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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 \AA , 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 $\text{Sc}_x\text{Y}_{1-x}\text{PO}_4$ and related ScVO_4 . Pure ScPO_4 exhibited a red luminescence (excit. $314, 445 \text{ nm}$; 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 $|1\rangle$ emission may then occur through a transition to the state $|0\rangle$, corresponding to the annihilation of an electron-hole pair. An alternative way to deal with this process is to consider the transition $|1\rangle \Rightarrow |0\rangle$ as an interband transition in which the state $|1\rangle$ would be associated with a spd type band and the state $|0\rangle$ 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 $|1\rangle$ and $|0\rangle$ 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 $|1\rangle \Rightarrow |0\rangle$ 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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