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Variations in the oscillator strength of the $^7F_0 \rightarrow {}^5D_0$ transition in Eu^{3+}: Y_2SiO_5 single crystals

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ABSTRACT

We report on the low temperature properties of the $^7F_0 \rightarrow {}^5D_0$ transition in Eu^{3+}: Y_2SiO_5 in a series of single crystals grown under different conditions. Inhomogeneous linewidths, peak absorption coefficients and homogeneous linewidths have been determined for ions in the two sites of the crystalline structure. Unexpected and strong variations of the peak absorption coefficients are observed for ions in site 1, but not in site 2. We attribute this effect to a combination of changes in inhomogeneous broadening and oscillator strength.

1. Introduction

Rare earth (RE) ions doped crystals are extensively used and studied for photonic applications. In particular, Eu^{3+} ions are widely found in red phosphors or as sensitive probes of their local environment for fundamental material studies. Recently, RE doped crystals have appeared as promising materials for solid state light–matter interfaces and processors in the field of quantum information processing (QIP) [1,2]. This is due to the long coherence lifetimes of the optical and spin transitions of RE ions at liquid helium temperature, which allow long lived superposition states to be created and manipulated [3,2]. Quantum storage, for example, has been demonstrated in several materials [4–7]. Eu^{3+} ions inserted into Y_2SiO_5 (YSO) crystals have been considered for QIP applications because of the long coherence lifetime (T_2=2.6 ms) or equivalently, the narrow homogeneous linewidth $\Gamma_h = 1/\pi T_2 = 122$ Hz of the $^7F_0 \rightarrow {}^5D_0$ transition [8]. In addition, the long ground state hyperfine coherence lifetime, up to 6 h [9–11], and the large ground and excited state hyperfine splitting are favorable to long storage time, multimode quantum memories [12–15].

The spectroscopy of Eu^{3+}: YSO crystals was reported in depth in Ref. [16]. Anisotropic absorption, fluorescence lifetimes and ^7F_J structures were studied as well as inhomogeneous and homogeneous linewidths for different Eu^{3+} concentrations and as a function of temperature. In Ref. [17], it was also suggested that growth conditions can modify the inhomogeneous broadening and coherence lifetimes in this material.

The main drawback of the $^7F_0 \rightarrow {}^5D_0$ transition is its low oscillator strength (1.3×10^{-8}), one order of magnitude lower than for other RE transitions used in QIP [18]. This low oscillator strength can be understood from selection rules. Indeed, in the framework of the Judd Ofelt theory, $J = 0 \leftrightarrow J = 0$ transitions are forbidden [19–21]. However, this selection rule is bypassed in many materials because of additional mechanisms: the breakdown of the closure approximation, the Wybourne–Downer process [22], and the so-called J-mixing, i.e. the mixing of the wave functions of $J \neq 0$ states with those of $J=0$ states by even parity terms of the crystal field [23–25]. Quantum storage efficiency is strongly dependent on the peak absorption α_0 of the absorbing transition and it is thus crucial to use hosts in which α_0 is as large as possible [1,2,26]. This is especially true for the weak $^7F_0 \rightarrow {}^5D_0$ transition of Eu^{3+} doped crystals.

In this paper, we report on large variations of the peak absorption coefficient for the $^7F_0 \rightarrow {}^5D_0$ transition in Eu^{3+}: YSO single crystals as the growth conditions were changed. This effect is only observed for ions in site 1 of the crystal structure, whereas ions in site 2 have identical properties in all samples. We discuss different mechanisms that could explain this result, using high resolution and coherent optical spectroscopy.

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2. Experimental

Several Eu^{3+}: YSO crystals (samples 1,3–7) were grown by the Czochralski method using an inductively heated iridium crucible. The starting oxides were at least of 99.99% purity (Alfa Aesar). Rather than starting the growth from a powder mixture, we used YSO ceramics obtained by solid state reaction as the starting material. Crystals were pulled from the melt along the [010] direction under nitrogen atmosphere. The crystals obtained were 1 in. in diameter, colorless and free from cracks. All boules were then oriented by Laue x-ray diffraction, cut perpendicular to the *b*-axis with a precision better than 1°, and polished to an optical finish.

Samples 1, 3 and 4 were grown from a stoichiometric ceramic. Sample 5 was grown from two previously prepared and purposely ground Y_2SiO_5 single crystals (boules 3 and 4). As the starting materials were doped with 0.1% Eu^{3+}, the europium concentration for sample 5 is lower, around 0.08% because of dopant segregation. Samples 6 and 7 were grown with additives for a better control of stoichiometry. Samples 2 and 8 properties have been taken from Ref. [16].

The Y_2SiO_5 host crystallizes in a monoclinic structure belonging to the space group C_{2h}^6 with eight formula units per unit cell. In this crystal Eu^{3+} ions substitute Y^{3+} ones in two sites of C_1 symmetry, with coordination numbers of 6 and 7 [27]. The optical and hyperfine level structures of Eu^{3+} in these two C_1 sites have been extensively studied [16,28,29]. The YSO crystal is biaxial. The crystallographic axis of order 2, *b*, is one of the principal dielectric axes, with the other two lying in the *a*–*c* plane and labeled *D*1 and *D*2. *D*1 is at 78.7° from the *a*-axis and 23.8° from the *c*-axis [30,31].

Optical experiments were performed in bath or closed cycle cryostats depending on the temperature required. The laser wavelength was centered at 580.038 nm and 580.2 nm (vacuum) in resonance with the Eu^{3+} $^7F_0 \rightarrow {}^5D_0$ transition for sites 1 and 2 respectively. Absorption coefficients were measured by monitoring the transmitted intensity of a 1 MHz linewidth dye laser (Coherent 899–21) at 15 K. Photon echo experiments were performed using 2 μs long pulses focused to a 100 μm diameter spot in the crystal. The laser power was 30 mW and the temperature was varied between 1.5 K and 7 K. An acousto-optic modulator (AOM), operating in a double pass configuration, provided pulse shaping of the excitation light. In order to minimize hole burning effects, the laser was continuously scanned over 1 GHz in 2 s.

3. Results

Typical Eu^{3+}: Y_2SiO_5 absorption spectra are presented in Fig. 1a. It clearly shows the anisotropic behavior of the absorption, which varies according to the polarization of light in the *D*1 – *D*2 plane. From these low temperature measurements, we determined the inhomogeneous linewidths and the peak absorption coefficients α_0 for all of our samples (Table 1). Large variations of α_0 are observed for site 1 in crystals of identical Eu^{3+} concentration, whereas α_0 is much more constant for ions in site 2 (Table 1, Fig. 2). For example, for 0.1% Eu^{3+}: YSO and light polarized along *D*1, α_0 is 37%, 34% and 6% lower for samples 3, 6 and 7 respectively, in comparison to sample 8. In the same samples, for site 2, α_0 is lower by only 18%, 6% and 6% with respect to Ref. [16]. In the following, we consider different possible explanations for the unexpected behavior of site 1:

1. Light is not polarized along the direction of maximum absorption.
2. The inhomogeneous broadening of the transition is varying.
3. Eu^{3+} concentrations in the crystals differ.
4. The transition oscillator strengths change from sample to sample.

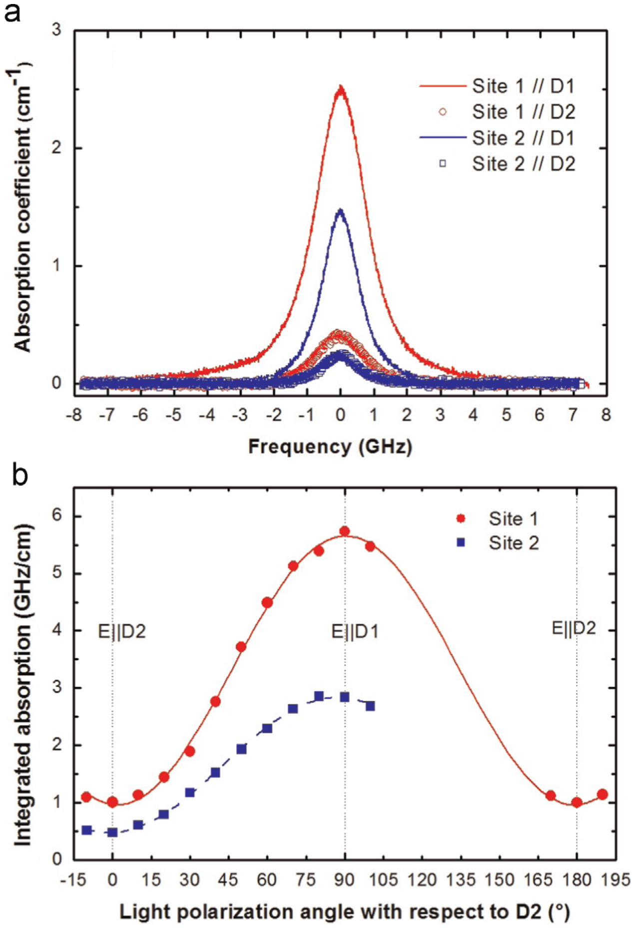

Fig. 1. Absorption of the $^7F_0 \rightarrow {}^5D_0$ transition in 0.1% Eu^{3+}: YSO for sites 1 and 2 at 15 K. (a) Spectra obtained for light polarized along *D*1 or *D*2 axes. (b) Integrated absorption coefficient as a function of the polarization angle with respect to *D*2.

First, monoclinic crystals like Y_2SiO_5 are biaxial and have three different refractive indices for light polarized along their principal dielectric axes. The extrema of absorption or fluorescence intensity are not necessarily obtained for light polarized along these principal axes [32]. However, in Eu^{3+}: YSO, both sites of Y_2SiO_5 present the largest (lowest) absorption for the $^7F_0 \rightarrow {}^5D_0$ transition when the incident light is polarized along *D*1 (*D*2) (Fig. 1b). These results confirm those of Könz et al. [16]. Eu^{3+} absorption varies by factors of about 4 and 6 between light polarized along *D*1 or *D*2 for site 1 and 2 respectively. However, Fig. 1b clearly shows that even a few degrees of misalignment could not explain the large variations of site 1 peak absorption coefficients for light polarized along *D*1. The same conclusion was reached when considering possible misalignments in the *D*1 – *b* plane.

We next investigated the transition inhomogeneous linewidth (Γ_{inh}), which affects peak absorption coefficients and is also a probe of crystal quality. Although the peak absorption coefficient strongly varies with polarization, inhomogeneous linewidths were found constant within 5% for light polarized along *D*1 or *D*2. The inhomogeneous linewidth increases with Eu^{3+} concentration for both sites (Table 1). For site 1, a linear dependence of Γ_{inh} on Eu^{3+} concentration with a slope of 21 GHz/unit concentration (expressed in mole %) has been reported [16]. This broadening arises from induced strains due to intrinsic defects and to the substitution of Y^{3+} by Eu^{3+} ions, which have different ionic radii (IR (Eu^{3+}, VI): 0.950 Å, IR (Y^{3+}, VI): 0.892 Å [33]). Absorption lineshapes were found to be Lorentzian for all samples, which is consistent with an inhomogeneous broadening induced by isolated point defects

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