Luminescence excitation spectra of TbX$_3$ (X = Cl$^-$, Br$^-$, I$^-$)

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ABSTRACT

A systematic study of the excitation spectrum of TbX$_3$ (X = Cl$^-$, Br$^-$, I$^-$) is presented in this work. In general, the excitation spectra of TbX$_3$ can be divided into three major regions: (1) the short-wave host lattice absorption region, (2) the intermediate absorption region where the Tb^{3+} 4f^8 → 4f^{7}5d^1 interconfigurational excitation transition are located, and (3) the long-wave excitation region where the Tb^{3+} 4f^8 → 4f^8 intraconfigurational excitation transition are located. The high spin and the low spin components of the Tb^{3+} interconfigurational excitation transition are clearly identified in the case of TbCl$_3$. The luminescence of TbX$_3$ (X = Cl$^-$, Br$^-$, I$^-$) is dominated by emission transitions emanating from the Tb^{3+} ^{5}D$_4$ state. A comparative study of the optical properties of TbX$_3$ (X = Cl$^-$, Br$^-$, I$^-$) with the properties of the Tb^{3+} ion in several halide host lattices is presented. Further, a comparative study of the fundamental host lattice optical transitions in terbium halides and other halide materials is also presented.

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1. Introduction

The Tb^{3+} 4f^8 → 4f^{7}5d^1 interconfigurational excitation transition in solids consists of a spin allowed component [low spin (LS) {4f^8 [^{7}F$_6$] → 4f^{7}5d^1 [^{7}D]} and a spin forbidden component [high spin (HS)] {4f^8 [^{7}F$_6$] → 4f^{7}5d^1 [^{9}D]} [1]. The Hund's rule places the spin forbidden transition at lower energy. The results available in the archival literature on the interconfigurational excitation transition of the Tb^{3+} ion in solids has been analyzed by Dorenbos [1]. The experimental data provides for an average energy difference (ΔE^{ex}) between the LS ($\Delta S = 0$) and HS ($\Delta S \neq 0$) components of 0.78 ± 0.11 eV (for 19 compounds) [2]. This splitting, which arises from the Coloumb interaction between the 4f and 5d electrons, is termed exchange splitting. The splitting does not correlate with the 5d crystal field splitting but correlates with the centroid shift [1]. The energy difference between the LS and HS components decreases (almost linearly) with increasing covalency between the 5d electron and the host lattice ligands [1].

There are two aspects of the Tb^{3+} 4f^8 → 4f^{7}5d^1 interconfigurational excitation transition that is of interest to this work. First, as previously stated, the exchange splitting (ΔE^{ex}) is strongly dependent on the host lattice [1,3]. Secondly, the energy position of the Tb^{3+} LS excitation transition can be determined from the corresponding energy of the first Ce^{3+} 4f^1 → 5d^1 excitation transition [1,2]:

$$E\{Tb^{3+}; (LS)4f^8[^7F_6] \rightarrow 4f^75d^1[^7D]\} = E[Ce^{3+};$$
$$4f^1 \rightarrow 5d^1] + 1.66 \pm 0.12 \text{ eV} \quad (1)$$

However, since the exchange splitting is strongly dependent on the type of compound, it is not possible to determine the energy position of the Tb^{3+} (HS) 4f^8[^{7}F$_6$] → 4f^{7}5d^1[^{9}D] transition by the average energy difference (ΔE^{ex}) of 0.78 ± 11 eV that has been derived in Ref. [1] even if the energy position of the Tb^{3+} (LS) 4f^8[^{7}F$_6$] → 4f^{7}5d^1[^{7}D] transition is successfully located through Eq. (1). As shown in Ref. [3], it is possible to calculate the energy position of the HS transition from structural data.

An examination of the data complied in Ref. [1] shows a paucity of data on the energy position of Tb^{3+} spin allowed and spin forbidden interconfigurational excitation transitions in the halide family of materials (chloride, bromide and iodide). Thus, the only halides in which these transitions have been documented are the octahedrally coordinated [TbX$_6$]$^{3-}$ (X = Cl$^-$, Br$^-$) complex in acetonitrile [1]. A more recent paper on the excitation spectrum of hexachloroelpasolite, Cs$_2$Na(Y,Tb)Cl$_6$ presents a detailed analysis of the Tb^{3+} 4f^8 → 4f^{7}5d^1 interconfigurational transitions [4]. The motivation of this study is to identify the Tb^{3+} 4f^8 → 4f^{7}5d^1 interconfigurational transitions in the excitation spectra of pure TbX$_3$ (X = Cl$^-$, Br$^-$, I$^-$) materials.

2. Experimental

All samples of TbX$_3$ were procured from Aldrich and were 99.9% pure. Since the halides are highly hygroscopic, precaution was taken to minimize exposure to air and moisture during optical characterization. All sample manipulations were carried out in drybox.

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The low temperature ($T = 80$ K) excitation spectra were recorded as described in Ref. [5]. We also synthesized Ce^{3+} doped TbX_3 with the formulation, $Tb_{0.99}Ce_{0.01}X_3$ (X = Cl^-, Br^-, I^-), by the procedure described in Ref. [5].

3. Results and discussions

3.1. X-ray diffraction results and crystal structure data

The result of the X-ray diffraction, which was performed to confirm the phase present in the commercial materials, is summarized below:

3.1.1. TbCl₃
The X-ray diffraction pattern was matched to the orthorhombic structure of $TbCl_3$ that is reported in the JCPDS files. The literature data suggests that at room temperature and pressure, $TbCl_3$ crystallizes in the $PuBr_3$-type orthorhombic structure with space group D_{2h}^{17} (CmCm) [6]. In this structure, the metal ion is present in a bicapped trigonal prismatic coordination of eight anions.

3.1.2. TbBr₃
The strong lines in the X-ray diffraction pattern matched very well with the rhombohedral structure of $TbBr_3$ that is reported in the JCPDS files. A few weak peaks could be attributed to the orthorhombic form of $TbBr_3$. According to Ref. [7], $TbBr_3$ illustrates the rhombohedral BiI_3 structure (space group: $R\bar{3}$), in which the metal ion is present in a distorted octahedral coordination of six anions.

3.1.3. TbI₃
The X-ray diffraction pattern can be matched to the rhombohedral structure of TbI_3. This material also crystallizes in the BiI_3 structure [7].

3.2. The excitation spectra of TbX₃ (X = Cl⁻, Br⁻, I⁻)

The energy of the transitions going to the two terms, ^9D and ^7D, which belong to the Tb^{3+} $4f^75d^1$ electronic configuration in TbX_3 (X = Cl^-, Br^-, I^-) and in other halides are assembled in Table 1. The crystal structure and the optical data pertaining to the host lattice excitation of TbX_3 and a few other selected halides are assembled in Table 2.

3.2.1. TbCl₃
The room temperature excitation spectrum of $TbCl_3$ is exhibited in Fig. 1. The excitation spectrum of $TbCl_3$ can be divided into three major regions: (1) the short wavelength region extending from 200 nm to 225 nm, (2) the intermediate excitation region extending from 225 nm to 290 nm, and (3) the long wavelength region extending beyond 290 nm.

The identification of the Tb^{3+} $4f^8 \rightarrow 4f^75d^1$ interconfigurational excitation transition is facilitated by the room temperature excita-

tion spectrum of $TbCl_3$:Ce^{3+}, which is presented in Fig. 2. The first Ce^{3+} $4f^1 \rightarrow 5d^1$ transition in $TbCl_3$ occurs near 340 nm (3.65 eV). Therefore, according to Eq. (1), the Tb^{3+} (LS) $4f^8[^7F_6] \rightarrow 4f^75d^1[^7D]$ transition can be anticipated at 5.31 ± 0.12 eV (233 ± 7 nm). The excitation spectrum of $TbCl_3$ indeed shows a broad band centered near 240 nm (5.16 eV) (Fig. 1). This band is assigned to the transition going to the ^7D level of the $4f^75d^1$ configuration. The narrow excitation band near 281 nm (4.41 eV; FWHM ~15 nm) in the intermediate region of the excitation spectrum is then assigned to the Tb^{3+} (HS) $4f^8[^7F_6] \rightarrow 4f^75d^1[^9D]$ transition. This yields the exchange splitting (ΔE^{ex}) in $TbCl_3$ of 0.75 eV, which is consistent with the average value of $\Delta E^{ex} = 0.78 \pm 0.11$ eV that has been obtained in Ref. [2]. For comparison, the exchange splitting in the hexachloroelpasolite, $Cs_2Na(Y,Tb)Cl_6$ is determined to be 0.87 eV [4]. We wish to point out that the values of exchange splitting in chlorides are smaller than those determined in fluorides host lattices (~1 eV) [1]. This is related to the higher covalency of the chloride lattice relative to the fluoride based lattices.

The sharp lines in the excitation spectrum which are mainly located in the long wavelength region extending beyond 290 nm (Fig. 1), are assigned to the Tb^{3+} $4f^8 \rightarrow 4f^8$ intraconfigurational excitation transitions. These transitions are weak due to their forbidden electric dipole character. Note that the excitation spectrum of Fig. 2 indicates energy transfer from Ce^{3+} to Tb^{3+} in $TbCl_3$.

The nature of the short wavelength region of the excitation spectrum that extends from 200 nm to 225 nm is difficult to unravel. It may be attributed to the host-crystal-absorption. Hence, for example, the onset at 225 nm (5.51 eV) can be assigned to the fundamental absorption edge (E^{fa}) of the host lattice and the first maximum in this short wavelength region at 223 nm (5.56 eV) to the creation of free excitons (E^{ex}), which may be regarded as bound electron–hole pairs. If this proposal is accepted then the edge of the conduction band (E^{VC}) can be estimated at ~$1.08 \times E^{ex}$ = 6.01 eV [8]. The E^{VC} corresponds to the creation of free electron and holes in the conduction and valence band of the host lattice, respectively [9]. However, this interpretation may not be justified for the following reason. The values for the energy of exciton creation in $LaCl_3$ and $LuCl_3$ are 6.5 eV [9] and 7.05 eV [10], respectively. Since the band gap increases with decreasing ionic radii of the host lattice cation, the exciton band in $TbCl_3$ may be anticipated at energies near or greater than 6.5 eV (190 nm). To clearly identify these bands would require the use of vacuum ultraviolet spectroscopy, which is beyond the scope of this work. Alternatively, the bands in the short wavelength region of the excitation spectrum that extends from 200 nm to 225 nm can be connected with transitions to higher 5d levels of the Tb^{3+} ion.

3.2.2. TbBr₃
The room temperature excitation spectrum of $TbBr_3$, which is exhibited in Fig. 3, can be divided into three major regions: (1) the strong short wavelength region extending from 200 nm to 260 nm, (2) the intermediate excitation region extending from

Table 1
The energy position (eV) of the $Tb^{3+}4f^8[^7F_6] \rightarrow 4f^75d^1[^7D]$ and $4f^8[^7F_6] \rightarrow 4f^75d^1[^9D]$ transitions in halides and the energy separation (ΔE^{ex}; in eV) (see text).

Halide	$4f^8[^7F_6] \rightarrow 4f^75d^1[^7D]$	$4f^8[^7F_6] \rightarrow 4f^75d^1[^9D]$	ΔE^{ex}	Refs.
LuI_3	4.61 ± 0.12^a	–	–	[10]
TbI_3	4.65 ± 0.12^a	4.05 ± 0.12^b	0.6^b	This work; see text
$TbBr_3$	5.03 ± 0.12^a	4.32	0.71 ± 0.12	This work
$TbCl_3$	5.16	4.41	0.75	This work
$[TbCl_6]^{3-}$	5.30	4.56	0.74	[1]
$[TbBr_6]^{3-}$	5.12	4.46	0.66	[1]
$Cs_2NaTbCl_6$	5.21	4.34	0.87	[4]

^a Energy position is estimated from the first Ce^{3+} $4f^1 \rightarrow 5d^1$ excitation transition (see text).
^b These values are estimated (see text).