MITT.ÖSTERR.MINER.GES. 149 (2004)

NATURE OF BENITOITE $BaTiSi_3O_9$ LUMINESCENCE

Gaft, M.[1], Nagli, L.[2] & Waychunas, G.[3]

[1] International Technologies Lasers (ITL), Rishon-Lezion, Hachoma 12, Israel
[2] Tel-Aviv University, School of Physics and Astronomy, Tel-Aviv, Israel
[3] Geochemistry Dept., Earth Sciences Division, MS 70-108B E.O. Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley, CA 94720
e-mail: michael_g@itlasers.com

Three broad bands and one narrow line have been detected in laser-induced luminescence spectra of benitoite. At 300 K the first band has λ_{max} = 420 nm, Δ = 80 nm and τ = 2.6 μs. The excitation spectrum consists of a narrow band peaking at 290 nm with a shoulder at 245 nm. At lower temperatures luminescence intensity and band shape remain practically the same, but τ becomes substantially longer, up to 1.1 ms at 40 K. It is proved that this blue band is connected with intrinsic isolated TiO_6 octahedra. The metastable level $^3T_{1u}$ is the emitting level at low temperatures with long τ. At higher temperatures an energy level with higher radiation probability must be involved in the emission process, and this level is situated at 0.06 eV higher than the lowest level. These two levels may be connected with $^3T_{1u}$ level splitting or with closely spaced $^3T_{1u}$ and $^3T_{2u}$ levels. Decay time shortening and thermal quenching are connected with non-radiative decay within the TiO_6 luminescence center, while energy migration does not take place at least up to room temperature.

At 300 K the second band has λ_{max} = 660 nm, Δ = 135 nm and τ = 1.1 μs. The excitation spectrum consists of an asymmetric band peaking at 350 nm. At lower temperatures the luminescence intensity is 10 times stronger and the emission band becomes narrower with longer τ (100 nm and 25 μs at 40 K, respectively). Such behavior may be connected with an intrinsic Ti^{3+} luminescence center. Excitation peaking at 355 nm is connected with the $^2T_2$-^2E transition, while the splitting of the ^2E state is a reason of the two shoulders present in the excitation spectrum. At lower temperature the opposite transition generates an intensive luminescence band peaking at 660 nm with τ = 20 μs. Thermal quenching and drastically reduced decay time with increasing temperature result from a non-radiative transition from excited to ground state.

At 300 K the third band has λ_{max} = 725 nm, Δ = 125 nm and τ = 100 μs. It is accompanied by a narrow line at 682 nm with similar τ. At lower temperatures the broad band is much weaker, while the narrow line becomes substantially stronger with longer τ, reaching 1.1 ms at 40 K. Such behavior is suitable for a d^3 luminescence center, possibly Mn^{4+} or Cr^{3+}