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### Effect of lithium intercalation on the crystal structure and magnetic property of layered FeWO<sub>4</sub>Cl

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Layered compounds such as graphite, metal calcogenides, metal oxide or oxyhydroxide, metal halides, and metal oxyhalides have attracted much interests due to their potential applications for adsorbents, ion exchange media, catalyst-supports, anisotropic semiconductors, and active materials for rechargeable batteries, etc.

LiFeWO<sub>4</sub>Cl has been prepared by reductive intercalation of lithium ion into FeWO<sub>4</sub>Cl. FeWO<sub>4</sub>Cl crystallizes in the tetragonal system (space group P4/nmm) with cell dimensions of  $a = 6.677(5)\text{\AA}$ ,  $c = 5.270(5)\text{\AA}$ , while lithium intercalation gives rise to the formation of monoclinic phase (space group P2<sub>1</sub>/m) with cell dimensions of  $a = 7.050(0)\text{\AA}$ ,  $c = 6.926(2)\text{\AA}$ ,  $\alpha = 5.043(0)^\circ$ , and  $\beta = 92.54(2)^\circ$ . According to the Fe K-edge X-ray absorption near edge structure spectroscopic analysis, only Fe<sup>3+</sup> ion in the FeWO<sub>4</sub>Cl lattice is reduced to Fe<sup>2+</sup> one with an increment of site symmetry from C<sub>4v</sub> to O<sub>h</sub> upon lithium intercalation. On the other hand, the white line intensity at the W L-edge X-ray absorption near edge structure spectroscopic analysis becomes slightly enhanced after intercalation, indicating an increase of the W(VI)-O bond covalency due to a decrease of the competing Fe(II)-O bond strength. Extended X-ray absorption fine structure analyses for FeWO<sub>4</sub>Cl and LiFeWO<sub>4</sub>Cl show that the tetrahedral symmetry of WO<sub>4</sub><sup>2-</sup> group in FeWO<sub>4</sub>Cl becomes distorted upon lithium intercalation indicating a modification of the first neighboring octahedral interlayer sites, where the half of them are occupied by the lithium ions with an ordered fashion.

Infrared spectroscopic analyses for FeWO<sub>4</sub>Cl and LiFeWO<sub>4</sub>Cl show that the symmetry of tetrahedral WO<sub>4</sub><sup>2-</sup> group in FeWO<sub>4</sub>Cl becomes lowered as the lithium intercalation into its two dimensional lattice, indicating an alternately ordered lithium occupancy of half of the octahedral interlayer sites.

Effective magnetic moments for FeWO<sub>4</sub>Cl and LiFeWO<sub>4</sub>Cl were estimated to be 5.95 and 5.10B.M., respectively, which ascribe to the selective reduction of high spin ferric ion to high spin ferrous one upon lithium intercalation. It was also found that the 2-dimensional magnetic property of FeWO<sub>4</sub>Cl was changed to the 3-dimensional one in LiFeWO<sub>4</sub>Cl owing to the c-axis contraction.

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### Tetravalent nickel in $\gamma$ -type nickel oxyhydroxides: X-ray absorption spectroscopic evidence

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Three different  $\gamma$ -type cobalt substituted nickel oxyhydroxides, containing tetravalent nickel were prepared by oxidative hydrolysis and cationic exchange reaction of NaNi<sub>1-x</sub>Co<sub>x</sub>O<sub>2</sub> in three different oxidizing media such as 4 : 1 mixture of 5M KOH and 1M NaClO solutions, 0.6M Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution, and 0.6M (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution for 10 hours, and stored in air with 60% relative humidity using a concentrated aqueous NaCl solution. As the X-ray absorption spectroscopy reference materials, LiNiO<sub>2</sub> was carefully prepared from a mixture of NiO and Li<sub>2</sub>CO<sub>3</sub> by solid state reaction at temperature range of 700-800°C.

The results of the chemical analyses suggest the following for three different  $\gamma$ -type cobalt substituted nickel oxyhydroxides :

Ni<sub>0.70</sub>Co<sub>0.30</sub>O<sub>2</sub>X<sub>0.30</sub>(H<sub>2</sub>O)<sub>0.45</sub>, Ni<sub>0.69</sub>Co<sub>0.31</sub>O<sub>2</sub>N<sub>0.30</sub>(H<sub>2</sub>O)<sub>0.46</sub>, Ni<sub>0.70</sub>Co<sub>0.30</sub>O<sub>2</sub>(NH<sub>4</sub>)<sub>0.30</sub>(H<sub>2</sub>O)<sub>0.34</sub>.

Structural and electronic properties of the  $\gamma$ -type cobalt substituted nickel oxyhydroxides have been investigated using X-ray absorption spectroscopy and compared with those of similar layered compounds with various nickel valencies. X-ray absorption near edge structure at Ni K-edge shows a shift of edge energies to higher values as the oxidation state of nickel increases. The valency of nickel was estimated from the shift of the edge energy. Its value for  $\gamma$ -type cobalt substituted nickel oxyhydroxide with interlayer potassium ions was found to be 4.00 while those for the compounds with interlayer ammonium and sodium ions was determined to be 3.94 and 3.90, respectively.

According to the extended X-ray absorption fine structure data, the Ni-O bond lengths in the first shell and the Ni-(Ni,Co) one in the second shell decrease with increasing nickel valency. The ionic radius for tetravalent nickel was estimated as 0.48Å from the Ni-O bond length in the first shell. The Co K-edge X-ray absorption spectroscopy shows the valency of cobalt remains unchanged during soft chemistry reaction.

The obtained  $\gamma$ -type cobalt substituted nickel oxyhydroxide should be expected to serve as a good tetravalent nickel reference compound in solid state chemistry and inorganic chemistry.