

Spectroscopic properties of Sr₂CeO₄ nanocrystals revisited

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Structure of Sr₂CeO₄ is characterized by chains of edge-sharing CeO₆ distorted octahedra [1]. Under excitation with UV light this crystal exhibits blue-white intense Stokes emission, which is due to Ce⁴⁺ - O²⁻ charge transfer (CT) transition [1,2]. At the same time the irradiation of Sr₂CeO₄ with a focused IR laser beam leads to broadband anti-Stokes white emission; this observation was tentatively ascribed to intervalence charge transfer between Ce³⁺ - Ce⁴⁺ pairs [3]. This interpretation was supported by the results of ab initio calculations performed for independent (CeO₆)⁹⁻ and (CeO₆)⁸⁻ clusters embedded in Sr₂CeO₄ lattice [3]. Whereas the intervalence charge transfer (IVCT) emission was obtained within ab initio approach, where the standard scaling of the ab initio vibrational frequencies turned out to be crucial, the Ce⁴⁺ - O²⁻ CT transition energies were highly overestimated within ab initio approach [3]. This work presents experimental spectra of Sr₂CeO₄ nanocrystals covering absorption, anti-Stokes emission as well as observed for the first time, Stokes IR emission induced by IR laser light. The interpretation of the observed spectra is revisited in the light of new ab initio calculations going beyond the minimal embedded clusters and independent Ce centers approximations.

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[3] Stręka W., Tomala R., Marciniak L., Lukaszewicz M., Cichy B., Stefański M., Hreniak D., Kędzior A., Krosnicki M. and Seijo L. (2016) *Phys. Chem. Chem. Phys.*, 18, 27921-27927.

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