

Yttrium(III) oxomolybdates(VI) as potential host materials for luminescence applications: an investigation of Eu^{3+} -doped $\text{Y}_2[\text{MoO}_4]_3$ and $\text{Y}_2[\text{MoO}_4]_2[\text{Mo}_2\text{O}_7]$.

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Rok wydania

2013

Czasopismo

New Journal of Chemistry

Numer woluminu

37

Strony

1919-1926

DOI

10.1039/C3NJ00166K

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

Two ternary yttrium(III) oxomolybdates(VI) are investigated, both structurally and spectroscopically. The crystal structure of $\text{Y}_2[\text{MoO}_4]_3$ was solved at room temperature in the orthorhombic space group $Pba2$ ($a = 1030.21(3)$, $b = 1032.41(3)$, $c = 1057.25(3)$ pm, $Z = 4$). In the unit cell, three discrete *ortho*-oxomolybdate(VI) units $[\text{MoO}_4]^{2-}$ and two Y^{3+} cations, both with CN = 7 featuring a monocapped trigonal-prismatic oxygen environment, can be distinguished. $\text{Y}_2[\text{MoO}_4]_2[\text{Mo}_2\text{O}_7]$ crystallizes monoclinically in the space group $P2_1/c$ ($a = 681.85(2)$, $b = 959.13(3)$, $c = 1052.99(3)$ pm, $\beta = 105.586(2)^\circ$) with two formula units per unit cell. In this compound the anionic environment of the crystallographically unique Y^{3+} cations also comprises seven oxygen atoms forming a monocapped trigonal prism. Furthermore, the crystal structure features both tetrahedral $[\text{MoO}_4]^{2-}$ and pyroanionic $[\text{Mo}_2\text{O}_7]^{4-}$ entities, the latter in staggered conformation, with the bridging oxygen atom between the two vertex-shared $[\text{MoO}_4]^{2-}$ tetrahedra residing on an inversion centre. Besides self-activated emission, resulting from the oxomolybdate(VI) units (maximum at around 600 nm), both compounds have the potential to be used as luminescence host materials, shown by spectroscopic studies involving Eu^{3+} as a sensitive probe. The emission spectra of $\text{Y}_2[\text{MoO}_4]_3:\text{Eu}^{3+}$ and $\text{Y}_2[\text{MoO}_4]_2[\text{Mo}_2\text{O}_7]:\text{Eu}^{3+}$ are dominated by the Eu^{3+} -typical $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition at 614 nm. In the excitation spectra, aside from 4f-interconfigurational Eu^{3+} transitions at lower energies, broad charge-transfer (CT) bands due to $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$ or $\text{O}^{2-} \rightarrow \text{Mo}^{6+}$ transitions dominate at higher energies. Comparing the diffuse reflectance spectra (DRS) of the undoped with the Eu^{3+} -doped materials, the $\text{O}^{2-} \rightarrow \text{Mo}^{6+}$ LMCT process proves to be crucial for the position of the broad CT band in the excitation spectra of both yttrium oxomolybdates(VI).

Adres publiczny

<http://dx.doi.org/10.1039/C3NJ00166K>

Strona internetowa wydawcy

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Plik został wygenerowany dnia 2026-10-09 12:00:07

Adres w repozytorium <https://old.chem.uni.wroc.pl/pl/repozytorium/OX7yUjg>.