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NEW LANGBEINITE PHOSPHATES, $K_2MTi(PO_4)_3$ (M = Er, Yb or Y)

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Three new potassium rare-earth/titanium phosphates $K_2ErTi(PO_4)_3$, $K_2YbTi(PO_4)_3$ and $K_2YTi(PO_4)_3$ have been structurally characterised by X-ray diffraction. They all belong to the langbeinite structure type, which has attained interest for a long time due to their ferroelastic and ferroelectric properties. Monophosphates with the chemical formula A_xM_2 $(XO_4)_3$ often crystallise in the cubic langbeinite $[K_2Mg_2$ $(SO_4)_3$] type structure or in the rhombohedral Nasicon $[Na_3Zr_2$ $(PO_4)(SiO_4)_3$] type. The langbeinite structure consists of isolated MO_6 octahedra connected to XO_4 tetrahedra by corner-sharing, thus forming a 3-dimensional framework. The A cations are located in cages formed by the framework. The title compounds can be regarded as modified KTi_2 $(PO_4)_3$ -structures where titanium have been partly replaced by a trivalent cation on both crystallographic independent sites, resulting in $K_2MTi(PO_4)_3$ (M = Er, Yb or Y) structures. An alternative approach describing the langbeinite structure using $[M_5X_6O_{39}]$ units will be presented. This new building unit is shaped as a trigonal pyramid with MO_6 octahedra in each corner and one in the centre of the pyramid. The new building mode has several advantages compared to using the conventional building block, $M_2X_3O_{18}$.

Keywords: LANGBEINITE MONOPHOSPHATE STRUCTURE DESCRIPTION

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APPLICATION OF RIETVELD METHOD TO XRD AND SAED PATTERN OF NANOCRYSTALLINE TiO_2 SAMPLES

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Two kinds of nanocrystalline TiO_2 samples were synthesised by the sol-gel method: iron doped TiO_2 (contains iron as a solid solution and poly(ethylene)glycol in anatase matrix) and undoped TiO_2. They were characterized by means of X-ray diffraction measurements (XRD) and selected area electron diffraction (SAED). Rietveld refinement of XRD and SAED data was applied in order to extract structural parameters such as unit cell parameters, bond lengths and angles. The obtained unit cell parameters a, c, bond lengths and angles from Rietveld refinement of XRD pattern are in a good agreement with obtained parameters from SAED pattern. Comparing our results with previous results obtained from neutron diffraction on coarse-grained TiO_2 powders, we found evident decrease of lattice parameter c and slight increase of lattice parameter a and enhancement of Debye-Waller parameters. The grain-size (in the range from 3 to 12 nm) dependencies of structural parameters can be explained by two-state model (presence of significant amount of grain boundaries in samples with nanocrystalline grains). Significant changes of lattice parameters were found between undoped and iron doped samples in parameter a for 0.4 % and c 0.5 % (XRD) and a 1.6 %, c 0.5 % (SAED). The changes are observed in bond lengths and angles. This can be explained by substitutional role of iron ions within unit cell of anatase. The reliability factor of the refinement is on average Rwp=10 % (XRD) and 15 % (SAED), indicating a good fit.

Keywords: RIETVELD, XRD, SAED

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ELECTRON DENSITY DISTRIBUTION IN MAGNESIUM-STABILISED CUBIC LITHIUM MANGANATE SPINEL

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Lithium manganate $Li_xMn_2O_4$ $(0 < x < 2)$ and its derivatives form a series of promising candidates for rechargeable batteries with a wide nonstoichiometry range necessary for reversibly intercalating Li ions. A synchrotron X-ray powder diffraction study on the electron density distribution of stoichiometric $Li(Mg_{1/6}Mn_{11/6})O_4$ cubic crystals revealed that (1) the structure is essentially of spinel-type with a faint diffuse scattering, (2) the Li atoms are not located at the ideal 8a site of the *Fd*3*m* spinel structure, but distributed among four positions slightly apart from the 8a, (3) the accumulation of residual electrons at the positions 0.35 Å apart from the 16c octahedral interstices suggests the existence of some portion of Li atoms at those positions, (4) the O atoms also show a statistical distribution around their ideal positions, and (5) the 3d electrons of Mn atoms are squeezed out toward the open space of the coordination octahedra with D3d distortion. The present results indicate an existence of many metastable positions available for Li, which possibly introduce a complicated hopping routes for Li in conjunction with local distortion of neighbouring atoms at least up to the second shell around Li. The distributions of Li and O atoms were supported by the molecular dynamics simulation. The electron density distribution around Mn was investigated by the molecular orbital calculation.
Synchrotron X-ray powder diffraction experiments were carried out at BL20B, Photon factory, Tsukuba.

Keywords: LITHIUM MANGANATE SPINEL ELECTRON DENSITY DISTRIBUTION LI DIFFUSION PATHWAY

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CORRELATION BETWEEN THERMAL VIBRATION AND CONDUCTIVITY IN $La_{0.9}Sr_{0.1}B_{0.9}Mg_{0.9}O_3$, B = Al, Ga, AND Sc

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In order to obtain a better understanding of the oxide ion conductivity in perovskites, the structure of $La_{0.9}Sr_{0.1}B_{0.9}Mg_{0.9}O_3$, B = Al, Ga, and Sc, have been investigated by time-of-flight powder neutron diffraction at room temperature, 270, 470, 850 and 950°C. For all compounds, at all temperatures, structural and an-isotropic thermal parameters were refined by full profile Rietveld methods. The changes in difference nuclear densities due to changes in temperature are illustrated by difference density maps around the atoms. The difference density maps are constructed from observed structure factors phased by calculated structure factors. Using observed structure factors, systematic errors due to model deficiencies and refinement are minimized. The nuclear difference densities are computed as the density at high temperature minus the density at room temperature. The difference density maps provide a direct picture of the average in space and time of changes in atomic thermal vibrations. The observed difference density distributions of the metal atoms may be described by zero and second order spherical harmonics, the natures of which vary with atomic sites. At the oxide ion sites, however, the difference density distributions are more smeared out and difficult to describe with second order spherical harmonics. The largest atomic vibration is found for the oxide ion positions. This is in good agreement with the fact that the oxide ions are the migrating ions. The conductivity of the materials has been measured at the same temperatures and correspondence is seen between high oxide ion conductivity and large atomic vibration.

Keywords: DIFFERENCE DENSITY MAPS PEROVSKITES THERMAL MOTION