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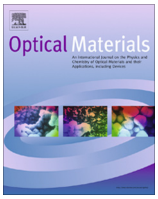

# The $H_2O/D_2O$ isotope effect in crystalline lanthanide sulfates at photo-, radio-, and triboluminescence

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ABSTRACT

We comparatively studied the $H_2O/D_2O$ isotope effect of lanthanide sulfate crystallohydrates on photo-, radio-, and triboluminescence and lifetimes of the excited $Ln^{3+}$ ions. Replacing $H_2O$ by $D_2O$ leads to an increase in the luminescence intensity whereas this process does not affect the maxima positions in photo-, radio-, and triboluminescence spectra. This isotope effect agrees with the known concepts of changes in luminescence quantum yields of the $Ln^{3+}$ ions being the main emitters. The bands of OH and OD radicals arise in triboluminescence spectra of lanthanide sulfate crystallohydrates (with $H_2O$ or $D_2O$) registered in argon atmosphere in UV region. This supports the proposition that water destruction occurs at the degradation of the crystallohydrates.

## 1. Introduction

It is known that under photoexcitation, the luminescence intensity of some lanthanide salts having crystallized water is less than that of the anhydrous ones [1,2]. The water molecules of the first coordination sphere of the $Ln^{3+}$ ions in crystallohydrates cause nonradiative deactivation of the electron-excited states of these ions. The change from the electron-excited energy of the ions to the high-frequency vibrations of the OH groups ($\nu = 3600\ cm^{-1}$) results in a strong luminescence quenching [3]. Nevertheless, the use of the waterless lanthanides salts, which are, therefore, perspective to produce various optical and luminescence devices, is problematic in air and normal conditions because of their high hygroscopicity. To decrease the quenching effect of water molecules, some methods that allow removing these molecules from the coordination sphere of the $Ln^{3+}$ ions can be used. The simplest one is to replace $H_2O$ by $D_2O$ that could provide increasing the luminescence quantum yields and lifetimes of excited $Ln^{3+}$ ions [3–5]. Increase in luminescence intensity under deuterosubstitution is associated with the change in deactivating the high-frequency oscillations (for OD groups surrounding the ion, $\nu = 2250\ cm^{-1}$).

There are some works describing the influence of heavy water on photoluminescence (PL) intensity and lifetimes of the excited-state lanthanide ions in solutions and crystallohydrates [3–8]. We assume that there could be a further study of H/D isotope effect by means of the other luminescence excitation methods. This would allow obtaining the extensive data on excitation mechanisms and deactivation of electron-excited states. The isotopic effect in water solutions was observed under the radioluminescence (RL) of the $Tb^{3+}$ ions [9] and sonoluminescence (SL) of the $Tb^{3+}$ and $Eu^{3+}$ ions [10–12]. The same effect was revealed at triboluminescence (TL) of the terbium sulfate crystallohydrate [13].

In this work, we study effect of the replacement of $H_2O$ by $D_2O$ on photo-, radio-, and triboluminescence intensities and lifetimes of the excited-states $Ln^{3+}$ ions in the lanthanide sulfate crystallohydrates.

## 2. Experimental section

Reagent-grade lanthanide sulfate crystallohydrates, $Ln_2(SO_4)_3\cdot 8H_2O$ (Ln = Eu, Tb, Dy) (Lanhit 99.99%), were used. Replacing $H_2O$ by $D_2O$ in these crystals was carried out in two stages. At the first stage, to dehydrate, the terbium and dysprosium, as well as europium crystallohydrates were kept in muffle furnace at 360 °C and 375 °C, respectively [14]. The second step involved gradual adding $D_2O$ with small excess to waterless salt cooled in dry argon to obtain $Ln_2(SO_4)_3\cdot 8D_2O$. X-ray diffraction data were performed with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at a nominal source power of 50 kV ∗ 40 mA on a four-cycle XCalibur Eos goniometer equipped with a CCD area a detector. Collection and processing of data was performed using the program CrysAlis Pro Oxford Diffraction Ltd., Version 1.171.36.20. The structure and refinement were performed by direct methods as implemented in the program SHELXS-97 [15]. The structure was refined by a

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full-matrix least-square technique using anisotropic thermal parameters for non-hydrogen atoms and a riding model for hydrogen atoms.

The crystals were placed in a standard quartz cell ($l$ = 1 cm) that was excited with xenon lamp at 450 W. The registration was carried out with "on reflection" geometry.

The triboluminescence of crystals (150–200 mg) was achieved in a cylindrical steel cell having quartz window at the bottom. For the TL excitation, 4-blade TPFE rod rotating at 1000 rpm was used [16,17]. In some cases, in recording TL spectra, argon was feed in cell at 10–15 ml/s using a tube. The cell was tightly closed to produce excess pressure.

The radioluminescence of crystals was excited with the use of microfocus X-ray tube BMS-1 equipped with Cu K$\alpha$ anode up to 45 kV [9].

The TL and PL spectra, as well as lifetimes of the excited-state $Ln^{3+}$ ions were recorded by means of Fluorolog-3 (Horiba Jobin Yvon) spectrofluorometer equipped with photomultiplier tube Hamamatsu R928P. The RL spectra were recorded on a Aminco–Bowman J4-8202 spectrofluorometer equipped with a Hamamatsu R3896 detector.

## 3. Results and discussion

The replacing $H_2O$ by $D_2O$ in lanthanide sulfate crystallohydrates did not change the positions of the maxima in PL spectra. A crystal structure of terbium sulfate crystallohydrate with heavy water (Fig. 1) and that with normal one [18] was identical. The intense band of the OD group at 2300–2500 $cm^{-1}$ in IR spectrum clearly indicates the replacement of normal crystallized water by the heavy one.

Comparing the deuterated and non-deuterated crystals (Fig. 2) clearly indicates an increase in photoluminescence intensity.

To compare correctly total luminescence intensity in the deuterated and non-deuterated samples, we calculated the area of the maxima in the spectra. For a single maximum, the normal or the Gaussian distribution can be used:

$$I(\lambda) = I_{\min} + I_{\max} \exp\left(-\frac{(\lambda - \lambda_{I_{\max}})^2}{2\sigma^2}\right) \qquad (1)$$

where $I_{\min}$ is the average intensity when luminescence is absent in the minimum point of spectrum (noise), $I_{\max}$ is the intensity of peak maximum in spectrum, $\lambda_{I_{\max}}$ is the wavelength at the maximum intensity; $\sigma$ is calculated as follows:

$$\sigma = \frac{1}{2}\left(\frac{\Delta\lambda_{I_{\max}}}{\sqrt{\ln 4}}\right) \qquad (2)$$

where $\Delta\lambda_{I_{\max}}$ is a width at the half-maximum.

The luminescence spectrum consisting of several peaks is represented as a superposition of all peaks:

$$I(\lambda) = I_{\min} + \sum_{i=1}^{n} I_{\max i} \exp\left(-\frac{(\lambda - \lambda_{I_{\max i}})^2}{2\sigma_i^2}\right) \qquad (3)$$

To compare the luminescence intensities, we calculated the ratio of the total integral luminescence intensities of the deuterated and normal crystallohydrates:

$$\frac{S_{I_{D_2O}}}{S_{I_{H_2O}}} = \frac{\int I_{D_2O}(\lambda)d\lambda}{\int I_{H_2O}(\lambda)d\lambda} \qquad (4)$$

These values are given in Table 1.

The decay curves of luminescence intensity at the pulsed photoexcitation, that inserted in Fig. 2, are well described by a simple exponential function:

$$I = I_0 \exp\left(-\frac{t}{\tau}\right) \qquad (5)$$

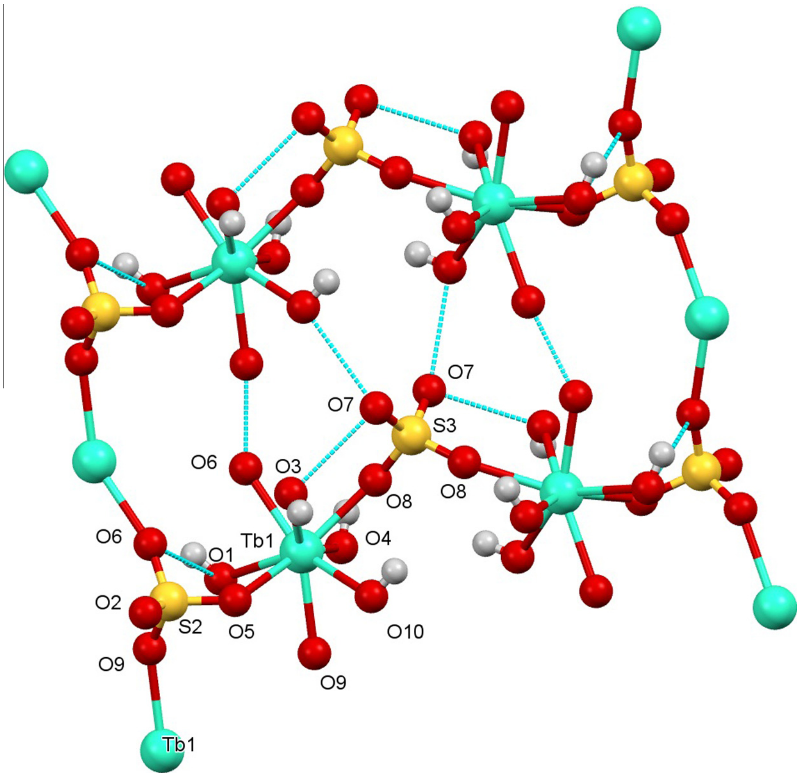

**Fig. 1.** Fragment of the crystal structure of terbium sulfate crystallohydrate after replacing $H_2O$ by $D_2O$. Crystal Data: $D_8O_{20}S_3Tb_2$, $M$ = 742.10, monoclinic, $a$ = 13.5027(4) Å, $b$ = 6.7172(3) Å, $c$ = 18.2369(5) Å, $\beta$ = 102.133(3), $V$ = 1617.15(9) $Å^3$, $T$ = 293(2), space group C2/c (no. 15), $Z$ = 4, μ(Mo K$\alpha$) = 9.165, 4211 reflections measured, 1811 unique ($R_{int}$ = 0.0205) which were used in all calculations. The final $wR_2$ was 0.1168 (all data) and $R_1$ was 0.0327 ($I$ > 2sigma(I)).