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Effects of high pressure on the fluorescence spectra of Cr³⁺ in GdAlO₃

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Abstract. The effect of high hydrostatic pressure, up to 100 kbar, on the emission spectra of Cr³⁺ ions in GdAlO₃ hosts was studied. A linear shifting (red-shift) of the single-ion line (the R line), the left-hand side (LS) line, right-hand side (RS) line and the neighbouring-pair line (NPL) was observed. The R line shows a pressure-induced shift of 0.082 nm kbar⁻¹, nearly 2.25 times that of ruby. The LS line, RS line and NPL show pressure-induced shifts of 0.0779 nm kbar⁻¹, 0.0864 nm kbar⁻¹ and 0.0933 nm kbar⁻¹, respectively.

1. Introduction

The optical and magnetic properties of GdAlO₃ with Cr³⁺ impurities substituting for Al³⁺ have been extensively studied both theoretically and experimentally [1–3]. The interest in this material derives from its potential application as a medium for a tunable laser [1, 4, 5]. The Al³⁺ site is octahedrally coordinated with six O²⁻ ions as nearest neighbours. When Cr³⁺ is added in small quantities, it will substitute for the Al³⁺ ions preferentially [1]. Only those Cr³⁺ ions substituted into the octahedral sites will give a fluorescence spectrum, with well defined peaks in the range 720 nm–740 nm [1, 3]. The effects of temperature and magnetic field on the fluorescence spectra for GdAlO₃:Cr³⁺ are well known [1–3, 6] but the effect of high pressure has not yet been investigated. Therefore, in the present paper we study the effect of high hydrostatic pressure (up to 100 kbar) on the fluorescence spectra of Cr³⁺ ions in GdAlO₃ hosts in order to obtain information about their optical properties as laser materials.

2. Experiment

A diamond-anvil cell (DAC) of the NBS type [7] with 1/3 carat stones was used to generate the pressure. The pressure was increased at room temperature, and the DAC was allowed to equilibrate for at least 12 h after each pressure was set up. The pressure used was in the range 0–100 kbar and the temperature was constant, 300 K. A small ($\approx 50 \mu\text{m}$) chip of ruby (0.1 mol% of Cr³⁺) and one of GdAlO₃:Cr³⁺ (with 0.7 mol% of Cr³⁺) were placed in the 300 μm hole in the preindented stainless steel gasket, together with a methanol–ethanol (4:1) mixture which served as the pressure medium and which remained hydrostatic up to 140 kbar [8]. A spectrofluorometer connected with a multiscaler card in a PC was used

as the measurement apparatus. The pressure was determined from the shift of the ruby R1 line ($0.0365 \text{ nm kbar}^{-1}$) [8, 9]. The positions of the ruby R1 line and sample R lines were determined using a double optical monochromator with 0.05 nm spectral resolution and a photon counter with a multiscaler. The samples were excited with a HeNe ion laser at 543.5 nm . In order to minimize the laser heating of the sample, the power of the laser was reduced to 3 mW .

3. Results and discussion

The starting point in the consideration of the fluorescence spectra of Cr^{3+} in GdAlO_3 was the similarity between the energy levels of ruby and those of $\text{GdAlO}_3:\text{Cr}^{3+}$ [1]. The above-mentioned assumption is confirmed by the excellent agreement between (i) the experimentally obtained temperature and magnetic field effects on the fluorescence decay of Cr^{3+} in GdAlO_3 and (ii) those predicted theoretically on the basis of the similarity between the energy levels of ruby and $\text{GdAlO}_3:\text{Cr}^{3+}$ [2].

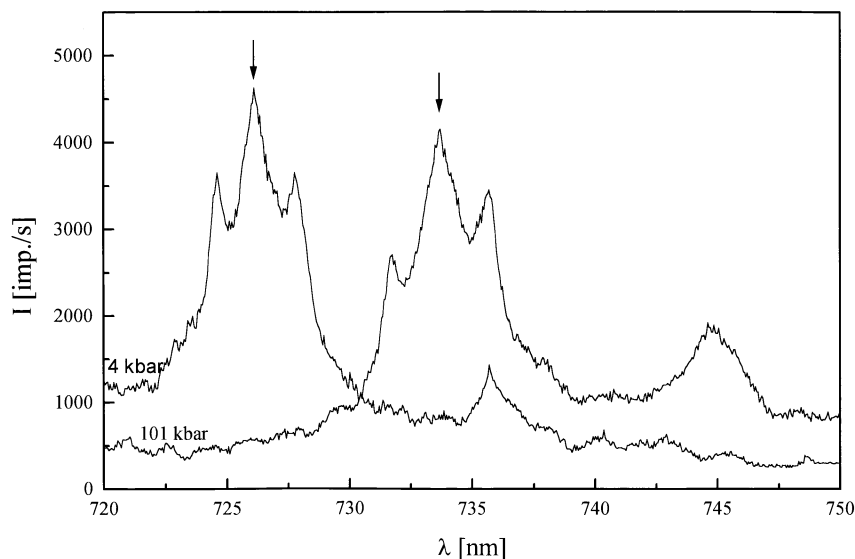


Figure 1. High-pressure fluorescence spectra of a $\text{GdAlO}_3:\text{Cr}^{3+}$ crystal (with $0.7 \text{ mol\% Cr}^{3+}$) at room temperature.

The room temperature emission spectra of $\text{GdAlO}_3:\text{Cr}^{3+}$, with $0.7\% \text{ Cr}^{3+}$ concentration, at two pressures, are shown in figure 1. The observed fluorescence spectra of Cr^{3+} in GdAlO_3 at room temperature and normal pressure are similar to the 4.2 K [10] and 70 K [1] spectra. The spectrum obtained shows four well-resolved strong lines. Three of them, at around 730 nm , are believed to be due to transitions between the Cr^{3+} states ${}^2\text{E}$ and ${}^4\text{A}_2$ that have been split by exchange interaction with the ${}^8\text{S}_{7/2}$ ground states of the eight surrounding Gd^{3+} ions [10]. One of them, the R line, at about 726 nm , corresponds to an electric dipole transition between the first excited state ${}^2\text{E}$ of the Cr^{3+} and the ground state ${}^4\text{A}_2$ [2]. On the left-hand side of the R line there is one line (denoted by LS) at about 724 nm , and there is another on the right-hand side (denoted by RS) at about 727 nm . We assume that the fourth line, at about 736 nm , is related to the energy transfer between so-called Cr^{3+} single

ions, which are nearly isolated from each other, and from the exchange-coupled Cr^{3+} pairs formed statistically by Cr^{3+} ions on neighbouring lattice sites. For consistency, we denote this fourth line as the NPL (the neighbouring-pair line) from now on. This kind of line was observed in several systems with high Cr^{3+} -ion concentrations: ruby [11, 12], $\text{GaAlO}_3:\text{Cr}^{3+}$ [13] and $\text{LaAlO}_3:\text{Cr}^{3+}$ [14]. In these crystals, the single ions and the neighbouring pairs have fluorescence line spectra that are easily distinguishable spectroscopically.

The linewidth of the R line at higher pressure increases by about 18% (unlike that for ruby, which is unchanged [16]). At zero pressure it is about 12.65 nm and at 101 kbar it is 14.95 nm. Comparing with the R1 linewidth of ruby, one can see that this R line is not as sharp as the R1 line of ruby (at 0.75 nm) [15]. The intensity of the R line is relatively high and changes slightly with pressure, unlike that of ruby which is almost unchanged [16]. The relative intensity (the background ratio) for the R line (0.24) is greater than that for the R1 line of ruby (0.01) [16]. The intensities of the R line and NPL at 4 kbar and 101 kbar are 3.23 and 2.17, respectively.

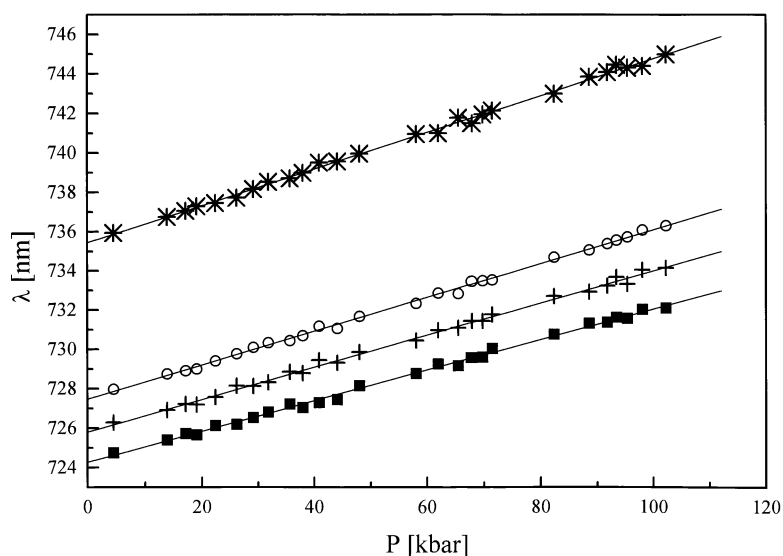


Figure 2. The effect of high pressure on the positions of the LS line, the R line, the RS line, and the NPL in the spectrum of $\text{GdAlO}_3:\text{Cr}^{3+}$ crystal, at room temperature. Key to symbols: ■: LS line; +: R line; ○: RS line; *: NPL.

The pressure dependences of the positions for the R line, LS line, RS line and NPL at room temperature are presented in figure 2. The positions of the LS and RS lines shift linearly under pressure towards the red, like that of the R line, but at different rates: $0.0779 \text{ nm kbar}^{-1}$ and $0.0864 \text{ nm kbar}^{-1}$, respectively.

The changing of the Cr^{3+} -ion R-line position with pressure is the same result as was obtained for ruby, a fact which is expected because of the above-mentioned similarity of the energy levels of $\text{GdAlO}_3:\text{Cr}^{3+}$ and ruby [2]. However, the R line of our samples is about 2.25 times more sensitive to pressure ($0.0820 \text{ nm kbar}^{-1}$) than the R1 line of ruby. This higher sensitivity of the R line for a GdAlO_3 host may be connected with the different crystal parameters relevant to the line positions. When Cr^{3+} ions are in octahedral surroundings in different crystal hosts—ruby [17], MgO [18] and alexandrite [19]—the changing of the R1-line positions with pressure can be expressed excellently as a function of the interionic

distance R [17]:

$$\lambda = \lambda_0 - \lambda_0 \{ [(R/R_0)^{-S} \exp[1.24(1 - R/R_0)^2 + 1.65(1 - R/R_0)^3] \}.$$

The validity of this equation is proved by the excellent agreement between the experimental and calculated line positions: the discrepancy is less than 2%. As in GdAlO₃ crystal the Cr³⁺ ion is also in octahedral surroundings [1], the change of the R1-line position with pressure can be expressed by the same equation. The fact that the parameter S is different for different crystal hosts [17–19] leads to the conclusion that for a GdAlO₃ host it must also be different. S is an adjustable parameter; it depends on the properties of the crystal. If one calculates the parameter S using the method described for ruby in [17], one obtains the value 0.849. If we insert the calculated value for the parameter S (0.849) in the equation given above, and suppose that a pressure of 101 kbar causes the same change of the R-line position as for ruby, we obtain that $\Delta\lambda/\Delta P$ is 0.078 nm kbar⁻¹. The discrepancy between the experimentally obtained and the calculated values of $\Delta\lambda/\Delta P$ is less than 5%. This agreement between the experimentally obtained and calculated values of $\Delta\lambda/\Delta P$ leads to the conclusion that the explanation given for the high sensitivity of the R line for GdAlO₃ is valid.

The rate of shift of the NPL is about 12% greater than that of the R line, namely 0.0933 nm kbar⁻¹. The great sensitivity of NPLs may be due to the effect of high pressure on single ions adding to the effect of high pressure on the neighbouring-pair ions. This difference in sensitivity will be the subject of further theoretical considerations.

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