Quantum confinement of electron-phonon interaction in luminescent nanocrystals

Spectral properties and luminescence dynamics of rare earth ions (Er^{3+} and Yb^{3+}) doped into nanocrystal of Y_2O_2S are being studied as a part of our effort to understand the electronic properties of f-element ions in nanostructured environments. It is known that size-dependent quantum confinement has significant effects on both radiative and nonradiative electronic transitions of optical centers in nanoparticles, and that modifying and controlling structure at the nanometer scale may induce novel properties for applications. In the case of rare earth ions doped into nanocrystalline materials, no confinement of electronic states should occur due to the localized electrons of such ions. However, confinement effects may be induced by inter-ionic electronic interaction and, particularly, through electron-phonon interaction [1]

We have observed that, at temperatures below 7 K, unusually strong and sharp hot bands of Er^{3+} originated from the upper crystal field levels of the $^4I_{15/2}$ multiplet at energy levels as high as 220 cm^{-1}. As shown in Figure 1, the hot band intensity increases as temperature decreases below 7 K, whereas above 10 K normal Boltzmann thermodynamic populations were observed. This anomalous thermalization phenomenon, which was not observed in the Er^{3+}:Y_2O_2S bulk counterparts, can be well explained based on the theory of ion-lattice interaction with consideration of confinement on phonon density of states, namely, reduction of phonon states in the low energy region. Due to the reduction of low-energy phonon modes (< 100 cm^{-1}) in the 20-40 nm crystals we studied, nonradiative relaxation of Er^{3+} between energy gaps less than 100 cm^{-1} is restricted, and as a result, the intensity of hot bands that originate from the upper crystal field levels in the $^4I_{15/2}$ ground state increases rapidly as temperature decreases below 7 K. This unusual increase in hot band intensity has been quantitatively interpreted by calculations of the temperature dependent multiphonon relaxation rates in the nanocrystals. It is expected that this phenomenon should occur at higher temperatures in smaller nanocrystals. Moreover, the confinement on electron-phonon interaction in nanocrystals should also impact phonon-assisted energy transfer and up-conversion processes that are technically important for applications.

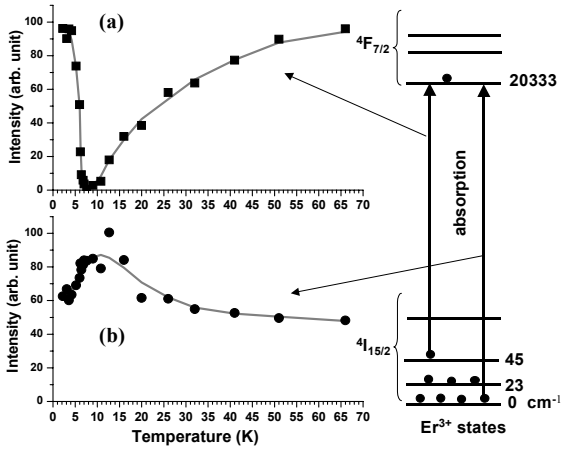

Figure 1. Temperature dependence of the excitation intensity of Er^{3+} in nanocrystals of Y_2O_2S: (a) the hot band originated from the crystal field level 45 cm^{-1} above the ground level, and (b) the normal excitation from the ground level.

1. G. K. Liu, H. Z. Zhuang, and X. Y. Chen, Nano Lett. 2, 535(2002)

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