

The Observation of Exciton Emission from Rutile Single Crystals

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In a recently published paper (1) we reported on the luminescence of semiconducting titanates. For all materials investigated, except TiO₂ (rutile), self-trapped exciton emission from a titanate group was observed at LHeT. For TiO₂ (rutile), band-gap excitation resulted in emission from Cr³⁺ impurity centers, even at LHeT.

To obtain further information on the luminescence properties of TiO₂ (rutile), measurements were performed on a single crystal. The TiO₂ (rutile) single crystal was kindly put at our disposal by Dr. L. H. Brixner of E. I. du Pont de Nemours and Company, Inc. (Wilmington, Delaware). This crystal was pulled from a very pure melt, so that the Cr³⁺ content is expected to be low in view of the favorable distribution coefficient. The luminescence measurements were performed on a Perkin-Elmer MPF-44L spectrofluorometer equipped with an Oxford Instruments CF204 liquid helium flow cryostat.

In Fig. 1 the emission spectrum of the rutile single crystal under band-gap excitation is shown. The emission spectrum starts on the shortwavelength side with a sharp line at 412 nm, followed by two other lines at 419 and 427 nm. The 412-nm emission line coincides within the experimental error

with the band gap of rutile, which is observed as the onset of the excitation spectrum. The emission lines are superimposed on a broad emission band with a maximum at about 485 nm. The line emissions are quenched very rapidly when the temperature is raised. Above 12 K these lines are no longer observed. The intensity of the broad-band emission is at 12 K about 35% of the intensity observed at 4.8 K. This suggests that the lines and the band originate from different luminescent centers. In view of their intensity ratio and the value of the Stokes shift of the band it is improbable that the 412 nm line would be a 0-0 transition belonging to the broadband emission (2).

Band-gap excitation at 4.8 K resulted also in emission in the near infrared. This is the emission from Cr³⁺ impurity centers we observed also for a TiO₂ (rutile) powder sample (1). Grabner *et al.* (3) reported this emission for rutile single crystals. The intensity of the Cr³⁺ emission increases with increasing temperature.

Following the argument of Toyozawa (4) discussed in Ref. (1), the sharp line at 412 nm can be ascribed to free exciton emission. This line coincides with the absorption band edge of TiO₂ (rutile) (see also Fig. 1 in Ref. (1)). The lines at 419 and 427 nm

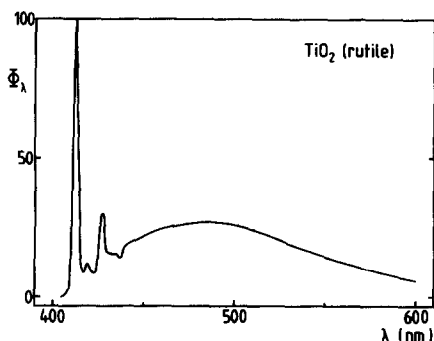


FIG. 1. Emission spectrum of a TiO_2 (rutile) single crystal at 4.8 K, recorded for excitation at 380 nm. Corrections have been made to account for the photomultiplier sensitivity. Φ_λ denotes the photon flux per constant wavelength interval in arbitrary units.

are situated at about 400 and 850 cm^{-1} lower energy, respectively. These values agree well with phonon frequencies reported for rutile (5). Therefore, they are attributed to phonon repetitions of the free exciton line.

Assignment of the broad emission band centered at 485 nm is less obvious. For the time being we ascribe this band to bound excitation emission due to trapping of free excitons by titanate groups near defects.

The results show clearly that in TiO_2 (rutile) we are dealing with a free state. As far as we are aware this is the first report of line emission from TiO_2 , although the compound has been studied many times before. From our research it is clear, that the line emission can only be observed at very low temperatures and Cr^{3+} concentrations. The free exciton state migrates over the lattice. At relatively high Cr^{3+} concentrations it will be effectively trapped by the Cr^{3+} impuri-

ties. If the Cr^{3+} concentration is low enough, trapping by defect states (resulting in broad band emission) or radiative free exciton recombination become also possible. The present observations confirm our qualitative model given before in Ref. (1).

Finally we would like to report in this context, that we also investigated the luminescence of the anatase modification of TiO_2 and found the same results as reported by Deb (6) for a sample of which it is not clear whether it is anatase or not. This shows that in the anatase modification the emission originates from self-trapped excitons, as is the case in SrTiO_3 . Localization probably prevails because the number of contacts between the titanate octahedra is lower in the anatase than in the rutile structure.

Acknowledgments

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