VUV studies of radiative recombination in rare-earth activated wide bandgap materials; BaF_2:Ce

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Open f-shell ions doped into a wide bandgap material provide an excellent vehicle to study carrier capture and recombination processes at structured impurities [1]. Much of the work on UV and VUV solid state luminescent materials was performed during the search for new, fast and efficient scintillator materials. One of the most interesting of these materials is BaF_2, the fastest known inorganic scintillator [2], which has been a major focus of effort at HASYLAB. As part of this effort we have conducted VUV studies of RE-activated BaF_2 and other wide bandgap materials. In this note we report initial results of our work on BaF_2:Ce.

EXCITATION SPECTRA. While radioluminescence spectra excited by gamma or X-radiation usually reflect the dominant radiative decay mode of the relevant electronic excitations of the material, photoluminescence oftentimes shows a strong dependence upon the wavelength of exciting light, indicating the existence of competing energy transfer channels to various emitting centers. Such a dependence is illustrated in Fig. 1, which shows excitation spectra obtained for STE- and Ce-emissions of BaF_2:0.2%Ce under synchrotron irradiation. At the short wavelength range of 50 to 150 nm the spectra reflect various processes by which the host-to-ion energy transfer can occur in BaF_2 [2]. Although 115-125 nm radiation excites STE-emission more effectively than Ce-emission, the opposite is true for longer wavelength excitation at 135-140 nm. For excitation at even shorter wavelengths, below 110 nm, Ce-emission prevails again.

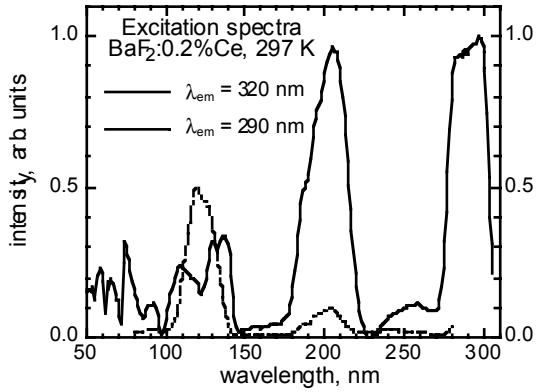

Figure 1: Excitation spectra of BaF_2:Ce. 320 nm - Ce-emission; 290 nm - STE-emission.

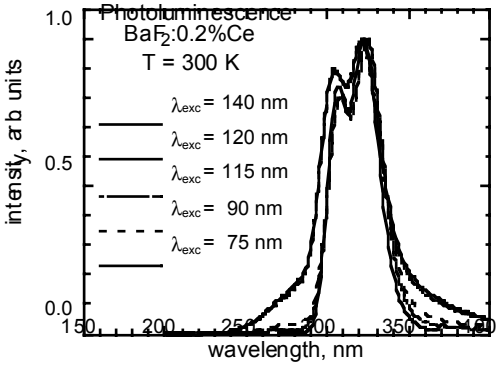

Figure 2: Emission spectra BaF_2:Ce for different excitation wavelengths, at 300 K.

EMISSION SPECTRA. The emission spectra shown in Fig. 2 demonstrate three important points: i) optical excitation at energy equal to or greater than the excitonic transition at 10 eV (123.9 nm) produces emission with significant contributions of both Ce and STE bands (Fig. 2, 120 and 115 nm excitations); ii) optical excitation at energy below that of the exciton produces a spectrum with almost no STE contribution (Fig. 2, 140 nm excitation); and, most importantly, iii) the shorter wavelength excitations at 90 and 75 nm produce spectra that consist almost entirely of Ce-emission. The low temperature spectra (10-25 K) are similar.

TIME PROFILES. In Fig. 3 we present selected time profiles from BaF_2:0.2%Ce measured under pulsed synchrotron radiation for a number of excitation wavelengths. The substantial diversity of rise and decay times of apparently multi-exponential time profiles indicate that different processes of host-to-ion energy transfer do exist and can be selectively activated by using different excitation wavelengths.

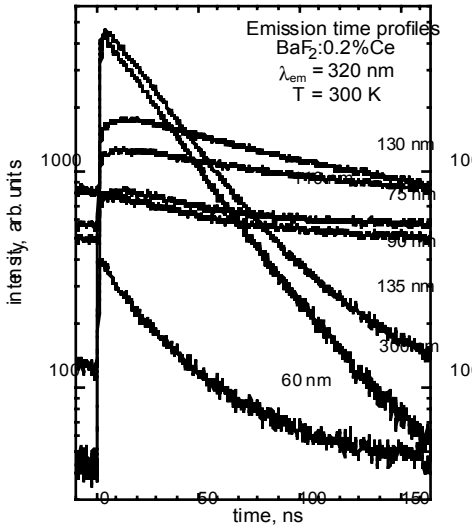

Figure 3: Time profiles of Ce-emission under VUV excitations at various wavelengths.

DISCUSSION. The profile excited at 300 nm shows single-exponential decay at about 30 ns (the Ce^{3+} radiative lifetime) while the similar 135 nm profile reflects fast energy transfer from the Ce-bound exciton. Decay profiles excited at 130 and 110 nm are much slower, with major contributions of STE-emission. At 75 and 90 nm the decays are slower yet, arising from separated carriers and hole self-trapping in the lattice of BaF_2. Finally, we attribute the surprisingly different and much faster 60 nm profile to fast consecutive hole and electron capture and radiative recombination at Ce ions. Apparently the 75 nm excitation creates a valence band hole and a hot conduction band electron that have an opportunity to separate. The 60 nm excitation, in contrast, creates a $Ba^{2+}5p$ core hole and a cold electron in the conduction band. After a CVL photon is emitted, relaxation could conceivably proceed by four different mechanisms: i) a hole self-traps and an electron is captured leading to STE-emission and/or Ce-emission after transfer (130 nm type profile); ii) a free band electron and hole recombine, creating an exciton which subsequently self-traps, generating STE-emission and/or Ce-emission, again with a 130 nm type profile; iii) a hole self-traps while an electron is captured by a nearby Ce^{2+} ion; the net coulombic attraction would then draw the self-trapped hole, which recombines with the Ce^{2+} ion. This could not, however, take place at temperatures below 108 K, where V_k centers are immobile, so that no low-temperature Ce-emission would occur; iv) a hole could be captured by a nearby Ce^{3+} ion, followed by attraction of a free electron and recombination with the Ce^{4+} ion. This would give rise to fast Ce-emission at any temperature. Thus only the last option is consistent with all experimental results presented in this note. A detailed account of this work will be published elsewhere. This work was supported by the TMR-Contract ERBFMGECT950059 of the European Community, ALEM Associates, Boston, and by the Polish Committee of Scientific Research, KBN (2P03B04914).

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