10-Physical and Chemical Properties of Materials in Relation to Structure (Superconductors, Fullerenes, etc)

(3) In reduced and oxidized catalysts, we found a Cu-O coordination peak (R=0.190nm, N=1) in RIF. But another peak at R=0.192nm, belonging to Cu-Cu coordination in CuO, was not found in the same RIF. We consider that this is evidence of a strong interaction between metal and r-Al2O3.

(4) Because of r-Al2O3, the reasons of deactivation are different for CZ and CZA. For CZ, deactivation is caused by enlargement and increase of crystalline Cu. For CZA, the r-Al2O3 may prevent the enlargement of Cu crystals, and stabilize in this way the activity of CZA. The reason of deactivation is the change of the dispersed Cu to the crystalline phase in the catalytic reaction, which leads to the loss of active regions.

XRD graphics and RIF figures are shown below.

Fig. 1 X-ray diffraction diagrams of the binary catalysts

The ternary catalyst 1-CuO 2.ZnO 3.Cu

Fig. 2 Cu-EXAFS

a.t-oxidized b.t-reduced c.t-oxidized d.t-reduced e.b-oxidized f.b-used g.CuO h.Cu

PS-10.03.07 ELECTRON DIFFRACTION STUDY OF THE SUBSTITUTION DISORDER OF THE Ti IONS IN Li1-xTi2O4

By C. Chailloit, E. Monopoulou, P. Bredet and J.J. Caproni, Laboratoire de Cristallographie, CNRS-UJF, BP 166, 38042 Grenoble cedex 09, France

The LiTi2O4 compound (spinel structure, space group Fd3m, a=8.41Å, Z=8) is known to be superconducting with Tc=11K. In the spinel oxides containing lithium, it has been observed that the small Li+ cations can move easily through vacant sites generated by the titanium-oxygen network. Therefore, by removing or inserting lithium, the stoichiometry of the compound can be varied. In the case of Li1-xTi2O4, Capponi et al. have shown (Acta Cryst. C, 1981, 47, 1530, 1531) that it is possible to extract lithium in a soft and controlled way by immersion in an HCl solution. In order to see if such a treatment induces a new kind of disorder, crystals treated in HCl solution for several days have been studied by electron diffraction. A Philips EM 400T microscope operating at 120kV was used.

Besides Bragg reflections, the presence of pronounced diffuse scattering was readily observed, and its geometry was studied by tilting around a-axis and a*b* directions from the (001) zone axis. Figure 1a shows an example of the diffuse scattering observed on the (001) zone axis.

To interpret the diffuse scattering patterns we have applied the theory of invariant clusters proposed by B通胀 et al. (J. Phys. Chem. Solids, 1972, 33, 1227) and developed by Sauvage et al. (Acta Cryst., 1974, A30, 239). This theory establishes that, if the diffuse scattering is confined to a geometric locus in reciprocal space, the ordering state can be described by the regular arrangement of identical polyhedra having an average composition of the sample. In the present case, we suppose that the diffuse scattering is due to a substitution disorder of Ti ions on the two types of octahedral sites in the spinel structure (16d and 16c). The displacement of Ti ions from a full 16d site to an empty 16e one being possible after the departure of the two neighboring Li ions. Then, the relevant polyhedron is a cube of edge dimension a/2 whose corners and centers of the faces correspond to the center of the octahedral sites occupied either by a Ti atom or by a vacancy. The composition of the sample implies that this disorder is present in one such cube unit. With this description, the equation of the surface of diffuse intensity is given by cos(πx/z)+cos(πy/z)+cos(z/2)+cos(πz/2)+cos(πz/2)cos(z/2)cos(πz/2) = 0

The calculated intersections of this surface with different reciprocal planes are in agreement with the experimental diffraction patterns as shown in Figure 1b. This observation confirms the presence of a Ti cation disorder between the 16d and 16e octahedral sites in the case of large lithium concentrations.

Figure 1. (a) Electron diffraction photograph along the [001] zone axis showing the diffuse scattering due to Ti cation network disorder.

(b) The intersection of the diffuse scattering surface calculated with the model described in the text and the [001] reciprocal plane.

PS-10.03.08 STRUCTURAL ASPECTS OF THE CRYSTALLOGRAPhic-MAGNETIC TRANSITION IN LaVO3 AROUND 140 K by P. Bordet 1, C. Chailloit 1, M. Mazzola 2, J. Q. Hu 3, A. Santoro 3, S. Strach 3, H. Takagi 3, C.S. Ogleby 3, J. B. Budgell 3, Laboratoire de Cristallographie CNRS-UJF, BP 166, Grenoble Cedex 9, France. 2 AT&T Bell Laboratories, Murray Hill, NJ 07974, USA. 3 Reactor Division, NIST, Gaithersburg, MD 20899, USA. 4 Dept. of Physics, University of Maryland, College Park, MD 20742, USA.
The perovskite-like compound LaVO₃ undergoes a crystallographic-austenite transition at about 140 K. Recently, it has been shown that under a magnetic field of a few hundreds Oe the crystallographic transformation occurring in LaVO₃ is accompanied by a magnetic transition into a large diamagnetic state below 135 K. In order to gain insight into the nature of this anomalous behavior, we have determined the structure of LaVO₃ at room temperature and just above (130 K) and below (100 K) the transition. Synchrotron x-ray and neutron powder diffraction techniques were used. The lattice parameter variation vs temperature and the structural refinements revealed that, above the transition, the structure of LaVO₃ of GdFeO₃ type, namely it is orthorhombic with lattice parameters at room temperature: a = 5.55548(4), b = 7.84868(6), and c = 5.55349(3) Å and space group Cmcm. The orthorhombic distortion of the structure is very similar to that of isostructural LaFeO₃. At 100 K, below the transition temperature, the structure is monoclinic with lattice parameters: a = 5.59360(4), b = 7.79851(3), c = 5.58690(3) Å, β = 90.151(4°) and space group P2₁/a. In the orthorhombic structure all V sites are equivalent, but two independent sites, V₁ and V₂, are observed in the monoclinic structure. These two sites form alternating layers along the b axis. Above the transition all the V octahedra are tilted around the three crystallographic axes and are elongated along the [110] direction. The elongation increas at the transition and occurs in different directions, with 90° apart, in the V₁ and V₂ octahedra. The low temperature magnetic structure and the results of field-cooling synchrotron x-ray and neutron powder diffraction experiments will be presented at the conference.

PS-10.03.09 TWO STRUCTURAL FORMS OF DI(DIMETHYL-TETRASELENAFULVALENIUM) TETRAFLUOROBORATE. By N. Therup, Chemistry Department B, The Technical University of Denmark, Lyngby, Denmark, L. Johannsen, NTNU Research Center, Trondheim, Norway, K. Borchgarden, CISMS, University of Copenhagen, Denmark, M.A. Beno, U. Geiser and J.W. Williams, Argonne National Laboratory, Illinois, USA.

The unsymmetrical organic diurea 2,3-dimethyl-1,4,5,8-tetraselenofulvalene formation with radical anion with inorganic anions. The 2:1 salt with tetrafluoroborate can be prepared by electrocrystallization, and two crystalline phases have been found. One form is tetragonal, space group 142d, a = 18.336 Å, c = 7.226 Å. The structure contains stacks of cations along the c axis. Within a stack, the cations are shifted along the long molecular axis in a zig-zag manner. The electrical conductivity is metallic at room temperature but at about 80 K a transition into a semiconducting behavior is observed. A Peierls type transition in a likely explanation and a structure determination below this temperature has been attempted. The other crystal form is triclinic, P₁, a = 7.284, b = 12.810, c = 13.826 Å, α = 83.44°, β = 80.16°, γ = 73.90°. This structure contains two independent cations which are rotated approximately 90° with respect to each other and no pronounced stacking is present. These cations are semiconducting in the temperature range studied. Polymorphism has been observed for many organic conductors (including superconductors) and as expected the physical properties are strongly related to the packing of the constituents in the crystal structure.

PS-10.03.10 EUROPID (III) MOSSBAUER SPECTRUM AS PROBE OF MAGNESIUM (II) SITES IN LITHIUM NIOBATE CRYSTALS.** By Hongxi Zhang, Lingchong Qiang and Chongqian Xu, Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150006, P. R. China.

Because of the advantages of magnesium (II) doped lithium niobate (Mg: LiNbO₃) crystal as electro-optic material, the local sites of Mg²⁺ in LiNbO₃ have been widely investigated by various methods (D. A. Bryan et al., Opt. Eng., 1995, 24), and L. Arizmendi et al., Phys. Rev., 1985, 31, 713) and several models were proposed (Zhang Qiao et al., Phys. Rev., 1991, B43, 2202, Zhou Yuxing et al., Phys. Rev., 1991, B43, 4374 and Zhang Hongxi et al., J. Chinese Ceramic Soc., 1991, 19, 523). But no direct evidence can be used to confirm the positions of Mg²⁺. In the present paper, we report the Mossbauer spectra of Eu⁺ in Eu:LiNbO₃ and Eu: Mg:LiNbO₃. Based on the Mössbauer parameter changes, the local site of Mg²⁺ is discussed.

Mossbauer absorbers were prepared from Czochralski-grown Eu: LiNbO₃ (2.5mol% Eu₂O₃) and Eu: Mg: LiNbO₃ (2.5mol% Eu₂O₃, 6mol% MgO) and Eu⁺ density was about 20μg/cm³. Mössbauer spectra were recorded at room temperature on an OXFORD MG-500 constant acceleration Mössbauer spectrometer with a 1024 multi-channel analyzer. The radiation source was solid state Eu(152) ⁹⁵Eu, about 100 mCi ⁹⁵Eu. A xenon proportional counter was used as detector. EuO₃ as standard absorber.

Based on L. Arizmendi's spectroscopic measurement, we fitted the spectra with two Lorentzian lines and obtained the isomer shifts (IS) of Eu⁺ in Eu: LiNbO₃ and Eu: Mg:LiNbO₃. The result is listed in the following table and it indicates that Eu⁺ can occupy both Li⁺ site (Eu(Li)) and Nb⁺ site (Eu(Nb)).

<table>
<thead>
<tr>
<th>Sample</th>
<th>IS</th>
<th>Line 1</th>
<th>Line 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu:LiNbO₃</td>
<td>0.3675</td>
<td>0.6182</td>
<td>0.444</td>
</tr>
<tr>
<td>Eu:Mg:LiNbO₃</td>
<td>0.2745</td>
<td>0.9143</td>
<td>0.521</td>
</tr>
</tbody>
</table>

** IS is very sensitive to Eu—O distance and increases with decreasing Eu—O distance (B. H. Osmon et al., Acta Cryst., 1969, 25, 2140). In LiNbO₃, average Nb—O distance is shorter than average Li—O distance (S. C. Abrahams et al., Acta Cryst., 1986, B42, 41) and XRD analysis showed that Eu⁺ doping does not cause structure changes. When Eu⁺ replaces Nb⁺ and Li⁺, Eu(Nb)—O distance is shorter than Eu(Li)—O. Therefore, it is deduced that, for Eu: LiNbO₃ or Eu: Mg: LiNbO₃, the lower IS corresponds Eu(Li) and the higher IS to Eu(Nb). From the relative intensities of the two subpeaks, we can estimate that about 56% (48%) Eu⁺ occupy Nb⁺ sites, 44% (52%) Eu⁺ occupy Li⁺ sites in Eu: LiNbO₃ (Eu: Mg: LiNbO₃). The results indicate that Eu⁺ and Mg²⁺ compete in Nb⁺ site and the doping of Mg²⁺ into Eu: LiNbO₃ increases the ratio of Eu(Nb). That means Mg²⁺ is preferred to occupy Nb⁺ site. From the conclusion, we also analyze the mechanism of the increased anti-photoconductivity of Mg: LiNbO₃.

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