. The system response was calibrated with a standard tungsten-halogen lamp to correct the emission spectra. Emission lifetime measurements and time resolved spectra were obtained by exciting the sample with a tunable dye laser (1ns pulse width). The spectra were processed by a EGG-PAR boxcar integrator.

EXPERIMENTAL RESULTS

The steady-state emission measurements were made under excitation in the peak of the $^4\text{A}_2 \rightarrow ^4\text{T}_2$ absorption band in the 4.2-625K temperature range. The luminescence spectra lie in the 690-1050nm wavelength range and are characterized by a broad band which corresponds to the $^4\text{T}_2 \rightarrow ^4\text{A}_2$ transition. At low temperatures, sharp lines and their vibronic replicas appear superimposed on the broad band but the lines intensity turns down rapidly when the temperature increases.

The fluorescence lifetimes of the broad emission band were studied as a function of temperature and emission wavelength. The decay curves were single exponential at all temperatures and wavelengths. Figure 1 shows the fluorescence decays at 77K (LNT) for different emission wavelengths obtained under pulsed laser action excitation at the center of the $4A_2 \rightarrow 4T_2$ absorption band. As can be observed, the decays present a strong monotonic variation, indicating that there is a large variety of crystal fields sites.

Figure 2 shows the emission lifetime and integrated emission intensities as a function of temperature between 4.2 and 625K. The rapid decline of lifetimes at high temperatures (above 400K) is well correlated with decreasing fluorescence intensity and is accordingly attributed to the dominance of nonradiative transitions.

Time-resolved emission spectra between 50 μ s and 700 μ s were obtained at 77K after exciting the sample at the peak position of the $4A_2 \rightarrow 4T_2$ absorption band. Figure 3 displays the first and the second moments calculated from the emission spectra as a function of time. A blue peak shift and a bandwidth narrowing as time increases can be observed. In particular, the second moment displayed in figure 3b shows a small declination at the first 200 μ s, then it is nearly constant between 200 and 400 μ s and finally strongly decreases above 400 μ s. This behaviour agrees with the existence of Cr^{3+} centers with a relaxation time of about 200 μ s (trigonal centers) and with another distribution of Cr^{3+} centers with higher relaxation times (cubic and/or tetragonal centers)(2).

Figure 1. LNT lifetimes at different emission wavelengths along the $4T_2 \rightarrow 4A_2$ emission band.

Figure 2. Lifetimes (o) and integrated emission intensities (x) as a function of temperature.

Figure 3. Time dependence of first (N_1) and second (N_2) moments obtained from the LNT corrected time-resolved emission spectra.

DISCUSSION

The emission spectra at different temperatures (4.2-625K) have been analyzed within the single configurational coordinate model (SCC)(linear coupling). The temperature dependence of the emission bandwidth allows us to estimate the effective frequency of the breathing mode phonon and the Huang-Rhys factor. The obtained values are $\hbar\omega_0=353\text{cm}^{-1}$ and $S_0=4.3$ respectively. The emission lineshapes can be fit by taking the finite temperature into account by using the equation of Struck and Fonger (3). The best fit was obtained, at different temperatures, using the cubic zero phonon line energy and the abovementioned values for $\hbar\omega_0$ and S_0 . As can be seen in figure 4, the good fit achieved seems to point out that the Cr^{3+} ions which are responsible for the broadband emission mainly belong to cubic sites.

As we have shown in figure 2, the Cr^{3+} fluorescence lifetimes and integrated emission intensities were significantly reduced at temperatures above 400K. This thermal quenching is most likely attributed to multiphonon emission processes. Theoretical models (4,5) based on linear coupling to modes of a_{1g} symmetry fail to explain the observed radiationless transition rate. However, if we assume different force constants in the ground and excited states(6), the obtained results are better. Figure 5 shows the measured temperature dependence of nonradiative transition probability W_{NR} and the predicted quenching in this model for a Manneback angle $\Theta=42.5$ ($A_{UV}=10^{13}\text{s}^{-1}$). As can be seen a good qualitative agreement for temperature dependence of W_{NR} is obtained. Table I shows the parameters values of the model for a Manneback angle $\Theta=42.5$.

Figure 4. Fit of the experimental emission line (solid line) with the theoretical shape (●) predicted by SCC with linear coupling at 77K, using the values $S_0=4.3$ and $\hbar\omega_0=353\text{cm}^{-1}$.

Figure 5. Temperature dependence of measured W_{NR} (o) and the predicted quenching assuming different force constants in the ground and excited states for $\Theta = 42.5$ (solid line).

Table I. Parameters of the SCC model with different force constants.

S_u	$\hbar\omega_u$ (cm^{-1})	S_v	$\hbar\omega_v$ (cm^{-1})	a_{uv}	U_0 (cm^{-1})	E_A (cm^{-1})
4.55	391	3.82	328	4.2	14144	9283

The experimental results on fluorescence lifetimes and time-resolved spectra, point to the existence of different Cr^{3+} centers in KZnF_3 . In order to obtain a deeper knowledge about this question, time-resolved excitation spectra were performed at 77K. Figure 6 shows two excitation spectra of the $^4\text{A}_2 \rightarrow ^4\text{T}_2$ band, performed at two delays (50 μs and 600 μs) for luminescence monitored at the peak position of the emission band (780nm). The features which appear in the excitation spectra can be interpreted as Fano antiresonances (7). As is easily seen, the excitation spectra monitored at high time delay is blue shifted as corresponds to emission losses from the low field sites (sites of shorter lifetimes). A strong antiresonance profile change from one spectrum to the other can be also observed which is related to the existence of different Cr^{3+} centers in the crystal (8). These results suggest further extensions of the study performed at 4.2K where the fine structure of the emission band is resolved.

Figure 6. LNT excitation spectra of the $^4\text{A}_2 \rightarrow ^4\text{T}_2$ band performed at two time delays (o) 50 μs and (x) 600 μs for luminescence monitored at the peak of the emission band.

In summary we have reported a detailed study of the spectroscopic properties of Cr^{3+} in KZnF_3 . The quantum mechanical SCC model with different constant forces gives a good qualitative agreement with the experimental temperature dependence of W_{NR} . From the emission lifetime measurements and time resolved spectra, we have shown the existence of inhomogeneous broadening associated with the presence of different sites for Cr^{3+} ions.

REFERENCES

- (1) U. Brauch and U. Dürr. *Opt.Comm.* **49**, 61 (1984).
- (2) O. Pilla et al. *Phys. Rev B* **38**, 3477 (1988).
- (3) C.W. Struck and W.H. Fonger, *J. Lumin.* **18-19**, 101 (1979).
- (4) N.F. Mott, *Proc. R. Soc. (London). Ser. A* **167**, 384 (1938).
- (5) W.H. Fonger and C.W. Struck, in *Radiationless Processes*, edited by B. DiBartolo (Plenum, New York 1980).
- (6) C.W. Struck and W.H. Fonger, *J. Lumin.* **10**, 1 (1975).
- (7) U. Fano. *Phys. Rev* **124**, 1896 (1961).
- (8) M.A. Illarramendi, R. Balda and J. Fernández, *Phys. Rev.* **47**, 8411 (1993).