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Analysis of the optical and magnetooptical spectra of non-Kramers $Pr^{3+}(4f^2)$ in $Y_3Al_5O_{12}$ complemented by crystal-field modelling

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ABSTRACT

The spectra of the absorption, luminescence, magnetic circular dichroism (MCD) and magnetic circular polarization of luminescence (MCPL) in the praseodymium yttrium garnet aluminate Pr^{3+}:YAG have been studied within the visible and near ultraviolet (UV) spectral range for temperature $T=90$ K and 300 K. Analysis of the spectral and the temperature dependences of the magnetooptical and optical spectra has made it possible to identify the optical 4f→4f transitions occurring between the Stark sublevels of the $^1D_2$, $^3P_0$ and $^3H_4$ multiplets in Pr^{3+}:YAG. It has been shown that for Pr^{3+}:YAG in the MCD within the UV spectral range for the absorption bands due to allowed 4f→5d transitions, and also in the MCPL for the luminescence bands, respectively, due to forbidden 4f→4f transitions within the visible spectral range, a significant role is being played by the effect of quantum mechanical "mixing" of the states of the three lowest energy Stark singlets of the ground state $^3H_4$ multiplet of the non-Kramers RE Pr^{3+} ion. A parameterized Hamiltonian defined to operate within the entire $4f^2$ ground electronic configuration of Pr^{3+} was used to model the experimental Stark levels, their irreducible representations (irreps) and wave functions. The crystal-field parameters were determined through use of a Monte-Carlo method in which nine independent crystal-field parameters, B_q^k, were given random starting values and optimized using standard least-squares fitting between calculated and experimental levels. The final fitting standard deviation between 61 calculated to experimental Stark levels is 18 cm^{-1}.

1. Introduction

The optical and magnetic properties of the rare-earth ions $RE^{3+}(4f^n)$ incorporated into various host materials have been investigated through analyses of their spectra [1,2]. The interpretation of the optical and magnetic features demonstrate that the RE^{3+} are effective microscopic probes in understanding the symmetry characteristics of the sites surrounding the ion, and their magnetic behavior in the media [3,4]. From the information so acquired, it has been possible to design and fabricate these materials into integral components essential in operating photonic devices [5]. The physical, mechanical, and thermal characteristics of the host are continually upgraded in the search for more efficient and less expensive material. Likewise, novel hosts are sought to improve and extend the optical response of these devices. The demand is promoted by rapid technical developments in communication, detection, and surveillance required by the medical, military, and commercial communities. An example of this evolution is the successful transition from the host single-crystal garnet to the ceramic form now used as a popular laser host material [6,7]. Recently, methods of synthesis and characterization have been directed toward new physical host forms such as nanowires of ZnO and ZnS doped with Tb^{3+}, Eu^{3+}, Er^{3+}, and Ho^{3+} that are presently being tested as components in magnetooptical devices [8].

The observed sharp-line absorption and emission spectra due to the $RE^{3+}(4f^n)$ ions, especially those incorporated into insulators (fluorides and oxides), and wide band-gap semiconductors (GaN and AlN), extend over a wide wavelength range from the ultraviolet (UV) to the infrared (IR) [9–11]. These spectra represent transitions within the $4f^n$ subshell of the ion [12,13]. According to electric dipole (ED) selection rules, these transitions are forbidden within the $4f^n$ subshell since there is no change in the orbital angular momentum l [14]. However, their observation, which appears as relatively weak spectra, is attributed to the mixing of states of opposite parity through the odd terms in the crystal-field

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Hamiltonian [12,13]. Transitions between levels in the $4f^n$ configuration and levels in the first excited configuration $4f^{n-1}5d$, can be observed in the UV spectrum if the transmission characteristics of the host lattice permit. The absorption and emission spectra involving the 5d levels of Ce^{3+}, Pr^{3+}, and Tb^{3+} have been investigated to some extent in fluoride and garnet hosts [9,15,16]. Within the $4f^n$ subshell, magnetic dipole (MD) transitions are also allowed between limited states (most likely between the ground and first excited $^{2S+1}L_J$ manifolds) [12,17].

Several studies have appeared in the past that have modeled the crystal-field splitting of the energy levels of $Pr^{3+}(4f^2)$ in single-crystal $Y_3Al_5O_{12}$ (YAG) [16–18]. Gruber et al. [16] reported an algorithm based on ED selection rules for D_2 symmetry that proved useful in assigning the irreproducible representations (irreps) of the crystal-field split energy (Stark) levels of the $Pr^{3+}(4f^2)^{2S+1}L_J$ multiplet manifolds, where a majority of the Pr^{3+} ions were found to substitute for Y^{3+} in D_2 sites during crystal growth. In D_2 symmetry RE^{3+} having an even number of equivalent electrons in the $4f^n$ subshell, are identified as non-Kramers ions. The crystal field splits each manifold J of these ions into $(2J+1)$ singlets with the resulting singlets labeled Γ_1, Γ_2, Γ_3, and Γ_4. ED selection rules preclude transitions between singlets having the same irrep. A set of closely spaced non-degenerate singlets is called aa a "quasi-doublet" [4]. Examples of "quasi-doublets" are found in the ground-state manifold of $Tb^{3+}(4f^8)$ and $Ho^{3+}(4f^{10})$ in garnets and oxides, where they exhibit large values of magnetic, magneto-elastic and magneto-optical effects in a magnetic field H [4,19]. So far, no "quasi-doublets" have been identified in the ground state manifold, $^3H_4$, in $Pr^{3+}(4f^2)$ in similar host materials.

More recently, Moune et al. [20] reported an analysis of the energy levels of Pr^{3+} in the ceramic form of YAG. By varying the Pr^{3+} concentration in the host, they were able to reduce the number of "extra" spectral lines attributed to Pr^{3+} in minority sites. The Stark level irreps for Pr^{3+} in D_2 sites were assigned by a method similar to one reported earlier [16]. The similarity between the Pr^{3+} spectra in the single-crystal and ceramic form of YAG has led to the use of the ceramic form as the laser host of choice for other RE^{3+} activator ions due to the optical quality and the reduced cost of preparation. However, some of the irrep. assignments made to the Stark levels and the crystal-field modeling results reported by Moune et al. [20] differ from those reported by Gruber et al. [16]. To verify the results obtained by both groups, we analyzed the experimental splitting and irrep. assignments reported by both groups to see if the host form could provide some explanation. The crystal-field splitting calculations utilize a Monte Carlo method to map out the local fitting minima of the crystal-field parameter space [21,22]. To this effect, the nine independent crystal-field parameters, B_q^k, were given random starting values and optimized using standard least-squares fitting between calculated and experimental levels. A parameterized Hamiltonian defined to operate within the entire $4f^2$ ground electronic configuration of Pr^{3+} was used to model the experimental Stark levels, their irreducible representations (irreps) and wave functions. Each local minimum determined from the fitting calculation corresponds to a specific ordering of the energy level irreps. Because there are a number of irrep. assignments made to closely spaced Stark levels whose separation is much less than the overall fitting standard deviation, the crystal-field calculations are unable to unambiguously determine the correct irrep identification for these levels. The best solution, which we used to determine wave functions for the magnetooptical calculations, has an overall standard deviation of 18 cm^{-1}, and broadly corresponds to the irrep assignments made by Gruber et al. [16] and Moune et al. [20]. However, a number of closely spaced singlet Stark levels are reversed in energy from the results reported by either group. The final set of CFP used in the present study is similar to the sets reported by Moune et al. [20] and Gruber et al. [16] (after the appropriate parameter transformation for different orientations of the quantization axes in D_2 symmetry [23]). Moreover, we found that CEF reported by Nekvasil et al. [24] and Fidancev et al. [25,26] did not improve the agreement between the calculated Stark and experimental assignments. From our modeling studies, it is clear that an independent experimental method of analysis and irrep assignment is required.

As an example, we have resolved part of the uncertainty in the irrep. assignments of closely spaced Stark-level singlets in non-Kramers $Pr^{3+}(4f^2)$ in YAG by an analysis of the magneto-optical spectra of multiplet manifolds such as $^3H_4$, $^1D_2$, and $^3P_0$, where sufficient resolution of the data is possible for analysis. We include in the present study the magnetic circular dichroism (MCD) in absorption and the magnetic circular polarization of the luminescence (MCPL). The analysis and modeling of these multiplets is relatively simple for given the number of Stark level transitions and selection rules operated on the $Pr^{3+}(4f^2)$ in an external magnetic field H. The Van Vleck "mixing" of the wave functions of closely spaced singlets in the magnetic field leads to the appearance of the magneto-optical properties useful in finding consistencies between the calculated and the experimental irreps [19]. This approach has been used by others as well [27,28] to interpret the magnetic and magneto-optical features of paramagnetic crystals of garnets, both aluminates and gallates doped with non-Kramers RE ions. The two lowest-energy Stark singlets in $^1D_2$ (16409 cm^{-1} and 16416 cm^{-1}) obtained from our present data (see Table 1) can be viewed as a "quasi-doublet", while the three lowest-energy singlets in $^3H_4$ (0, 19, and 50 cm^{-1}), that are relatively isolated from the rest of the manifold in Table 1, can be treated as a "quasi-triplet" according to Nekvasil et al. [24]. The energies of the Stark singlets and the irreps listed in Table 1 come from our reexamination of the experimental levels given in Ref. [16] and the wave functions that match each irrep. come from our present crystal-field splitting calculations for the multplets $^3P_0$, $^1D_2$, and $^3H_4$.

2. Measurement technique and samples

Single crystals of praseodymium–yttrium garnet–aluminate Pr^{3+} in $Y_3Al_5O_{12}$ (YAG:Pr^{3+}) were grown by the method of spontaneous crystallization from a solution-melt (Czochralski

Table 1
The energies and wave functions of the some Stark sublevels $^3H_4$, $^3P_0$, and $^1D_2$ multiplets.

The energies of Stark sublevels (in cm^{-1})	Irreducible representations of the D_2 group	Wave functions in the $\|J, M_J\rangle$ -basis
0	Γ_3	$\|\Psi_1\rangle = -0.66\left(\|^3H_4, 3\rangle - \|^3H_4, -3\rangle\right)$
19	Γ_1	$\|\Psi_2> = 0.69\left(\|^3H_4, 2\rangle + \|^3H_4, -2\rangle\right)$
50	Γ_4	$\|\Psi_3\rangle = -0.67\left(\|^3H_4, 3\rangle + \|^3H_4, -3\rangle\right)$
515	Γ_2	$\|\Psi_4\rangle = -0.62\left(\|^3H_4, 2\rangle - \|^3H_4, -2\rangle\right)$
528	Γ_3	$\|\Psi_5\rangle = 0.65\left(\|^3H_4, 1\rangle - \|^3H_4, -1\rangle\right)$
546	Γ_1	$\|\Psi_6\rangle = -0.95\|^3H_4, 0\rangle + 0,18\|^3H_4, -4\rangle$
560	Γ_4	$\|\Psi_7\rangle = 0.65\left(\|^3H_4, 1\rangle + \|^3H_4, -1\rangle\right)$
766	Γ_2	$\|\Psi_8\rangle = -0.62\left(\|^3H_4, 4\rangle - \|^3H_4, -4\rangle\right)$
780	Γ_1	$\|\Psi_9\rangle = 0.65\left(\|^3H_4, 4\rangle + \|^3H_4, -4\rangle\right)$
16409	Γ_1	$\|\Psi_{64}\rangle = 0.93\|^1D_2, 0\rangle - 0,24\|^3P_2, 0\rangle$
16416	Γ_2	$\|\Psi_{65}\rangle = -0.67\left(\|^1D_2, 2\rangle - \|^1D_2, -2\rangle\right)$
20528	Γ_1	$\|\Psi_{69}\rangle = 0.99\|^3P_0, 0\rangle$