

Polaron- and Self-Trapped Exciton Formation in Anatase and Rutile TiO₂ Studied by Temperature Dependent Photoluminescence

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Because of its high quantum yield and a suitable electronic band structure, titania (TiO₂) is a very promising semi-conducting material for photo-conversion applications such as photocatalytic reactions and as transport material in photovoltaic. From many studies performed on electronic and optical properties on TiO₂, some experimental facts and some typical features have been evidenced and are the basis of our understanding: a very large Stokes shift, a very efficient separation of photoexcited charges (electron and hole), a strong charge-phonon coupling, and a high density of oxygen vacancies. Nevertheless, a comprehensive picture of the carrier behavior, that could unify all the experimental observations by involving those mechanisms, is still missing. Even if many hypotheses about the photoluminescence (PL) origin were published since the first studies of light emission in TiO₂, a large set of different interpretations is still proposed where the electron-hole recombination mechanisms show various physical origins as: self-trapped excitons, recombination from surface states, or oxygen vacancies.

Our paper aims thus at giving some insight into the processes that the carriers come across after their excitation and at clarifying, which mechanism is dominant: We attempt in this work to clarify the origin of the PL in TiO₂ crystals and the way the carriers are trapped or the way they move. Our work involves a method that we successfully used on nanocrystals [1-3] and that we now apply to study bulk crystals because they preserve the ability to observe intrinsic processes. Our analysis is based on the measurement of PL spectra as function of temperature: indeed, radiative recombination of the photo-induced carriers is in competition with charge transfer towards surface sites.

We show that, in anatase and rutile, weakly bound self-trapped excitons are made out from carrier polarons and give rise to a broad emission in the visible spectral range. The thermal activation of carrier motion allows their hopping to distant sites that leads to the observed

quenching of luminescence. Both crystalline phases show thus a very strong interaction between the photogenerated carriers and the lattice. In the specific case of rutile TiO₂, the PL spectral shape and its intensity-quenching scenario reveal the presence of dark trap states. Moreover, an additional narrow line structure shows up at low temperatures. The latter is due to localized impurity states that can be attributed to oxygen vacancies and obeys to a Franck-Condon model that fits nicely experimental curves with a large Huang-Rhys parameter $S=2.5$.

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References:

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