Short Communication

Fluorescence decay times of rare earth ions in silicate glass as functions of temperature

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1. Introduction

The fluorescence decay times of rare earth ions in inorganic hosts are affected by a variety of parameters including the ion concentration, the temperature and the presence of other similar or different ions with possible radiative or non-radiative energy transfer to the rare earth ions. With the exception of cerium the fluorescence emissions observed by excitation with UV light, with cathode rays or with charged particles occur from transitions within the 4f shell and are mainly of the forced electric dipole and the magnetic dipole types. The theory of these transitions has been described extensively [1 - 6]. Inorganic glass systems make attractive hosts for rare earth ions because of their comparative ease and low cost of manufacture, because of the opportunity to mould and shape scintillators for particular applications, and because of the possibility of changing the basic manufacturing ingredients to suit particular problems. It is therefore important to know how the fluorescence decay times are affected by changing one or more of the aforementioned parameters. In this work we investigate the behaviour of the decay times of some of these rare earth ions in a series of silicate glass hosts as a function of temperature.

2. Experimental

The cerium-doped glasses were either manufactured by Levy—West Ltd., London, or were part of Nuclear Enterprises range of scintillators used as neutron detectors. The composition and the physics of these glasses have been described previously [7, 8]. The europium-doped glasses were similar in composition to the cerium-doped glasses and the compositions of the terbium-doped glasses are shown in Table 1.

For measurements of the decay times the samples were held in a home-built double-walled cryostat of simple design and the temperature was

TABLE 1

Composition of terbium-doped glasses

Oxide	Composition (wt.%)				
	Glass no. 10	Glass no. 11	Glass no. 12	Glass no. 13	Glass no. 14
SiO_2	57.1	59.7	61.6	56.9	54.3
Li_2O	13.1	9.56	6.97	9.22	8.89
SrO	31.5	22.5	23.2	21.5	20.5
Al_2O_3	3.4	3.56	3.66	3.4	3.25
Tb_2O_5	4.88	4.96	4.56	9.04	13.1

monitored continuously using a thermocouple attached to the inside of the sample holder. UV excitation pulses of about 3 μs duration (or 5 ns for the cerium-doped samples) were passed via a monochromator to the sample. The luminescence was passed through a second monochromator at right angles to the sample and was monitored by a Philips photomultiplier tube. The output was fed to a PAR 113 pre-amplifier and then to a PAR 160/162 boxcar integrator which enabled the average of many decay curves to be plotted on a chart recorder.

3. Results and discussion

The results of the UV excitation measurements are shown in Table 2. All the decays could be fitted to simple exponentials. The degree of "forbiddenness" in the europium-doped and terbium-doped samples can be estimated from the increase, by almost five orders of magnitude, in the decay times compared with those for cerium in similar hosts. The 4f−5d transition of the cerium ion is an electric-dipole-allowed transition and thus a simple exponential decay is expected in the absence of any energy transfer from the excited cerium activator to other ions. Energy transfer between cerium ions has also been found to be insignificant for other systems [9, 10]. Since a glass does not have any long range order, it is expected that there will be a variation of rare earth sites and ion−ion distances with a corresponding effect on the transition probability and thus the decay times of individual ions. It has been proposed [11] that, for the rare earths to exhibit a single simple exponential decay, they must be strongly coupled together so that the rate of radiationless energy transfer between the ions is fast compared with their fluorescence lifetimes. In this model the excitation belongs to the coupled system of ions as a whole and the measured lifetime is characteristic of this system with a subsequent exponential decay. This type of energy transfer in glass systems is thought to be predominantly phonon assisted [12, 13].

4. Conclusion

The measurements of the decay times of the cerium ions indicate that they act in isolation from each other with little transfer between them. The

TABLE 2

Decay times

Temperature (K)	Decay times (ns) for cerium-doped glasses			Decay times (ms) for europium-doped glasses			Decay times (ms) for terbium-doped glasses		
	NE902	NE905	NE912	1/77/902	2/77/905	3/77/912	10	13	14
300	58.1	59.3	59.1	2.43	2.70	2.85	3.40	3.24	3.21
250	57.8	–	59.4	2.57	–	–	–	–	3.20
195	58.2	59.3	58.2	2.63	–	–	–	–	3.25
150	58.4	59.5	59.1	2.63	–	–	–	–	3.30
103	58.4	59.5	58.7	2.69	–	–	–	–	3.32
77	57.8	59.4	–	2.79	–	–	–	–	3.43
30	57.2	58.4	–	–	–	–	–	–	–
7.5	56.5	58.4	57.8	–	–	–	–	–	–

increase in the decay times of the europium and terbium ions at low temperatures and with the decrease of the concentration of these ions suggests that some form of energy transfer occurs in these cases. The mechanism is probably phonon assisted.

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