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MS17 O3

Positive Electrode Materials Based On Moroccan Mineral Resources (Co, Mn, Ni) : Structural And Electrochemical Properties I. Saadoun¹, M. Aklalouch¹, M. Dahbi¹, J.M. Amarilla², K. Edstrom³ And T. Gustafsson³. ¹ ECME, LP2E2M, Université Cadi Ayyad, Morocco. ² ICMC CSIC, Madrid, Spain. ³ Angström Lab., Uppsala University, Sweden

Keywords: Rietveld Refinement, Functionally graded Materials, Energy storage

Intense research is worldwide devoted to the synthesis and characterization of positive electrode materials for lithium ion batteries owing to their high energy density and excellent power performances. Most of the efforts are concentrated on the two-dimensional layer-structure LiMO_2 (M : Co, Mn, Ni), the three-dimensional LiMn_2O_4 spinel and the LiFePO_4 olivine type structure. Fortunately, Morocco produces cobalt, manganese, nickel and is the main phosphate producer in the world. For the layered LiMO_2 oxide, Li^+ and M^{3+} cations are supposed to be orderly arranged along the (111) direction of the rock salt cubic lattice leading to a 2D layer structure, isostructural with $\alpha\text{-NaFeO}_2$ (space group R-3m). Li^+ cations reside at Wyckoff 3a (0 0 0) octahedral sites, Ni^{3+} cations are located in octahedral 3b (0 0 1/2) and oxygen anions are in a cubic close-packing, occupying the 6c (0 0 z) sites. Stoichiometric LiNiO_2 (Li/Ni = 1) is difficult to synthesize. Some extra-nickel ions are present in the Li plane leading to $[\text{Li}_{1-z}\text{Ni}_z]_{3a}[\text{Ni}]_{3b}[\text{O}_2]_{6c}$ true formula. This results in a lower initial capacity as well as severe capacity loss upon cycling. Co substitution for Ni leads to strictly two-dimensional $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ oxide without extra-nickel in the lithium plane. We have selected the $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ composition for the electrochemical study. In order to increase its electronic conductivity and to make easier the lithium diffusion during the intercalation process, two ways were chosen: i) synthesis by the combustion method which leads to small particle sizes, ii) substitution of Mn for Ni and Co, which leads to the existence of mixed valence system. The results of structural study were discussed in relation with magnetic and electrochemical properties.

On the other hand, LiMn_2O_4 adopts the spinel structure (space group $\text{Fd}\bar{3}m$) consisting of a cubic close packed oxide ions with the manganese ions in one half of the octahedral site (16d wyckoff site) and Li^+ ions in one-eighth of tetrahedral sites (8a site). Although of its low cost and good environmental benignity, this oxide suffers from a serious capacity deterioration problem after cycling at high temperatures which seems to be related to the existence of Jahn-Teller Mn^{3+} ions. In order to improve the rate capability of the materials and to keep the oxidation state of manganese as Mn^{4+} , we have carried out the synthesis of nanocrystalline double substituted spinels $\text{LiNi}_{1.5-y}\text{Ni}_{0.5-y}\text{Cr}_{2y}\text{O}_4$. The samples have been characterized at first by X-ray diffraction. The Scherrer method has been used to elucidate the thermal evolution

of the average crystallite sizes. The relationship between the structural data and the electrochemical performances of the studied samples will be presented during the ECM meeting.

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MS17 O4

High-pressure structural studies of energetic compounds C. R. Pulham,^a A. J. Davidson,^a I. D. H. Oswald,^a D. I. A. Millar,^a F. P. A. Fabbiani,^b D. J. Francis,^b W. G. Marshall,^b A. S. Cumming,^c D. R. Allan,^d A. R. Lennie^e and T. J. Prior.^e ^aSchool of Chemistry and Centre for Science at Extreme Conditions, University of Edinburgh, UK. ^bISIS Neutron Facility, Rutherford Appleton Laboratory, UK. ^cDstl, Fort Halstead, Sevenoaks, UK. ^dDiamond Light Source, UK. ^eSRS, Daresbury Laboratory, Warrington, UK
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Keywords: energetic materials, high-pressure diffraction, polymorphism

The effective modelling of the properties and performance of solid energetic materials (propellants and explosives) under operational conditions requires detailed knowledge of the crystal structures of these compounds. In many cases, the crystal structure of the compound obtained under ambient conditions is used as the basis for modelling properties at higher temperatures and pressures because structural information is often not available under more extreme conditions. However, such extreme conditions can lead to substantial changes in intermolecular interactions and molecular geometries, and can even induce phase transitions leading to dramatic changes in properties such as detonation velocity, shock sensitivity, and reactivity. There is therefore a requirement to obtain *detailed* structural information about these materials under extreme conditions. Using a combination of X-ray and neutron diffraction techniques, augmented by vibrational spectroscopy, we have studied a series of energetic ammonium salts and have obtained detailed structural information for these materials at pressures up to ~8 GPa. Under hydrostatic conditions ammonium perchlorate undergoes a first order phase transition at 3.98 GPa in agreement with the results of a previous study [1]. We have successfully solved and refined the structure of this new orthorhombic phase, which features a more close-packed structure with more extensive hydrogen bonding. Contrary to a previous report [2], no evidence was found for a pressure-induced phase transition in ammonium dinitramide up to 4.03 GPa – an equation of state up to this pressure has been obtained. Significant changes were observed in the intermolecular contacts involving N-H...O-N interactions, and in the torsional angles of the dinitramide ion. We have also studied the effects of pressure on the widely used secondary explosives HMX and RDX. Structural information on the β -form of HMX up to ~8 GPa has been obtained. Neutron powder diffraction studies of RDX up to ~8 GPa confirm the previously observed α - γ transition at ~4 GPa [3,4] and suggest a significant conformational change in the high-pressure polymorph.

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MS17 O5

Magnetic and crystal structure of the BiCrO₃ multiferroic compound. Pierre Bordet^a, Céline Darie^a, Céline Goujon^a, Maria Bacia^a, Holger Klein^a and Emmanuelle Suard^b, ^a *Institut Néel, CNRS-UJF, BP166, 38042 Grenoble cedex 9, France*, ^b *Institut Laue-Langevin, BP156, 38042 Grenoble cedex 9, France*
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Keywords: multiferroics, perovskite, neutron diffraction

Bi-based perovskites are the subject of a renewed research interest due to the coexistence of magnetic and electric orders observed in BiMnO₃ and BiFeO₃. This rare phenomenon is thought to originate from the structural distortion induced by the 6s² electron lone pairs of the Bi³⁺ cations. Another consequence is the instability of many of these compounds at room pressure. We report here the synthesis at high pressure and the crystallographic/magnetic investigation of BiCrO₃, an up-

to-now less studied material [1], using electron microscopy and temperature dependent x-ray and neutron powder diffraction.

Polycrystalline samples of BiCrO₃ were synthesized by high pressure solid state reaction in a Conac anvil-type apparatus at 2 GPa and 750°C. Magnetic susceptibility measurements show the onset of magnetic order at 114K followed by a large increase below 80K. X-ray powder diffraction measurements were carried out up to 900°C under inert gas or air. Neutron powder diffractograms were collected on the D20 and D2B instruments of the ILL-Grenoble between 2K and 470K. BiCrO₃ is found to be isostructural to BiMnO₃ at room temperature, with monoclinic space group C2, and 3 independent Cr³⁺ cation sites. It transforms to the orthorhombic GdFeO₃ type at 405K. Although the observed magnetic neutron scattering is confined to the nuclear Bragg peaks, solution and refinement of the neutron diffraction data indicate the appearance of G-type anti-ferromagnetic order at the 114 K transition temperature, with all spins aligned along one of the unit cell axes, spins on different Cr sites being anti-parallel. This is followed by a progressive spin re-orientation between 80 K and 60 K. The low temperature value of the magnetic moment is 2.5 μB as expected for Cr³⁺ cations. Detailed results of these investigations and comparison with dielectric measurements will be presented at the meeting.

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