

Inhomogeneous Broadening: Symmetry of Centers and Disorder in Solid Solutions and Nanocrystals

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Abstract. Zero-phonon electronic transitions of Cr³⁺ impurity ions in solid solutions and nanocrystals are studied. In the series of Lu_{3x}Y_{3-3x}Al₅O₁₂ (0 < x < 1) garnet solid solution crystals the modification of zero-phonon R-line (²E–⁴A₂) fluorescence spectra of Cr³⁺ ions with changing x occurs in a discrete fashion and is not accompanied by strong inhomogeneous broadening. The effect is ascribed to high C_{3i} symmetry of Cr³⁺(Al³⁺) sites. The fluorescence line narrowing experiments were performed for the inhomogeneously-broadened R-line of cubic Cr³⁺ centers in MgO nanocrystals. The inhomogeneous broadening in nanocrystals is attributed to spatial confinement.

Keywords: fluorescence, impurity ions, inhomogeneous broadening, solid solutions, nanocrystals.

The talk reports the results of the experimental studies of the role of disorder and spatial confinement in inhomogeneous broadening of zero-phonon lines (ZPL) in the impurity ions spectra in insulating solid solutions and nanocrystals.

1. Usually, the inhomogeneous broadening of electronic transitions ZPL in rare-earth and transition metals impurity ions in solid solutions (mixed crystals) is, due to structural disorder of the matrix, much larger than in single-component crystals and similar to that observed in glasses (see e.g. [1]). We studied zero-phonon electronic transitions in Cr³⁺ and Ce³⁺ impurity ions in the series of Lu_{3x}Y_{3-3x}Al₅O₁₂ (0 < x < 1) garnet solid solution crystals [2]. It was observed that in contrast to the case of Ce³⁺, the modification of zero-phonon R-line (²E–⁴A₂) fluorescence spectra of Cr³⁺ ions with changing x occurs in a discrete fashion and is not accompanied by strong inhomogeneous broadening. The effect is ascribed to high C_{3i} symmetry of Cr³⁺(Al³⁺) sites that allows only a limited number of non-equivalent Cr³⁺ centers in mixed environment. The disordered system in which impurity ions occupy high-symmetry sites provides a unique opportunity to study locally identical impurity centers inside mixed matrices of different composition. The energies and radiative lifetimes of ²E states of locally identical Cr³⁺ centers in mixed garnet matrices were studied and the observed dependences on Lu content x are discussed in terms of lattice compression and dilation according to the Vegard's law.

2. The inhomogeneous broadening of electronic transitions of rare-earth and transition metal impurity ions in nanocrystals is typically significantly larger than that in the bulk crystals of the same

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composition. This additional broadening is usually ascribed to the increased role of the surface and to the larger number of defects in these materials.

MgO:Cr³⁺ and MgO:Mn⁴⁺ are crystalline materials which due to the necessity of charge compensation host a few types of 3d³ centers with different symmetry and thus may serve as a model for studies of the inhomogeneous broadening mechanisms. Sol-gel technology-produced MgO:0.1%Cr nanocrystals (particles size ~5 nm) were studied with laser spectroscopy techniques [3]. The low-temperature fluorescence line narrowing (FLN) experiments were performed for the inhomogeneously-broadened (FWHM ~0.2 nm) magnetic dipole R-line of cubic Cr³⁺ centers. The observed fluorescence spectra consist of a narrow resonantly excited component and non-resonant one, which is due to splitting of the excited ²E states of cubic centers under the random stress. The non-resonant fluorescence spectrum reveals the distribution of the distortions of the cubic crystal field for Cr³⁺ centers in nanocrystals. The observed spectra and their dependence on excitation wavelength are drastically different from that observed in [4] in bulk single crystals, and thus demonstrate specific inhomogeneous broadening mechanisms in nanocrystals. The nature of inhomogeneous broadening of spectral lines of impurity ions in nanocrystals is discussed.

In conclusion: we observed new effects in inhomogeneous broadening of fluorescence lines that enable to understand the role of the local symmetry of impurity centers in solid solutions spectra and to make conclusions about the nature of inhomogeneous broadening in nanocrystals.

References

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