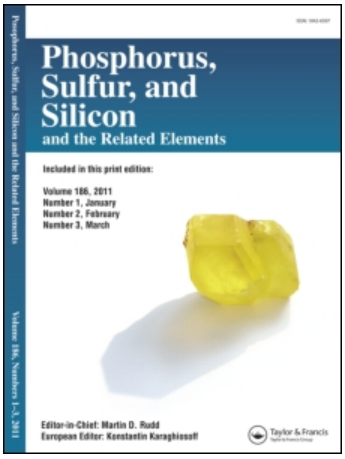

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Luminescent Properties of Some Rare Earth Phosphates

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LUMINESCENT PROPERTIES OF SOME RARE EARTH PHOSPHATES

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Abstract Luminescent properties of scandium and yttrium phosphates are discussed and mechanisms involving their emissions proposed.

Key Words: Scandium, Yttrium, Lanthanides, Luminescence, Inorganic Materials.

The tetrahedral PO_4 group is considered "transparent"in the visible and ultraviolet spectrum, up to about 1750 Å, so the possibility that $LnPO_4$ may display their own optical properties was scarcely admitted [1]. The aim of the present work is to study the luminescent activity of the dynamic matrix $Sc_xY_{1-x}PO_4$, and related $ScVO_4$. Pure $ScPO_4$ exhibited a red luminescence (excit. 314, 445 *nm*; emis. 680 *nm*), while pure YPO_4 showed only a weak blue emission. Intermediate solid solutions with $x = 0.25$; 0.5 and 0.75 reproduce $ScPO_4$ emissions while relative intensities increase with x. The phosphates were regarded as systems in which optical activity is due to an interaction between the cationic and anionic orbitals. The xenotime structure implies a D_{2d} site symmetry for Sc in a distorted octahedral environment. So, the non-occupied ***d*** orbitals are split into four levels belonging to the irreducible representations A_1, B_1, B_2 and E, while the non-occupied ***s*** orbital transforms as A_1. The highest occupied molecular orbitals of the complex have essentially characteristics of the ligands. Thus, the absorption of radiation by the system corresponds to a charge transfer process. After fast internal relaxations to the state $|1>$ emission may then occur through a transition to the state $|0>$, corresponding to the annihilation of an electron-hole pair. An alternative way to deal with this process is to consider the transition $|1> \Rightarrow |0>$ as an interband transition in which the state $|1>$ would be associated with a ***spd*** type band and the state $|0>$ would correspond to a band of the ***sp*** type. The YPO_4 emission can be rationalized by the fact that, since the ***d*** and ***s*** orbitals of Y^{3+} are higher in energy, the gap between the states $|1>$ and $|0>$ is larger than in the case of Sc^{3+}. In the case of $ScVO_4$ an additional low lying energy level belonging to the VO_4^{3-} group must be considered within the scheme: if it is close to the cationic ***d*** and ***s*** orbitals a quenching effect on the $|1> \Rightarrow |0>$ emission might take place. This explains the fact that no red emission is observed and the band agrees in position with the optical activity of the VO_4^{3-} ion.

REFERENCE

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