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# Rare Earth Materials for Population Density Control with Ultra-High-Speed Optical Pulses

D. C. Dai, Q. Luo, R. H. Li, X. Y. Yu, Z. R. Qiu, J. Y. Zhou, and Y. S. Yang

**Abstract**—The rare earth materials,  $\text{KNdFe}(\text{CN})_6 \bullet 3\text{H}_2\text{O}$  (KNFCN),  $\text{NdFe}(\text{CN})_6 \bullet 4\text{H}_2\text{O}$  (NFCN), and  $\text{NdFeO}_3$  (NFO) are characterized by absorption and fluorescence spectra. The dephasing times ( $T_2$ ) and the fluorescent lifetimes ( $T_1$ ) of the materials are determined. The critical bit rate ( $W_{\text{crit}}$ ) for ultra-high-speed population density control is discussed. The feasibility of using the materials for ultra-high-speed, all-optical switching devices is presented.

**Index Terms**—All-optical switching, coherent control, dephasing time, lifetime, rare earth material.

COHERENT optical control in semiconductor quantum wells (QW) for ultra-high-speed, all-optical switching has attracted a great deal of research attention in recent years [1], [2]. Nevertheless, real world application of the QW for the ultra-high-speed switching has not yet been possible due to the restrictions imposed by the exciton's long population recovering time ( $T_1$ ) [subnanosecond to nanosecond] and low working temperature (4 K) requirement. Various methods have now been proposed, including use of microcavity [3], or use of semiconductors with reduced quantum dimension [2]. Although limited success has been achieved, it will be of great importance to search for new types of materials suitable for ultra-high-speed switching operating at room temperature or at liquid nitrogen temperature (77 K). The trivalent rare earth (RE) ions in a solid is shown to be a suitable material for the purpose of optical switching.

An important parameter for ultra-high-speed optical switching for coherent control, the critical bit rate,  $W_{\text{crit}}$ , is given by [4]

$$W_{\text{crit}} = \frac{T_2}{\tau \cdot T_1} \quad (1)$$

with  $T_2$  the dephasing time of the material,  $T_1$  the population recovery time, and  $\tau$  the optical pulse width used for coherent control. To obtain a significant contrast ratio,  $W \ll W_{\text{crit}}$  is required. For example,  $W/W_{\text{crit}} = 0.1$ . In this case, the switching operative speed should be  $0.1W_{\text{crit}}$ . Equation (1) suggests that the material with the slow dephasing rate and large population

recovery rate is ideal for the purpose of coherent control. As the population recovery rate can by definition never exceed the dephasing rate, a so-called "strong" collision system, where collision can simultaneously destroy the coherence as well as populations in the excited state, is most desirable.

RE ions show sharp intra-4f electronic spectral lines even in the room temperature, as their 4f electrons are very well shielded by the outside 5s5p electrons. As a result, individual RE ions can be regarded as single quantum dot, presenting large  $T_2$  suitable for coherent control [5]. On the other hand, RE ions generally present long lifetimes in metastable states ranging from millisecond to microsecond [6]. Substantial reduction of the metastable states lifetimes is then essential to achieve ultra-high-speed population density control [4], [5].

It is now known that the energy transfer from the excited energy levels of RE ions to other RE ions or to optical traps can dramatically decrease their lifetimes [6], [7], which is generally called fluorescence quenching (FQ). The FQ of RE ions by the 3d-transition metal ions were investigated by Sakamoto [8] and Piguet [9]. The FQ of RE ions was also studied in superconductors by Flores [10]. In those works, no information was provided on the  $T_2$  and  $T_1$  of the RE ions' energy levels. Here we will report the results of spectroscopic properties of  $\text{Nd}^{3+}$  ions in RE-iron compounds. We estimate the values of  $T_2$  and  $T_1$  and demonstrate the feasibility of using the materials as a high-speed, all-optical switching device.

The materials  $\text{KNdFe}(\text{CN})_6 \bullet 3\text{H}_2\text{O}$  (KNFCN),  $\text{NdFe}(\text{CN})_6 \bullet 4\text{H}_2\text{O}$  (NFCN) and  $\text{NdFeO}_3$  (NFO) are studied in this work with the reflectance spectra and the fluorescence spectra with continuous-wave excitation, pulse excitations with nanosecond (ns) and picosecond (ps) resolutions, respectively.

The fluorescence spectra is studied with a Ti:sapphire laser (Spectra-Physics Co.). The fluorescence lifetime for the metastable state ( ${}^4\text{F}_{3/2}$ ) of  $\text{Nd}^{3+}$  ion is measured at the emission wavelength 860 nm with an excimer laser pumped dye laser (FL2002, Lambda Physik Co.) at 580 nm, which is in resonance with  ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{5/2}$ ,  ${}^2\text{G}_{7/2}$  transition of  $\text{Nd}^{3+}$  ion. The temporal resolution of the measurement system with a PMT (Hamamatsu R928) and a BOXCAR system is 10 ns. For ps time-resolved fluorescence spectrum, the experiment setup is the same as that described in [11].

Fig. 1 shows the typical reflectance absorption spectrum for NFO. The clear transition lines at about 880, 800, and 750 nm are correspondent to the  ${}^4\text{I}_{9/2} \rightarrow {}^4\text{F}_{3/2}$ ,  ${}^4\text{I}_{9/2} \rightarrow {}^4\text{F}_{5/2}$ ,  ${}^2\text{H}_{9/2}$  and  ${}^4\text{I}_{9/2} \rightarrow {}^4\text{F}_{7/2}$ ,  ${}^4\text{S}_{3/2}$  transitions of  $\text{Nd}^{3+}$  ions, respectively. The intra-4f transitions multiplets of  $\text{Nd}^{3+}$  ions located at wavelength shorter than 560 nm are covered by strong d-d transition bands of iron ions.

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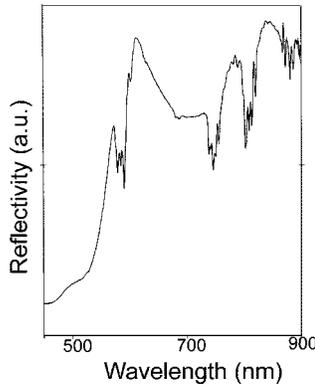


Fig. 1. Reflectance absorption spectrum of NFO.

The dephasing time of the excited levels of  $\text{Nd}^{3+}$  ions can be estimated for a homogeneously broadened two-level system by [12]

$$T_2 = \frac{\lambda^2}{\Delta\lambda \cdot c} \quad (2)$$

where  $\Delta\lambda$  and  $\lambda$  are the full-width at half maximum (FWHM) and the center wavelength of the absorption transition lines, respectively,  $c$  is the speed of light in the vacuum. The estimated  $T_2$  of  $\text{Nd}^{3+}$  ions in these materials are shown in Table I. The accuracy of this estimation is proved by our recent femtosecond (fs) experimental measurement on rare earth ions [13].

The fluorescence spectra of  $\text{Nd}^{3+}$  ions in these materials are shown in Fig. 2. Weak fluorescent emission is observed with KNFCN and NFCN, but no fluorescence could be detected for NFO with the maximum sensitivity of our experiment system. The lifetimes of  $\text{Nd}^{3+}$  ions in NFCN and NFO are too short to be resolved by the ns dye laser and PMT system. However, it is possible to estimate the lifetimes through the measurement of fluorescence quantum yield,  $\Phi_f$ , given by

$$\Phi_f = \frac{A_{21}}{A_{21} + Q_{21}} \quad (3)$$

where  $A_{21}$  is the spontaneous emission rate and  $Q_{21}$  is the collision quenching rate [14]. The radiation lifetime is

$$\tau = \frac{1}{A_{21} + Q_{21}}. \quad (4)$$

Thus, the yield  $\Phi_f$  can also be presented as

$$\Phi_f = \frac{\tau}{\tau_{rad}}. \quad (5)$$

Using KNFCN as a reference, it is possible to estimate the population lifetime as

$$\frac{\Phi_{KNDCN}}{\Phi_x} = \frac{\tau_{KNDCN}}{\tau_x} \quad (6)$$

where  $x$  represents the samples of interest, NFCN or NFO.

With (6), we assume that the absorption cross sections by each  $\text{Nd}^{3+}$  ion in different host are in the same order of magnitude, which can be estimated from the reflectivity measurement and from material structure analyses. As a result, the population

TABLE I  
DEPHASING TIME, FLUORESCENT LIFETIME  
AND BIT RATE FOR OPTICAL SWITCHING IN KNFCN, NFCN, AND NFO.  
\* INDICATES THE LIFETIME ESTIMATED WITH FLUORESCENT QUANTUM  
YIELD EFFICIENCY

Material	KNFCN	NFCN	NFO
Dephasing time ( $T_2$ ) (ps)	0.2	0.5	1
Lifetime ( $T_1$ ) (ns)	80	8*	<0.8*
$W_{\text{crit}}$ (GHz)	0.05	1.25	>25
$W$ (GHz)	0.005	0.125	>2.5
$W_{\text{LT-crit}}$ (GHz)	1.0	10	100

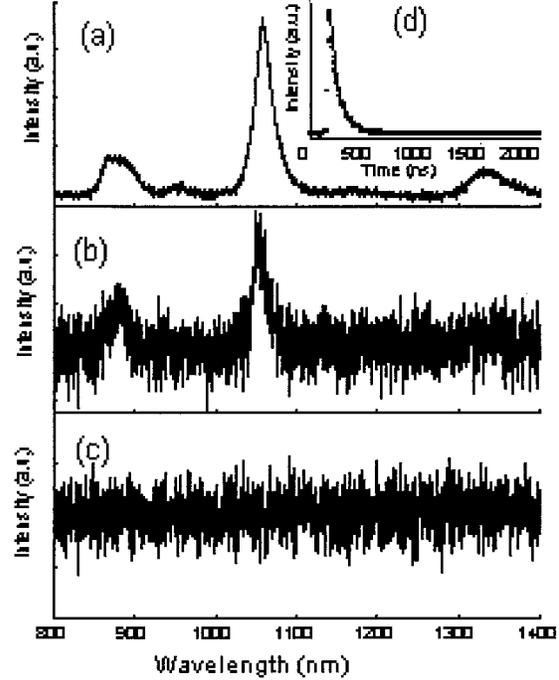


Fig. 2. Typical fluorescence spectra of  $\text{Nd}^{3+}$  ions in the materials. (a) KNFCN. (b) NFCN. (c) NFO. (d) The fluorescence decaying curve of  $\text{Nd}^{3+}$  ion in KNFCN.

lifetimes of  $\text{Nd}^{3+}$  ions for NFCN and NFO can be estimated with (5), as shown in Table I.

Under the same experiment conditions, the integrated luminescence intensity is 100 : 10 :  $y$  ( $y < 1$ ) for KNFCN, NFCN, and NFO. The measured lifetime of  $\text{Nd}^{3+}$  ion in KNFCN is 80 ns [shown in Fig. 2(d)]. Table I shows the estimated values of  $T_1$  and  $T_2$  as well as the values of  $W_{\text{crit}}$  and  $W$  for each material. We conclude that 2.5-GHz coherent population density control is possible for the material NFO at room temperature.

For the material working at 77 K, the  $T_2$  can be increased to up to 4 ps. In this case, the critical bit rate of these materials,  $W_{\text{LT-crit}}$ , can be increased to 100 GHz for NFO, which is also shown in Table I.

The mechanism of energy transfer in RE solids was discussed in earlier work [6]. The FQ is due to the efficient energy transfer from RE ions to iron ions through the  $C = N$  bridge in KNFCN and NFCN, in which the d electrons of iron ions are delocalized through the  $C = N$  group even up to the outer electron orbitals of  $\text{Nd}^{3+}$  ions. The delocalization of electron reduces the actual interaction distance between the  $\text{Nd}^{3+}$  ion and  $\text{Fe}^{3+}$  ion, and then strengthens the exchange interaction and the dipole-dipole

interaction, which are based on the spatial overlap of the electronic wavefunction of  $\text{Nd}^{3+}$  ion and Fe ions [15]. As a result, the ultrafast energy transfer occurs efficiently, and the fluorescence of  $\text{Nd}^{3+}$  ions is quenched dramatically [15], [16]. The mechanism of FQ for  $\text{Nd}^{3+}$  ion in NFO is believed to be caused by the efficient energy transfer from  $\text{Nd}^{3+}$  to  $\text{Fe}^{3+}$  through  $\text{O}^{2-}$ -bridge providing delocalized electronic pair, as the actual distance between  $\text{Nd}^{3+}$  and  $\text{Fe}^{3+}$  in NFO is smaller than NFCN and KNFCN.

The interesting results appear for the excitation wavelength at 580 nm measured with a ps dye laser and a streak camera. It is shown that the population relaxation time is as short as 44 ps for KNFCN, which is shown to be determined by the relaxation time of  $[\text{Fe}(\text{CN})_6]^{3+}$  [5]. Using the 0.4 ps dephasing time at room temperature, we estimate using (1) that  $W_{\text{crit}} = 100$  GHz. For the material working in a liquid nitrogen region, the dephasing time can be an order of magnitude larger, giving rise to the  $W_{\text{LT-crit}} = 1000$  GHz. The practical working rate for population density control can be as high as 100 GHz.

The materials described in this work can be prepared either as thin films or as optical crystals. Optical switching can be implemented with an experimental configuration similar to that described in [2].

In conclusion, we demonstrate the dramatic decrease of the RE ion lifetimes in synthesized RE-iron compounds, which is useful for population density control using ultra-high-speed optical pulses.

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