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(54) **TEMPLATED, LAYERED MANGANESE PHOSPHATE**

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(58) **Field of Search** 423/311; 556/24

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,089,881 A * 5/1978 Lukehart
4,497,743 A * 2/1985 Brisset et al.
5,780,003 A 7/1998 Lewis
6,156,931 A 12/2000 Lewis

OTHER PUBLICATIONS

Escobal, et al., "A New Manganese(II) Phosphate Templated by Ethylenediamine: $(C_2H_{10}N_2)[Mn_2(HPO_4)_3(H_2O)]$. Hydrothermal Synthesis, Crystal Structure, and Spectroscopic and Magnetic Properties", *Chem. Mater.*, (2000), 12, 376–382.

Serre, et al., "Synthesis and characterization of MIL-43 and MIL-44, two new layered templated tetravalent phosphates: $Zr(PO_4)_2 \cdot N_2C_2H_{10}$ and $Ti_2(PO_4)_2 \cdot (HPO_4)_2 \cdot N_2C_2H_{10}$ ", *Solid State Sciences* 3 (2001), 623–632.

Simon, et al., "Synthesis and crystal structure of MIL-32: a new chiral layered aluminophosphate templated with non chiral tris (2-aminoethyl)amine: $Al_3(PO_4)_4 \cdot N_4C_6H_{21} \cdot H_2O$ ", *Solid State Sciences* 3 (2000), 389–395.

Yao-Hua Xu, et al., "An Open Framework Aluminophosphate with Unique 12-Membered Ring Channels: $Al_9(PO_4)_{12} \cdot (C_{24}H_{91}N_{16}) \cdot 17 H_2O$ ", *Journal of Solid State Chemistry* 145, (1999), 220–226.

Serpaggi, et al., "A New Gallium Phosphate Templated by Tris(2-aminoethyl)amine: $[Ga(HPO_4)(PO_4(OH))[(C_2H_7N)_3N] \cdot H_2O]$ ", *Acta Cryst.*(1997), C52, 1568–1570.

S. Ayyappan, et al., "A Novel Monomeric Tin(II) Phosphate, $[N(C_2H_5NH_3)_3]^{3+} [Sn(PO_4)(HPO_4)]^{3-} \cdot 4H_2O$, Connected through Hydrogen Bonding," *Journal of Solid State Chemistry* 139, (1998), 207–210.

Simon, et al., "Synthesis and crystal structure of MIL-27: a new oxyfluorinated three-dimensional framework metallo-phosphate obtained with aluminum in four, five and sixfold coordination and templated with the tris (2-aminoethyl)amine", *Solid State Sciences* t. 1 (1999), 339–349.

* cited by examiner

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(57) **ABSTRACT**

A new crystalline manganese phosphate composition having an empirical formula:



The compound was determined to crystallize in the trigonal space group P-3c1 with $a=8.8706(4) \text{ \AA}$, $c=26.1580(2) \text{ \AA}$, and $V(\text{volume})=1783 \text{ \AA}^3$. The structure consists of sheets of corner sharing $Mn(II)O_4$ and PO_4 tetrahedra with layers of $(H_3NCH_2CH_2)_3N$ and water molecules in-between. The protonated $(H_3NCH_2CH_2)_3N$ molecules provide charge balancing for the inorganic sheets. A network of hydrogen bonds between water molecules and the inorganic sheets holds the structure together.

12 Claims, 2 Drawing Sheets

