

A(x)(H₃O)(2-x)Mn-5(HPO₃)(6) (A = Li, Na, K and NH₄): open-framework manganese(II) phosphites templated by mixed cationic species

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[Ver ResearchID y ORCID](#)

DALTON TRANSACTIONS

Volumen: 45

Número: 30

Páginas: 12188-12199

DOI: 10.1039/c6dt01610c

Fecha de publicación: AUG 14 2016

[Ver información de revista](#)

Resumen

A(x)(H₃O)(2-x)Mn-5(HPO₃)(6) (A = Li, x = 0.55 (1-Li); A = Na, x = 0.72 (2-Na); A = K, x = 0.30 (3-K); A = NH₄, x = 0.59 (4-NH₄)) phases were synthesized by employing mild hydrothermal conditions. 1-Li was studied by single crystal X-ray diffraction, while sodium, potassium and ammonium containing analogues were obtained as polycrystalline samples and characterized by powder X-ray diffraction. The four compounds were characterized by ICP-Q-MS, thermal analysis and XPS, IR, UV/Vis and EPR spectroscopy. Single crystal data indicate that 1-Li crystallizes in the P3c1 space group with lattice parameters a = 10.3764(1) angstrom and c = 9.4017(1) angstrom with Z = 2. The crystal structure of these phases is constituted by a three-dimensional [Mn(II)(5)(HPO₃)(6)](2-) anionic skeleton templated by alkali metal and ammonium cations together with protonated water molecules. Such an inorganic framework is formed by layers of edge-sharing MnO₆ octahedra placed in the ab plane and joined along the c direction through phosphite pseudotetrahedra. The sheets display 12-membered ring channels parallel to the c-axis, ca. 5 angstrom in diameter, where the extra framework species display a strong disorder. EPR measurements point to the existence of short range ferromagnetic interactions around 12 K. Magnetic susceptibility and heat capacity measurements show that all the compounds exhibit long range antiferromagnetic order below circa 4 K, with a significant magnetocaloric effect around the Neel temperature.

Palabras clave

KeyWords Plus: CRYSTAL-STRUCTURES; MAGNETIC-PROPERTIES; CATHODE MATERIAL; IRON PHOSPHITE; HEAT-CAPACITY; ION BATTERY; TRANSITION; CHANNELS; FE; ANTIFERROMAGNETISM

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Financiación

| Entidad financiadora | Número de concesión |
|--|---------------------------------------|
| Ministerio de Economía y Competitividad | MAT2013-42092-R MAT2014-55049-C2-R |
| Gobierno Vasco | IT630-13 |
| UPV/EHU | UFI11/15 |
| National Program for the Promotion of Human Resources within the National Plan of Scientific Research, Development and Innovation, "Ministerio de Ciencia y Educacion" | |
| CONICYT | 3150455 |

[Ver texto de financiación](#)

Editorial

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Categorías / Clasificación

Áreas de investigación:Chemistry

Categorías de Web of Science:Chemistry, Inorganic & Nuclear

Información del documento

Tipo de documento:Article

Idioma:English

Número de acceso: **WOS:000381328100032**

ID de PubMed: 27412966

ISSN: 1477-9226

eISSN: 1477-9234

Información de la revista

- Impact Factor: [Journal Citation Reports®](#)

Otra información

Número IDS: DT2RM

Referencias citadas en la Colección principal de Web of Science: **52**

Veces citado en la Colección principal de Web of Science: **0**