

SYNTHESIS AND CRYSTAL STRUCTURE OF
A NEW LAYERED HYBRID GALLOPHOSPHATE CONTAINING OXALATE GROUPS

by

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The field of open framework materials has expanded dramatically during the last few years by introducing suitable organic ligands as part of the crystal structures, thus allowing a more flexible tailoring of the atomic architecture. The resulting materials can be described as hybrid inorganic-organic frameworks [1].

We have investigated the use of oxalic acid as an organic ligand having four potential donor sites for cation coordination. The compound $(C_2N_2H_{10})_3[Ga_4(C_2O_4)_4(HPO_4)_4(H_2PO_4)_2]$ was prepared by hydrothermal synthesis under autogenous pressure using ethylenediamine (*en*) and oxalic acid as organic structuring agents. The title compound was accompanied by a second new oxalate-bearing gallophosphate, $(C_2N_2H_{10})_2[Ga_2(C_2O_4)_2(HPO_4)_3] \cdot H_2O$, described elsewhere [2]. The starting mixture, corresponding to the molar composition $0.5 Ga_2O_3, 2 H_3PO_4, 2 H_2C_2O_4 \cdot 2 H_2O, 4 H_3BO_3, 2 en$ and $202 H_2O$, was placed in a Teflon-lined stainless-steel autoclave and heated at $165^\circ C$ for five days. The structure was determined by single-crystal X-ray diffraction (CCD detector, MoK α radiation, room temperature).

It crystallises in triclinic space group P1 with $a = 8.730(1), b = 11.575(1), c = 11.696(1) \text{ \AA}$, $\alpha = 115.12(1), \beta = 90.07(1), \gamma = 111.23(1)^\circ$, $V = 950.52(16) \text{ \AA}^3$, $Z = 2$, $R(F) = 5.63 \%$ for 2452 observed data with $F_0^2 > 2\sigma(F_0^2)$. The compound consists of anionic chains built of corner-linked alternating GaO_6 octahedra and PO_4 tetrahedra. Parallel chains are corner-linked to form corrugated sheets parallel to (011). Each GaO_6 octahedron is coordinated to four mono- or di-protonated PO_4 tetrahedra and one bidentate oxalate group. Charge neutrality is achieved by the incorporation of *en* in its diprotonated form. The *en* molecules, situated between and within the polyhedral sheets, interact with the inorganic framework via multipoint hydrogen bonding. Slight orientational disorder is observed for one of the three PO_4 groups, and two of the three *en* molecules. These disorder features are interrelated. Thermogravimetric analyses indicate that the structure remains stable until $\sim 250^\circ C$, when the loss of *en* leads to a collapse of the structure. The total mass loss of 39.2 % corresponds to the weight of oxalate and *en*. A further characterisation using IR absorption and Raman spectroscopy is in progress.

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References

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