

P11.02.77*Acta Cryst.* (2008). A64, C531**Electron density distribution in anatase (TiO₂) under UV-irradiation: Observation and calculation**

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Anatase-phase TiO₂ is widely recognized as an effective photocatalyst. This photocatalytic activity is ascribed to an excited electron and a hole under UV light. Asahi *et al.* (2000) has reported molecular-orbital bonding structure for anatase using first-principles calculations. Their calculation indicated that the excited electrons occupy Ti 3d t_{2g} d_{xy} non-bonding orbital, while this has not been confirmed experimentally. Natural single crystal of anatase (Tisey, Norway) was spherically ground in 200 μm in diameter and used for the experiments. A Rigaku AFC-5S four-circle diffractometer with monochromatized MoKα radiation was used for data collections. Three sets of diffraction intensities were collected; set 1 was collected under no light, set 2 under UV (λ = 253.6 nm: 4.9 eV) plus fluorescent light, and set 3, again, under no light. Structural parameters (with harmonic ADP) were preliminarily refined to attain most reliable scale and extinction factors for Fourier summation. Some of ADPs, particularly U₁₁ at O site showed small but notable increase with UV irradiation. There was no notable difference among electron densities ρ_{set1} and ρ_{set3}. On the other hand, characteristic differences were found on ρ_{set2} - ρ_{set3} (ρ₂₋₃) in the vicinity of both the Ti and O site positions. Positive densities beside the O site correspond to increase in harmonic ADP by heat with relaxation. On the other hand, appearance of positive density around the Ti site positions could not be explained by change only in harmonic ADP: electron cloud of Ti was deformed in <110>. Maximum in ρ₂₋₃ (0.24eÅ⁻³) was found at 0.28 Å from the Ti position in <110>. These positions correspond to those of the maxima of wavefunction of Ti 3d t_{2g} d_{xy} orbital calculated by a DV-Xα method.

Keywords: anatase, UV irradiation, excited electron

P11.02.78*Acta Cryst.* (2008). A64, C531**Structure determination of metallic nanoparticle catalysts by atomic scale *in-situ* environmental TEM**

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Catalyst chemical vapor deposition (CVD) is now known as the best method for large scale production of carbon nanotubes (CNTs). Metal nanoparticles absorb carbon from a source gas such as acetylene and expel CNTs. Since electronic properties of CNTs can be varied from metal to semiconductor by their atomic structures, there have been a number of theoretical and experimental studies on the role played by nanoparticle catalysts (NPCs). However, actual nucleation and growth process of CNTs from NPCs has never been observed at atomic scale. We show atomic-scale *in-situ* environmental transmission electron microscopy observation of the nucleation of CNTs followed by continuous growth in metal catalyzed CVD with the spatial resolution better 0.2nm. Surprisingly, CNTs grow from solid state NPCs of complex structures. Based on this finding, we succeed in solving long-standing problems on the CVD growth of CNTs.

Keywords: carbon nanotubes, catalyst structure, environmental transmission electron microscopy

P11.05.79*Acta Cryst.* (2008). A64, C531**Nanocrystalline structure of an active phase in V-Mo-Nb-O catalysts for ethane (amm)oxidation**Tatyana U. Kardash, Ludmila M. Plyasova, Valentina M. Bondareva, Svetlana V. Cherepanova, Dmitry I. Kochubey
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Development of catalysts based on nanomaterials and characterization of their structure has become the great deal of scientific attention in material science in the last time. The present study is devoted to the investigation of structural features of an active phase in V-Mo-Nb-O catalysts for selective transformations of ethane to ethylene, acetic acid and acetonitrile [1-2]. The catalysts were synthesized by mixing aqueous solutions of ammonium paramolybdate, ammonium metavanadate and niobium oxalate with further drying and calcination in air at 400 °C. Samples were analyzed by XRD, HREM and EXAFS. The active component of these catalysts is a triple compound with Me₅O₁₄-like structure (Me=Mo, V, Nb) and variable composition [1-2]. The active catalyst is XRD amorphous and characterized by the presence of both narrow reflections at d = 4.00, 2.00 Å, and broad reflection at d = 3.40 Å. HREM investigation reveal 1D-ordered nanostructure with block size <5 nm and interlayer distance of 0.40 nm. In perpendicular plane, networks are built by disordered Me₅O₁₄-like subunits, which consist of MeO₇-bipiramides connected by edge with five octahedra [3]. Model of active nanocrystalline phase was proposed according to HREM data, XRD pattern modeling by DFA method and local structure investigation by EXAFS. Authors acknowledge the financial support of RFBR (project 07-03-00203)

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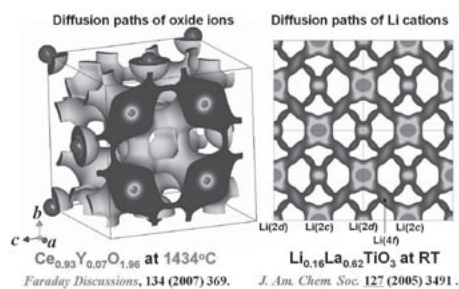
Keywords: V-Mo-Nb-O catalysts, nanostructure, Mo₅O₁₄**P11.13.80***Acta Cryst.* (2008). A64, C531-532**Structure and ionic conduction in inorganic materials through nuclear/electron density analysis**

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The development of improved electrolyte and electrode materials requires a better understanding of the mechanism of ionic conduction, and crucial to this is a comprehension of the crystal structure at high temperatures. Our group has developed new high-temperature neutron and high-resolution synchrotron diffraction techniques to study the precise crystal structures, nuclear and electron density in inorganic materials up to 1900 K [JAmCeramSoc85(2002)2925,89(2006)1395, JApplCryst37(2004)786, 38(2005)854]. Here we review our recent works on the positional disorder and diffusion path of mobile ions in Bi₂O₃ [CPL378(2003)395],

(La_{0.8}Sr_{0.2})(Ga_{0.8}Mg_{0.15}Co_{0.05})O_{2.8} [CPL380(2003)391], CeO₂ [APL84(2004)526], Bi_{1.4}Yb_{0.6}O₃ [APL87(2005)221909], Ce_{0.93}Y_{0.07}O_{1.96} [Farad.Discuss.134(2007)369], and La_{0.64}(Ti_{0.92}Nb_{0.08})O₃ [Chem.Mater.19(2007)32604], Y_{0.79}Ta_{0.21}O_{1.72} [ChemMater19(2007)3539], La_{0.6}Sr_{0.4}CoO₃ [JApplCryst40(2007)1166], (La_{0.6}Sr_{0.4})(Co_{0.8}Fe_{0.2})O_{3-x} [SolStIon179(2008)1939], (Pr_{0.9}La_{0.1})₂(Ni_{0.74}Cu_{0.21}Ga_{0.05})O_{4+x} [JACS139(2008)2662], La_{0.62}Li_{0.16}TiO₃ [JACS127(2005)3491] and CuLi [JMaterChem16(2006)4393] (Figure). It was found that the disorder and path depend on the crystal structure.



Keywords: neutron and X-ray diffractometry, *in-situ* powder diffraction, ionic conductors

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Short-range to long-range order structure change of Mg-Fe alloys

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We performed structure analysis of Mg-Fe alloy system prepared by mechanical alloying. For Mg concentrations up to about 15 mol%, mechanical alloying can produce single-phase bcc alloys. By using the conventional average structure analysis and X-ray pair-distribution function method, we can bridge the long-range and short-range order structure of Mg-Fe alloys. The substituted Mg atoms arranged randomly in the low-Mg composition, but Mg atoms came to have the order structure as the Mg composition increases. It can explain this new finding as a kind of short-range order to long-range order phase transition.

Keywords: Mg-Fe, mechanical alloying, pair-distribution function

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Development of a new type of Li-battery materials based on the milarite-family

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Over the last three decades, enormous efforts have been devoted to advance Li-ion based batteries by exploiting a variety of electrode and electrolyte materials [1]. However, demands for lighter and

smaller batteries exceed the dimension offered by the modern technology. In this respect, it is try-worthy continuing to develop new battery materials. The milarite-family (A₂B₂C[T(II)₃T(I)₁₂O₃₀): A = Sn⁴⁺, Ti⁴⁺, Zr, Al, Fe³⁺, ...; B = Na, H₂O; C = Na, K; T(I) = Si, Al; T(II) = Li, Be, Mg, ... [2, 3] is a highly interesting candidate due to: 1) the presence of short pathways available for conducting Li; 2) the presence of a crystal-chemical basis for the formation of solid-solutions and defect-engineering; 3) a high thermal stability up to 1200 K. In fact, our recent studies showed ionic conductivity in Li-bearing milarite-type minerals, sogdianite and sugilite, for the first time [4, 5]. The ionic conductivity in sogdianite could be assigned to site exchange processes of Li between T(II) and A sites parallel to the (001)-plane at elevated temperatures. Interestingly, the ionic conductivity in this topology is proportional to the amount of Na cations at B sites [5]. These Na cations may play a relevant multiple role, as carrying and transferring charges for the negative-charged framework [Li₃Si₁₂O₃₀]⁹⁻. Here, the state of the art development of Li-Na-bearing milarite-type Li-battery materials will be presented.

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Keywords: ionic conductors, milarite, sogdianite

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Optimization of energy parameters indemnification of impurity levels in lead and bismuth

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In impurity semiconductors except for the impurity giving the basic carriers of a charge, there are compensating impurities. Usually for their characteristic the measure of indemnification is entered and properties of semiconductors in a wide interval of a degree of indemnification are investigated. Influence of indemnification on properties of alloys is expressed that in the forbidden zone there are additional resolved power levels. Indemnification influences dispersion of carriers of a charge. These two factors strongly change such characteristics, as concentration and mobility of carriers of a charge (including electro-conductivity and thermoelectromotive of semiconductors). Influence of indemnification on properties of chalcogenides of bismuth and lead is investigated. Crystals PbTe-PbCl₂-B and Bi₂Te₃ <CdCl₂-B with low concentration of the hole carriers of current. The measured and calculated parameters (electro-conductivity, thermoelectromotive, concentration of carriers of current testify the strong compensating influence of boron. Adjusting with complex impurity (PbCl₂-B) and (CdCl₂-B) it was possible to receive a set of samples with concentration of the hole carriers down to P=6,2-1017 cm⁻². The reason of strong indemnification is, on seen, linkage of vacancies of lead in complexes with ions of chlorine (in case PbS and PbTe). In Bi₂Te₃, strong p-type influence of boron results in indemnification of donor levels of chlorine.