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# Optical spectroscopy of $Pr^{3+}$ in the weberite, $NaGdSb_2O_7$: High covalence of $Pr^{3+}$–$O^{2-}$ bonding

A.M. Srivastava [a],*, S.J. Camardello [a], H.A. Comanzo [a], M. Trevisani [b], M. Bettinelli [b]

[a] GE Global Research, One Research Circle, Niskayuna, NY 12309, USA
[b] Luminescent Materials Laboratory, Department of Biotechnology and Instm, Udr Verona, University of Verona, Strada Le Grazie 15, I-37134 Verona, Italy

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ABSTRACT

The spectroscopic properties of the $Pr^{3+}$ ion in $NaGdSb_2O_7$ are discussed in this paper. The host crystallizes in the orthorhombic weberite crystal structure with the general formula, $A_2B_2O_7$. The $Pr^{3+}$ luminescence is dominated by emission transitions emanating from the $^1D_2$ state. Transient fluorescent decay of the $Pr^{3+}$ luminescence is indicative of random distribution of $Na^+$ and $Gd^{3+}$ ions in $NaGdSb_2O_7$. The remarkable feature in the spectroscopic properties of the $Pr^{3+}$ ion is the very low energy of the interconfiguration $Pr^{3+}$ $4f^2 \rightarrow 4f^15d^1$ excitation transition (3.63 eV; 342 nm). The large red shift of the $Pr^{3+}$ $4f^15d^1$ configuration is connected with significant covalent contribution to the crystal field and the high covalence of the $Pr^{3+}$–$O^{2-}$ bonding is tentatively assigned to chemical covalent bonding within the $A_3B$ tetrahedral moieties which surround the $O_{8h}^{2-}$ anion in the weberite structure. A comparative study of the optical properties of $Pr^{3+}$ in $NaGdSb_2O_7$ and $La_2Hf_2O_7$, which crystallizes with the pyrochlore structure, is also presented.

## 1. Introduction

The crystal structure of weberite with the general formulation $A_2B_2X_7$ (A and B are cations and X is either $O^{2-}$ or $F^-$) and space group Imma is an anion-deficient fluorite-related superstructure [1]. The A-cations of the weberite structure occupy the 4a and 4d atomic positions with site symmetry, $C_s$ (m). The primary coordination sphere of the two A-cations is very different. The cation occupying the atomic position 4d ($A_{4d}$) occur in distorted cube coordination with two different $A_{4d}$–X bond-lengths. The coordination can be described as (4+4). The cation occupying the atomic position 4a ($A_{4a}$) are in di-hexagonal pyramidal coordination with three different $A_{4a}$ –X bond-lengths. This coordination polyhedron can be described as being (2+4+2). The B-cation is present in six-fold coordination of oxygen ligands.

The antimonates $NaLnSb_2O_7$ (Ln=La, Pr–Dy) crystallize in the orthorhombic weberite structure [2]. X-ray diffraction data indicate random distribution of the $Na^+$ and $Gd^{3+}$ ions over the 4*a* and 4d sites. The luminescence of pure and $Eu^{3+}$, $Bi^{3+}$ and $Tb^{3+}$ doped $NaGdSb_2O_7$ was reported by Srivastava [3]. The $Eu^{3+}$ luminescence data confirmed the random distribution of the A-site cations while the $Bi^{3+}$ ($6s^2$) luminescence confirmed the very different coordination polyhedral of the two A-site cations. The spectroscopic properties of $Tb^{3+}$ (and $Eu^{3+}$) ion indicated that the crystal-field strength was strong at the site of the rare earth ion in $NaGdSb_2O_7$.

In this paper we examine the optical properties of the $Pr^{3+}$ ion in $NaGdSb_2O_7$. Our goal is to elucidate the influence of chemical bonding and cation distribution (over the 4a and 4d sites) on the spectroscopic properties of the $Pr^{3+}$ ion. Another goal of this paper is to provide a comparative study between the optical properties of the $Pr^{3+}$ ion substituted in materials with the weberite and the cubic pyrochlore structures. This comparative study is initiated because (1) both structures can be considered as superstructures of the fluorite lattice ($AX_2$) [1] and, (2) we have systematically examined the optical properties of rare earth and transition metal ions in the pyrochlore family of materials [4–9], which facilitates such a comparative study.

## 2. Experimental

Polycrystalline samples of pure $NaGdSb_2O_7$ and doped with $Pr^{3+}$ (substituting for $Gd^{3+}$) were synthesized using a solid state reaction from $NaHCO_3$ (Aldrich, 99.5%), $Gd_2O_3$ (Aldrich, 99.99%), $Sb_2O_3$ (Aldrich, 99.999%) and $Pr_6O_{11}$ (Aldrich, 99.999%). An excess of 10% of $Sb_2O_3$ was used to ensure the formation of the pure phase. Appropriate amounts of the reagents were mixed and heat treated in a horizontal furnace in air for 5 h at 650 °C and 10 h at 950 °C. The samples were reground and heated at 1100 °C for 5 h, reground and finally heated at 1200 °C for an additional period of 12 h.

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* Corresponding author.
*E-mail addresses:* srivastava@ge.com, srivastava@crd.ge.com (A.M. Srivastava).

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The presence of a $NaGdSb_2O_7$ single phase was checked by X-ray powder diffraction (XRPD).

Luminescence measurements at room and low temperatures were done as previously described [10]. The spectra have been corrected for the wavelength dependent variations in the Xe lamp intensity and for the monochromator and photomultiplier response. Room temperature decay curves were measured with a Fluorolog 3 (Horiba-Jobin Yvon) spectrofluorimeter, equipped with a Xe ozone-free pulsed lamp (450 W), a double excitation monochromator (Czerny-Turner), a single emission monochromator (mod. HR320) and a photomultiplier in photon counting mode for the detection of emitted signal (mod. R928P).

## 3. Results and discussions

### 3.1. *The excitation spectrum of $Pr^{3+}$ activated $NaGdSb_2O_7$*

Fig. 1 exhibits the room temperature diffuse reflectance spectrum (DRS) of pure $NaGdSb_2O_7$ along with the excitation spectrum of the $Pr^{3+}$ doped composition. The DRS shows an optical absorption edge at 280 nm (4.43 eV). This is consistent with the low temperature excitation spectrum that exhibits a broad band centered near 280 nm [3].

Fig. 1 shows that the host lattice excitation band is also present in the excitation spectrum of $NaGdSb_2O_7$:$Pr^{3+}$. This indicates the occurrence of efficient energy transfer from the host lattice to the $Pr^{3+}$ ion. In the excitation spectrum, the $Pr^{3+}$ intraconfigurational excitation transitions, $^3H_4 \rightarrow {}^3P_J$ and $^3H_4 \rightarrow {}^1D_2$ can be identified (Fig. 1). Further, the excitation spectrum shows the presence of a broad-band centered near 330 nm. The energy of this band is determined more precisely by decomposing the room temperature excitation spectrum into a sum of Gaussians by the procedure previously described [11]. A satisfactory fit ($R^2 = 0.998$) was obtained when the excitation spectrum was decomposed into three Gaussians bands centered at 5.54 eV (224 nm), 4.38 eV (283 nm) and 3.63 eV (342 nm), respectively (see the inset in Fig. 1). The two high energy bands are assigned to the host lattice excitation transitions. The lowest energy band at 3.63 eV (342 nm) is assigned to the $Pr^{3+}$ $4f^2 \rightarrow 4f^15d^1$ excitation transition. This assignment can be further confirmed by examining the optical properties of $NaGdSb_2O_7$:$Pr^{3+}$ at low temperatures.

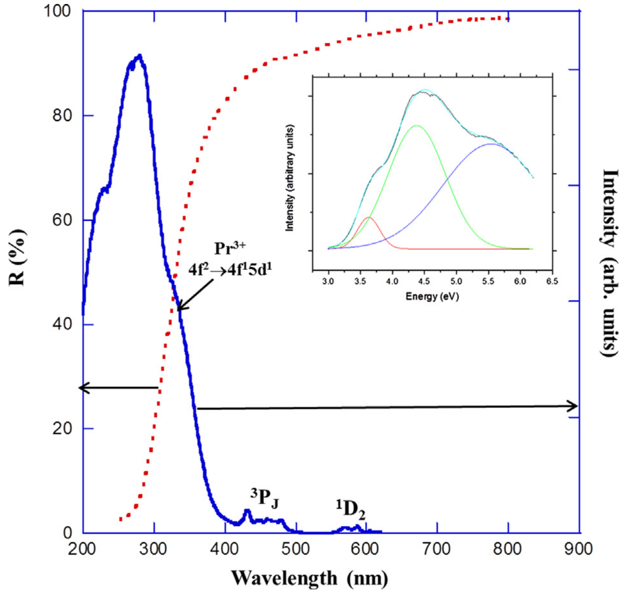

**Fig. 1.** The room temperature diffuse reflectance spectrum of pure $NaGdSb_2O_7$ and the excitation spectrum of $NaGdSb_2O_7$:0.1%$Pr^{3+}$. The inset shows the decomposition of the broad excitation band into three Gaussian functions (the black curve is the experimental data and the turquois is the Gaussian fitting; see text for details).

Fig. 2 exhibits the low temperature ($T = 10$ K) emission spectrum of $NaGdSb_2O_7$:$Pr^{3+}$ for $\lambda_{ex} = 270$ nm (host lattice excitation). The broad emission band centered near 600 nm is due to the host lattice luminescence [3]. Superimposed on host lattice emission band are sharp line transitions which are attributed to emission from the $Pr^{3+}$ $^1D_2$ state (see Section 3.3). Fig. 3 illustrates the excitation spectrum that is obtained when monitoring the emission at 550 nm and 652 nm, respectively. The former wavelength ($\lambda_{em} = 550$ nm) monitors the host lattice emission while the latter

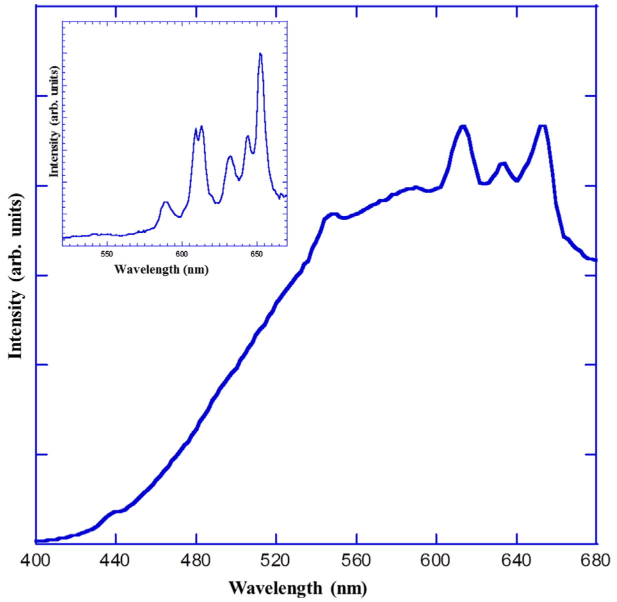

**Fig. 2.** The emission spectrum of $NaGdSb_2O_7$:0.1%$Pr^{3+}$ at $T = 10$ K ($\lambda_{ex} = 270$ nm). The inset shows the emission spectrum at room temperature for $\lambda_{ex} = 435$ nm ($^3H_4 \rightarrow {}^3P_J$).

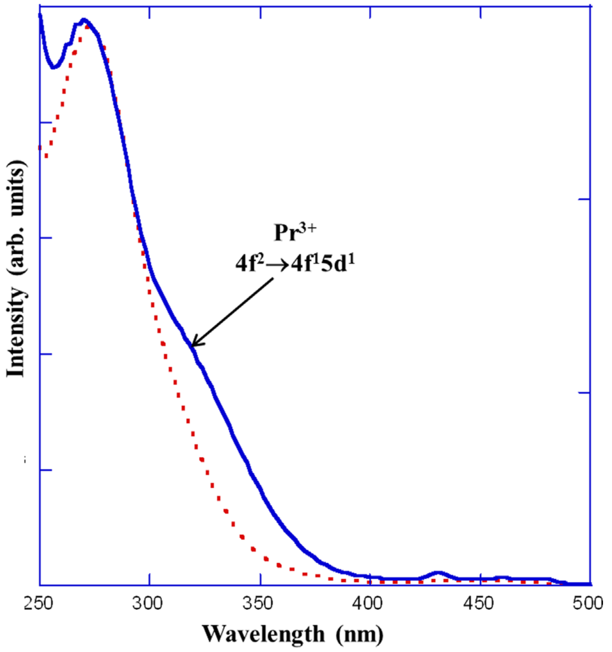

**Fig. 3.** The excitation spectrum of $NaGdSb_2O_7$:0.1%$Pr^{3+}$ when monitoring the host lattice emission at $\lambda_{em} = 550$ nm (red dotted curve) and the $Pr^{3+}$ $^1D_2$ emission at $\lambda_{em} = 653$ nm (blue solid curve) at $T = 10$ K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)