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The effect of high pressure on R1 line fluorescence lifetime in $Al_2O_3:Mn^{4+}$

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Abstract. The lifetime τ of the R1 fluorescence line, $^2E(\bar{E}) \rightarrow {}^4A_2$ of α-$Al_2O_3:Mn^{4+}$, has been measured under high pressure conditions (up to 107 kbar). The study shows that τ rapidly increases with pressure and that this increase is primarily caused by a rapid changing in the wavenumber of the R1 line, compression rate and refractive index of the crystal. The presented measurements agree qualitatively with the theoretically predicted increase in τ with pressure.

1. Introduction

Since the first solid-state laser demonstration, i.e. ruby as Cr^{3+} ions doped into Al_2O_3 [1], hundreds of crystals, glass and even plastic materials have been used as hosts to demonstrate lasing. Today, the optical properties of ($3d^3$) ion-doped crystalline host materials are still of continuing interest for applications in the field of solid state laser materials. Aluminium oxide α-Al_2O_3 (corundum) is a important type of host material. The Mn^{4+} ion, in corundum, is a very promising system for tunable laser application [2]. So, when Mn^{4+} is substituted for Al^{3+} in α-Al_2O_3 one expects it in some way to be analogous to ruby, because the Mn^{4+} ion has the same electronic structure of the open shell as Cr^{3+} ($3d^3$). The effect of high pressure on the position of the R line in α-$Al_2O_3:Mn^{4+}$ has been investigated [3] a lot but the effect of high pressure on the R line fluorescence lifetime has not yet been the subject of research. Therefore, the aim of this paper is to assess the effect of high pressure on the R line fluorescence lifetime in α-$Al_2O_3:Mn^{4+}$ and in this way increase our knowledge of optical properties of α-$Al_2O_3:Mn^{4+}$ under pressure.

2. Experiment

The effect of high pressure on the fluorescence lifetime for the R1 line, $^2E(\bar{E}) \rightarrow {}^4A_2$ transition, in single crystals $Al_2O_3:Mn^{4+}$ (0.04% Mn) was investigated in a diamond anvil cell of the NBS type with 1/3 carat stones with inconel gasket materials. The gasket is pre-indented to the thickness of 80–90 μm. Methanol–ethanol mixture (4:1) is used as a pressure transmitting medium to generate hydrostatic conditions to at least 110 kbar. The decay curve was measured with the sample at least 24 hours under pressure. The pressure was determined by the shift of the ruby R1 line (0.0365 nm $kbar^{-1}$) [4]. The sample ($\approx$30 μm chip) were excited using an argon ion laser at 488 nm. In order to diminish laser

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heating of the sample the power of the laser was reduced to 3 mW. The decay curves were measured for each pressure at the maximum of the R1 line using well known methods for fluorescence lifetime measurement. Laser light was chopped by a mechanical chopper. The illumination lasted about 1 ms and the total measuring time for each scan was 10 ms. The data collected by the multiscaler after 50 000 excitation pulses were transferred to the PC to obtain the decay curve and calculated lifetime.

3. Result and discussion

The change of the measured fluorescence lifetime τ for the R1 line, $^2E(\bar{E}) \rightarrow {}^4A_2$ transition, is presented in table 1. It can be observed that the fluorescence lifetime τ rapidly increases with pressure. The rate of τ at 100 kbar and normal pressure (τ/τ_0), in Al_2O_3:Mn^{4+}, is about 3.2 and in ruby it is 2 [5]. With increasing pressure the fluorescence lifetime for the R1 line changes in the same manner as was observed in other ions with a $3d^3$ electronic configuration in a corundum host i.e. as Cr^{3+} ions doped into Al_2O_3 [5]. But on the other hand the rate of change of τ with pressure is different for Mn^{4+} and Cr^{3+} ions. Or in other words, τ for the R1 line in Al_2O_3:Mn^{4+} is more sensitive to pressure than τ for ruby's R1 line.

Table 1. Pressure, wave-number of emitted light, compression rate, refractive index, oscillator strength measured and calculated fluorescence lifetime for the R1 line.

P [kbar]	$W(^2E)$ [cm^{-1}]	k	n	$f \times 10^{-6}$	τ(exp.)10^{-3} [s]	τ(calc.)10^{-3} [s]
0.00	14 743	1.0000	1.7650	1.200	0.80	0.80
8.24	14 735	0.9989	1.7645	1.141	0.89	0.85
15.07	14 728	0.9980	1.7642	1.092	0.97	0.89
19.18	14 724	0.9975	1.7639	1.062	1.02	0.91
27.40	14 716	0.9964	1.7635	1.003	1.17	0.97
35.62	14 709	0.9954	1.7630	0.944	1.24	1.03
45.21	14 700	0.9942	1.7625	0.875	1.41	1.11
53.43	14 693	0.9932	1.7621	0.815	1.53	1.19
61.65	14 685	0.9922	1.7616	0.756	1.71	1.29
72.61	14 675	0.9909	1.7610	0.677	1.82	1.44
82.20	14 667	0.9898	1.7605	0.608	2.13	1.61
95.90	14 655	0.9882	1.7597	0.510	2.47	1.92
104.12	14 649	0.9873	1.7593	0.450	2.52	2.18
106.86	14 646	0.9870	1.7591	0.431	2.59	2.28

The similarity between the Al_2O_3:Mn^{4+} and ruby crystal and the fact that the Mn^{4+} ion is isoelectronic with Cr^{3+} (configuration $3d^3$) [2] lead to the assumption that the same considerations which successfully described the effect of high pressure on ruby can also be used on Al_2O_3:Mn^{4+} [6]. Thus, in the general case the fluorescence lifetime of the R1 line for Mn^{4+} in corundum can be expressed by [6]:

$$\tau_R = K n^{-1} W(^2E)^{-2} f_R^{-1} \tag{1}$$

$W(^2E)$ and f_R are the wavenumber and oscillator strength for the R1 line respectively. n is the refractive index for the corundum crystal. K is a constant and has the value of 0.3698 which was obtained by fitting (1) to normal pressure for τ_0 (0.0008 s) [7] using $(f_R)_0$, n_0 and $W(^2E)_0$ for the $^2E(\bar{E}) \rightarrow {}^4A_2$ transition. The mentioned similarity between Al_2O_3:Mn^{4+} and ruby crystal leads to the conclusion that the pressure-induced oscillator strength for the

R1 line and refractive index for Al_2O_3:Mn^{4+} is the same as for ruby crystal, so one has $f = (1200 - 7.2P) \times 10^{-9}$ [6] and $n = 1.765 - 5.5 \times 10^{-5}P$ [8] (pressure P is in kbar).

The pressure dependence of the wavenumber of ^2E for Mn^{4+} in Al_2O_3 can be expressed as a pressure dependence of the mentioned level for any $3d^{3+}$ ion in corundum [9]:

$$W(^2\mathrm{E}) = \{6783 + 6783 \times [k^{-S_0} - 1]\}^{-1} \times 10^8 [\mathrm{cm}^{-1}] \tag{2}$$

where k represents the linear compression rate defined as a ratio of the distance between the central metal ion and the ligand at any normal pressure (R/R_0). From low pressure experiments with $A = 2.213$ kbar Å^{-1} [3], B_0 (isothermal bulk modulus) $= 2504.1$ kbar [9] and $\Delta\lambda \ll \lambda$, the value of 0.5 is obtained for S_0 from $S_0 = 3B_0(\lambda_0 A)^{-1}$ [9]. k can be calculated for the corundum structure using a Murnaghan equation [10, 11], where pressure P is expressed in kbar:

$$k = (0.001597P + 1)^{-0.0833}. \tag{3}$$

Inserting in (1) the mentioned relation for: the oscillator strength, refractive index pressure dependence, constant K, wavenumber of ^2E and after rearranging τ_R can be expressed as

$$\tau_R = 3.698 \times 10^{-8}[1.765 - 5.5 \times 10^{-5}P]^{-1}[6783 + 6783(k^{-S_0} - 1)]^2[1200 - 7.2P]^{-1} \text{ [s]}. \tag{4}$$

Equation (4) was used for calculating the fluoresence lifetime for the R1 line. Reasonable agreement of the calculated and measured values were observed. Deviations between the calculated and measured data may be due to the simplicity of the used model, particularly due to the used estimation that the increase of τ is primarily caused by changes in the wavenumber of the R1 line, compression rate and refractive index of the crystal. Therefore, in further theoretical investigation the effect of other relevant factors on τ must be considered.

4. Conclusion

High pressure has a significant effect on the fluorescence lifetime τ for the R1 line, $^2E(\bar{E}) \rightarrow {}^4A_2$ transition. The study shows that τ rapidly increases with pressure. At 100 kbar the fluorescence lifetime is about 3.2 times longer than at normal pressure. The study shows that increase of τ is primarily caused by a rapid change in the wavenumber of the R1 line, compression rate and refractive index of the crystal. The presented measurements agree qualitatively with the theoretically predicted increase in τ with pressure.

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