



Resonant energy transfer and cross relaxation between Sm^{3+} ions in LiYF_4 crystals

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ABSTRACT

Luminescence decay curves of Sm^{3+} ions in LiYF_4 crystals doped with 1, 5 and 10 mol% Sm^{3+} are multi-exponential, whereas that in a LiYF_4 crystal doped with 0.1 mol% Sm^{3+} is well approximated by a single exponential function with a decay time of 4.8 ms. The average luminescence decay times decrease from 4.8 to 0.60 ms with the increasing Sm^{3+} concentrations between 1 and 10 mol%. The decay curves for all crystals are found to be almost independent of the temperature between 15 and 300 K. The decrease of the decay times for the higher Sm^{3+} concentrations indicates energy transfer between two Sm^{3+} ions. Taking the crystal structure of LiYF_4 into account, it is deduced that a single-step energy transfer process for the 1 and 5 mol% Sm^{3+} concentrations occurs from a Sm^{3+} ion at the origin of (0 0 0) to one of the Sm^{3+} ions substituting for the first nearest neighbor Y^{3+} sites and beyond within a sphere with an approximate radius of less than 0.7 nm. On the other hand, a multi-step energy transfer process dominates for the highest concentration (10 mol%) because the calculated average distance between two Sm^{3+} ions in the 10 mol% Sm^{3+} sample is comparable with the migration length of the single-step energy transfer process estimated from the 1 and 5 mol% Sm^{3+} samples.

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1. Introduction

LiYF_4 is a tetragonal fluoride crystal with the scheelite structure [1]. Each Y^{3+} ion is surrounded by a dodecahedron of eight F^- ions and has a point group symmetry of D_{2d} . This compound is favorable for the introduction of trivalent rare earth ions as they substitute for the Y^{3+} ions without charge compensation [2–4]. Rare earth doped LiYF_4 has been shown to be a useful host crystal for studies of quantum upconversion [5,6]. Indeed, upconversion lasing has been demonstrated using $\text{LiYF}_4:\text{Er}^{3+}$ [7], $\text{LiYF}_4:\text{Nd}^{3+}$ [8] and $\text{LiYF}_4:\text{Tm}^{3+}$ [9]. Additional applications of rare earth doped LiYF_4 include their use as phosphor materials [10]. In order to improve the luminescence efficiency of phosphors, it is very important to have a detailed understanding of energy transfer mechanisms between rare earth ions especially in higher concentrations [11–13].

In previous work [4,14,15], we performed crystal growth investigations, polarized excitation, electron paramagnetic resonance (EPR) and crystal-field analyses of Sm^{3+} -doped LiYF_4 . Only the trivalent ionic species is present in $\text{LiYF}_4:\text{Sm}$, which is not

necessarily the case for nominally comparable complex fluorides such as KY_3F_{10} [15–17].

In this paper, we report on the luminescence decay dynamics for Sm^{3+} ions in LiYF_4 single crystals. A variety of Sm^{3+} concentrations (0.1–10 mol%) were studied in the temperature range between 15 and 300 K. We have examined the concentration dependence of the inferred decay times and the integrated intensities estimated from the luminescence decay curves of the ions. We interpret the data in terms of nonradiative energy transfer between equivalent Sm^{3+} ions, taking the LiYF_4 crystal structure into account.

2. Experimental procedure

The scheelite structure of the LiYF_4 crystal belongs to the space group of $C_{4h}^6(I4_1/a)$ [1]. The lattice parameters are $a=b=0.517$ nm, $c=1.075$ nm and $(x, y, z)=(0.2815, 0.085, 0.044)$ [18]. Fig. 1 shows a unit cell of the LiYF_4 crystal structure, where a yttrium site is located at the origin of (0 0 0). Y^{3+} ions, denoted by large black solid circles, occupy dodecahedral sites. Li^+ ions, denoted by medium-size gray solid circles, occupy tetrahedral sites. F^- ions are denoted by small gray solid circles. Sm^{3+} ions enter the LiYF_4 crystal structure, substituting for Y^{3+} ions.

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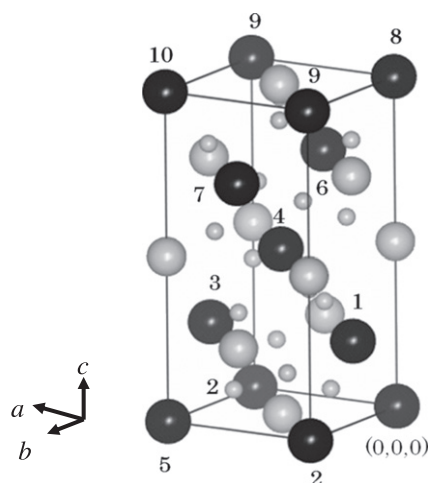


Fig. 1. LiYF_4 crystal structure with a unit cell. Dodecahedral yttrium sites and tetrahedral lithium sites are represented by large and medium-size solid circles, respectively. Fluoride sites are represented by small solid circles. Number of yttrium sites denoted by 1,2,- - - represents the first and second, - - -, shortest distances from the origin, respectively.

LiYF_4 single crystals doped with Sm^{3+} ions ($n=0.1, 1, 5$ and 10 (mol%)), where n means a composition of n mol% SmF_3 and $(100-n)$ mol% YF_3 in the starting charge, were grown by the Bridgman–Stockbarger technique [4,14]. LiYF_4 melts incongruently at a temperature of 819°C with a composition of 49 mol% YF_3 and 51 mol% LiF . The slight excess of LiF ensures nucleation and growth of doped crystals under the desired phase. In order to avoid constitutional supercooling, the crystals were grown in a temperature gradient of $40^\circ\text{C}/\text{cm}$ with a translation rate of 0.8 mm/h. The Sm^{3+} concentration in the as-grown crystals had a slight gradient along the crystal growth direction. The segregation coefficient of Sm^{3+} in LiYF_4 was estimated to be 0.96 by comparing the Sm^{3+} absorption coefficient of two slices taken from the top and the bottom of the boules [14]. The value close to 1 reflects the isoelectronic nature and the low ionic radii mismatch involved in the substitution of Sm^{3+} for Y^{3+} .

Optical absorption spectra were measured at 300 K using a Hitachi A3000 spectrophotometer. Luminescence/excitation spectra and quantum yield of luminescence were measured at 300 K using a Horiba FluoroMax-4 spectrophotometer. Luminescence decay curves were measured using the third harmonics (355 nm) of a Spectra-Physics GCR100 pulsed Nd:YAG laser with output pulse width of ~ 10 ns, a Jasco CT-25C monochromator, and a Hamamatsu Photonics R943-02 photomultiplier tube, connected with a Yokogawa DL1740 digital oscilloscope and a personal computer. Sample temperature between 15 and 300 K was achieved using an Iwatani CA201 cryo-refrigerator.

3. Theory

3.1. Formation of Sm^{3+} pairs

First, we estimate the distance from the origin (a yttrium site) to the other yttrium sites in LiYF_4 . The first nearest neighbor yttrium site located at the coordinates $(0, 1/2, 1/4)$, denoted by 1 in Fig. 1, has the closest proximity. The distance increases with the yttrium site number as shown in Fig. 1. The distribution function, $N(R)$, is defined as the number of yttrium sites contained in a sphere with a radius of R (nm) from the origin. A numerical simulation of the distribution function, $N(R)$, using the LiYF_4 crystal structure parameters and an increment ($\Delta R=0.05$ nm) of R yields a result approximately proportional to R^3 as shown in

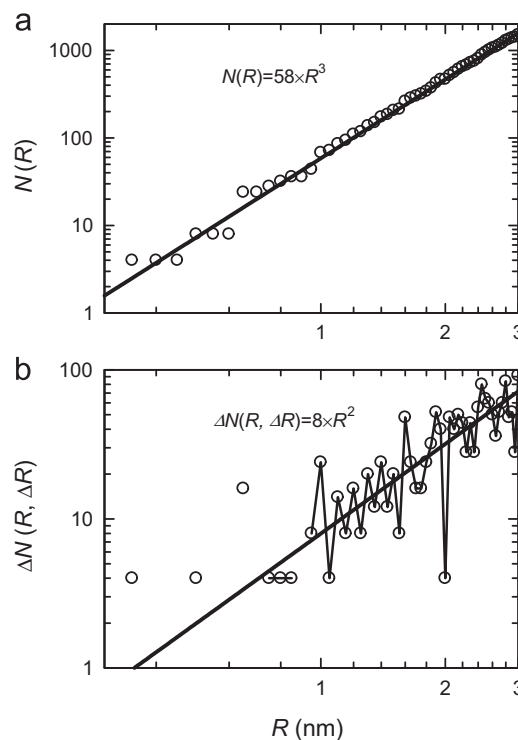


Fig. 2. (a) Distribution function, $N(R)$, defined as the number of yttrium sites contained in a sphere with a radius of R where the origin of $(0\ 0\ 0)$ is a yttrium site. (b) Partial distribution function, $\Delta N(R, \Delta R)$, defined as the number of yttrium sites contained in a shell with a volume of $4\pi R^2 \Delta R$ between R and $R+\Delta R$.

Fig. 2(a). The partial distribution function, $\Delta N(R, \Delta R)$, which is defined as the number of yttrium sites contained in a shell with a volume of $4\pi R^2 \Delta R$ between R and $R+\Delta R$, is discontinuous and proportional to R^2 as shown in Fig. 2(b). The function has three discrete values below 0.7 nm.

Next, we calculate the probability of Sm^{3+} -pair formation in LiYF_4 with a parameter c being defined as the probability that a yttrium site is occupied by a samarium ion, namely, being equal to $n/100$ of the samarium n mol% concentration in LiYF_4 . In the present treatment we will consider that one Sm^{3+} ion of the pair is located at the origin and the other Sm^{3+} ion at a distance of R away substitutes for one of the Y^{3+} ions contained within a volume of $4\pi R^2 \Delta R$ between R and $R+\Delta R$. The probability of Sm^{3+} -pair formation as a function of R , with the assumption that Sm^{3+} ions substitute randomly for Y^{3+} ions in the crystals and distribute uniformly, is given by product of probabilities for three independent events in the form of

$$\begin{aligned} W(R, \Delta R) &= c(1-c)^{N(R)} \{1-(1-c)^{\Delta N(R, \Delta R)}\} \\ &= c\{(1-c)^{N(R)} - (1-c)^{N(R)+\Delta N(R)}\}. \end{aligned} \quad (1)$$

A similar calculation of the formation probability of the stable self-trapped excitons in $\text{AgBr}_x\text{Cl}_{1-x}$ mixed crystals was carried out by Yamaga et al. [19]. As Eq. (1) includes a discontinuous function of $N(R)$, the right hand side in Eq. (1) cannot be represented in the infinitesimal deformation. A numerical simulation of the probability function, $W(R, \Delta R)$, can be carried out using Eq. (1) with values of c ($=0.001, 0.01, 0.05$ and 0.1). In this calculation, ΔR is set to the same increment (0.05 nm) of R as in Fig. 2. A decrease of the value of ΔR improves resolution of the probability, but has a limit of the resolution because of the discontinuous function $N(R)$. The results in Fig. 3 show three discrete possible sites below 0.7 nm the same as in Fig. 2(b). The three discrete peaks are located at $R=0.4, 0.5$ and 0.65 nm.

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