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Photoluminescence and Circularly Polarized Luminescence Spectra of Optical Active Terbium (III) ODA Crystals and Complex-doped SiO_2 Xerogels

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ABSTRACT : Highly resolved total luminescence (TL) and circularly polarized luminescence (CPL) spectra of trigonal $Tb(ODA)_3$ single crystals and teteragonal Tb-cyclen derivatives complex-doped SiO_2 xerogels are measured at room temperature and 10 K to discuss fine structures and CPL spectral patterns specific to site symmetry of the chiral complexes.

Keywords : luminescence, CPL, terbium (III) , ODA, cyclen

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1. INTRODUCTION

Quantum confinements effects in restricted media of nano-meter sizes have been currently reported in II-VI semiconductor nanoparticles [1]. In the advancement of nanotechnology, optical characterization of new materials properties using unusual spectroscopic methods has become quite essential in nanotechnology [2]. We have recently reported strong and broad luminescence of sol-gel silica glasses doped with transition metal ions ((M= Ti^{4+}, V^{5+}, Cr^{6+}, Zr^{4+}, Nb^{5+}, Mo^{6+}, Hf^{4+}, Ta^{5+}, W^{6+} etc)[3]. They are due to LMCT (ligand-to-metal charge transfer) transitions of transition metal ions with closed shell electronic structures which were generated in a long term of redox reactions. Some vanadium and chromium complexes dispersed in sol-gel silica glasses were found to show various luminescence spectra due to different valences. Physico-chemical control of valence can be done by change of thermal annealing conditions [4]. In sol-gel zirconia thin films doped with CdS: Mn^{2+} or Eu^{3+}, surface bound defects of nanocystals in the restricted ceramic host were observed [5]. Numerous reports on luminescence of Eu^{3+} and other rare earth (RE) ions doped in sol-gel SiO_2 glasses appeared in the last decade [6]. New information is available for RE (15-crownether –5) complexes dispersed into sol-gel glasses[7].

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In this paper, photoluminescence (total luminescence , TL) and circularly polarized luminescence (CPL) spectra of chiral Tb(III) cyclen derivative complexes embedded in xerogel SiO2 are reported in order to investigate electronic structures of rare earth complexes in nano-porous rigid matrices. Using circularly polarized luminescence spectroscopy, excited-states structures of chiral Tb(III) complexes were investigated as a function of temperatures between 10 and 300K [8]. In comparison with this, single crystals of tris (oxodiacetato)gadolinate(III)- terbate(III) mixed single crystals $Na3[Gd_{1-X}Tb_X(ODA)_3]$ $2NaBF_4$. $6H_2O$ were investigated by CPL spectroscopy[9]. Principal emission lines in the $^5D_4 \rightarrow {}^7F_J$ transition of two complexes are assigned to discuss molecular structures of the chiral complexes at low temperatures.

2. RESULTS AND DISCUSSION

We have been interested in luminescence of optically active metal complexes in solution. Excited-state chirality can be solely detected by CPL spectroscopy. Luminescence as well as lifetime measurements can supply us information on electronic structures of metal complexes in general, but configurational, conformational and vicinal effects of optical activity are considered in terms of the luminescence dissymmetry factor g and associated spectral changes of the CPL spectra. Preparation of materials and measurements of TL/CPL spectra are described elsewhere [8, 9]. TL(broken line) and CPL (solid line)spectra of Tb-(R)-cyclen derivative in methanol are shown in Fig. 1. The CPL spectra covering the principal $^5D_4 \rightarrow {}^7F_5$ transition represent three CPL peaks of positive

g-factors and two peaks of negative ones. Since the central Tb ion has a tetragonal axial symmetry with the coordination ligand, the observed CPL spectral pattern is characterized by the presence of three CPL peaks of different signs. The g-factor of the strongest peak at 18, 300 $cm^{-1}$was found to be +0.10.

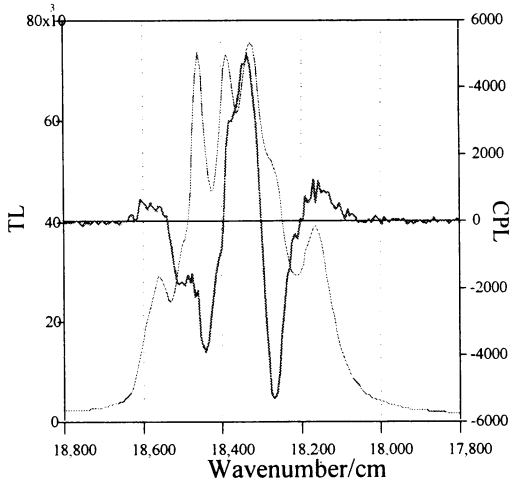

Fig.1 Total luminescence (TL broken line) and CPL (solid line) spectra of Tb(III)-R-cyclen derivative complex in methanol at room temperature in the $^5D_4 \rightarrow {}^7F_5$ transition

Fig. 2 shows luminescence (TL, broken line) and CPL (solid line) spectra in the $^5D_4 \rightarrow {}^7F_5$ transition of a Tb(III)-(S)-cyclen embedded in xero-gels at r.t. The positive CPL sign at 18300 cm^{-1} of R-enantiomer in Fig. 1 is reversed in sign in this figure by holding the three peaks pattern. The luminescence dissymmetry *g*-factor was found to be ~-0.02 at 18.300 cm^{-1} in xerogels at room temperature (r.t.). In solution this g value is–0.12. Since spectral profiles in solution and in xerogels are similar to each other, the chiral structure is partially preserved in xerogels. By lowering the temperature from 300 K to 10 K, the broad band due to the host silica , centered at 20, 000 cm^{-1} , was found to be more increasing in intensity in comparison with Tb^{3+} emission

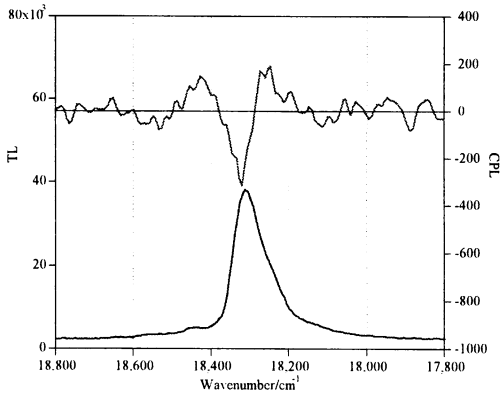

Fig.2 TL (broken line) and CPL (solid line) in the $^5D_4 \rightarrow {}^7F_5$ transition of Tb-(S)-cyclen in Xero-gel at r.t.

TL/CPL spectra of trigonal dihedral $Tb(ODA)_3$ single crystals demonstrate fine structures due to configurational optical activity. Therefore, we can not detect CPL signals in solution and from ortho-axial crystal faces by consideration of polarization configurations [9].

Single crystal Tb $(ODA)_3$ represents a different CPL spectral pattern Fig. 3. There are two prominent peaks with different CPL signs and the same intensity at r.t. By lowering the temperature to 10K, the degeneracy of these two peaks is lifted to deduce four peaks of two positive and two negative CPL signs , as shown in Fig.3. Fig. 4 displays spectral profiles in all the $^5D_4 \rightarrow {}^7F_J$ (J=0, 1, 2....6) transition at 10 K. We also notice the presence of a single peak at 14, 700 cm^{-1} due to the $^5D_4 \rightarrow {}^7F_0$ transition. If we neglect a small shoulder at a higher energy side, we could assume the presence of a single site in luminescence and CPL spectra. This is consistent with the crystallo-graphical assignment of Z=1 and the calculation of the lowest excited state [9]. The g-factor was found to show an unusual temperature change at about 120 K. This is because of the distortion of the trigonal dihedral structure in D_3 point symmetry through the structural phase transition at low temperature. These results give evidence of the fact that CPL-technology can reveal subtle structural changes in the excited state of chiral Tb(III) complexes.

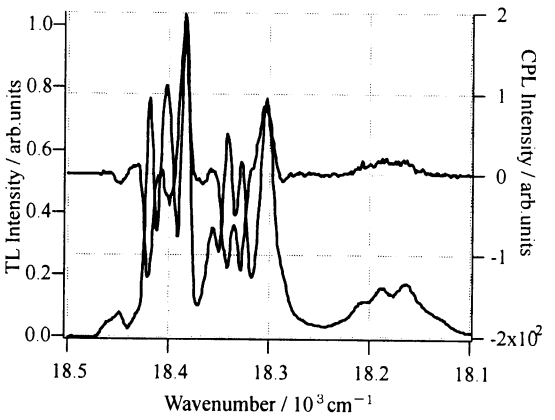

Fig. 3 TL (broken line) and CPL (solid line) spectra of Tb $(ODA)_3$ single crystal in the $^5D_4 \rightarrow {}^7F_5$ transition at 10 K under an Ar^+ ion laser (488 nm) excitation.

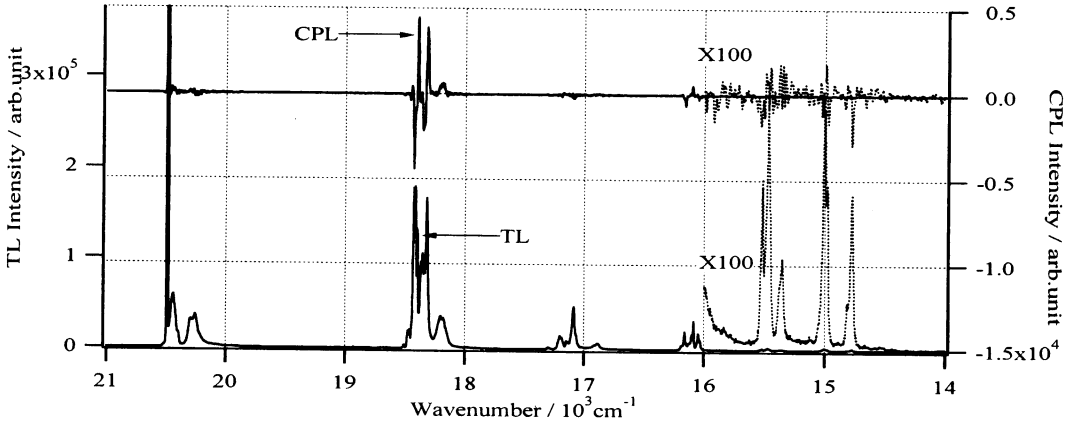

Fig.4 TL(lower half) and CPL (upper half) spectra of $Tb(ODA)_3$ single crystal in the $^5D_4 \rightarrow {}^7F_J$ (J=0, 1, 2....6) transition at 10K under an Ar^+ laser (488nm) excitation.

In summary, Tb(III) complexes are found to be stabilized in nano-porous and transparent xerogels . Luminescence/CPL spectral profiles of chiral Tb(III) complexes are characteristics of trigonal and tetragonal symmetry of the corresponding ODA and cyclen ligands, respectively.

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