

## Relating Localized Electronic States to Host Band Structure in Rare-Earth-Activated Optical Materials

Charles W. Thiel, Herve Cruguel,<sup>\*</sup> Huasheng Wu,<sup>†</sup> Yongchen Sun, Gerald J. Lapeyre, and Rufus L. Cone

*Department of Physics, Montana State University, Bozeman, MT 59717*

Randy W. Equall

*Scientific Materials Corporation, 310 Icepond Road, Bozeman, MT 59715*

Roger M. Macfarlane

*IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120*

<sup>\*</sup> Present address: Département de Recherche sur l'Etat Condensé, CEA/Saclay, F-91191 Gif-sur-Yvette Cedex, France

<sup>†</sup> Present address: Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong, China

Rare-earth ions have a multitude of technological applications as optically active impurities in insulators and semiconductors. Knowledge of the energies of the host crystal's electronic band states relative to the  $4f^N$  or  $4f^{N-1}5d^1$  states responsible for the ion's optical transitions is important for understanding the properties and performance of each material since energy and electron transfer between these states influences the material's efficiency and stability.<sup>1</sup> Little is known about the relationships between these states, but there is growing motivation to explore these properties for developing ultraviolet laser materials, phosphors for applications including plasma displays and mercury-free lamps, scintillator materials for medical imaging, and optical data processing and storage technologies based on photorefractivity or photon-gated photoionization holeburning. Continued advances in optical technologies require knowledge of the systematic trends and behavior of rare-earth energies relative to crystal band states so that the properties of current materials may be fully understood and new materials may be logically developed.

We have recently initiated a systematic study of the relative energies of the rare-earth ions' electronic states and the host band states in optical materials using resonant electron photoemission spectroscopy (RPES).<sup>2,3</sup> RPES directly determines the energies of all occupied electronic states relative to a common energy reference and can unambiguously separate and assign spectral features to a particular electronic state.<sup>4</sup> Figure 1 presents results for yttrium aluminum garnet (YAG), the most important host crystal for solid-state lasers. Circles represent measured binding energies of the rare-earth  $4f^N$  ground state relative to the valence band maximum (the host's highest energy occupied state).

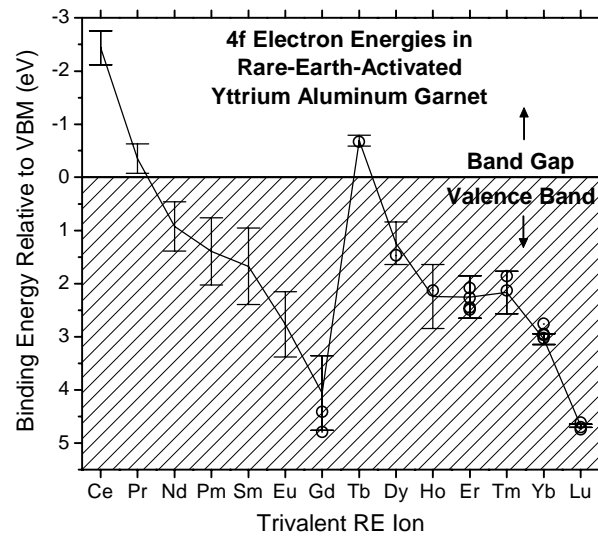
These results have led to an empirical model that successfully describes the rare-earth binding energies in optical materials with two parameters: one describes a constant shift experienced by all rare-earth ions and the second describes a smaller dependence on the rare earth's ionic radius. These empirical parameters may be determined from measurements on just two different rare-earth ions, or, in certain cases, simply from measurements on the host crystal itself. With parameters determined from our measured

data, this model predicts the energies of the remaining ions as is shown by the solid line in Figure 1.

This information is directly relevant to understanding and predicting properties critical for applications, such as excited-state absorption energies to the conduction band and relaxation pathways involving ionization. For example, the results for YAG predict that ionization of  $\text{Nd}^{3+}$  occurs at energy larger than the band gap and that ionization from 1.064  $\mu\text{m}$  laser photons would require a very low probability five-photon absorption from the upper laser level. In contrast, the results for  $\text{Ce}^{3+}$  predict that excited-state absorption to the conduction band would overlap emission wavelengths from the  $5d^1$  to  $4f^1$  transition, resulting in parasitic absorption that prevents its use as a tunable blue laser. All of these results suggest that systematic studies of additional host compounds will rapidly lead to a clearer picture for the host's effect on the rare-earth ion's  $4f$  electron binding energies that will motivate fundamental theoretical analysis and accelerate development of new optical materials.

## REFERENCES

1. See, for example, G. Blasse and B. C. Grabmeier, *Luminescent Materials* (Springer, Berlin, 1994).
2. C. W. Thiel, H. Cruguel, H. Wu, Y. Sun, G. J. Lapeyre, R. L. Cone, R. W. Equall, and R. M. Macfarlane, "Systematics of  $4f$  electron energies relative to host bands by resonant photoemission of rare-earth ions in aluminum garnets," *Phys. Rev. B* **64**, 085107-1—085107-13 (2001).
3. C. W. Thiel, H. Cruguel, Y. Sun, G. J. Lapeyre, R. M. Macfarlane, R. W. Equall, and R. L. Cone, "Systematics of  $4f$  electron energies relative to host bands by resonant photoemission of rare-earth-doped optical materials," Accepted for publication in *J. Lumin.* (2001).
4. J. W. Allen, "Resonant Photoemission of Solids with Strongly Correlated Electrons," in *Synchrotron Radiation Research: Advances in Surface and Interface Science*, edited by R. Z. Bachrach (Plenum Press, New York, 1992), Vol. 1, pp. 253—323.



## FIGURE CAPTION

**Relating Localized Electronic States to Host Band Structure Figure 1.** Circles represent measured 4f electron binding energies relative to the Valence Band Maximum (VBM); negative binding energies are within the band gap of the host and positive energies are below the VBM. The solid line is the fit of the model to our measured values. The error bars on the model are due to uncertainty in the input parameters and can be improved with further measurements on more materials. Note that the bottom of the conduction band lies at about  $-6.5$  eV.