Unravelling Superstructure and Electronic Ordering in $LiNiO_2$ bulk single crystals grown by Optical floating zone technique

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Ni rich, layered oxides are promising cathode materials for Li-ion batteries since they fulfil the energy density requirements of the automobile industry [1,2]. They offer capacities higher than 180 $mAhg^{-1}$ (commercial Li-ion batteries have capacities of 140 $mAhg^{-1}$) at relatively high mean voltages of 3.6-4.0 V with outstanding efficiencies and sufficient power densities, but they tend to degrade relatively fast. In these rhombohedral structures, transition metals (TMs) and Li ions occupy edge-sharing oxygen octahedra in alternating layers. However, the magnetic and electronic properties of the materials have been under discussion since their discovery, though this knowledge is essential in understanding their functionality and the reasons for failure upon long-term operation [2]. In $LiNiO_2$, 23% of Ni show a Ni^{2+}-configuration (t_{2g}^6 e_g^2, s=1), 46% a Ni^{3+}-configuration (t_{2g}^6 e_g^1-low spin, s=1/2) and 31% a $Ni^{2+}L$ configuration (t_{2g}^6 e_g^2 L-low spin, L: electron-hole at oxygen sites), determined with Ni $L_{2,3}$ edge X-ray absorption spectroscopy (XAS) and charge transfer multiplet calculations [3]. The S=1 and S=1/2 spin of Ni^{2+}/$Ni^{2+}L$, Ni^{3+} should give rise to an anti-/ferromagnetic moment along the *c*-direction of the structure. Upon charging, Li-ions are deintercalated while the Ni-O host structure is oxidized. The oxidation of Ni (19% Ni^{2+}, 49% Ni^{3+}, 32% $Ni^{2+}L$ for charged $Li_{0.4}NiO_2$) changes the spin to S = -0.3) and thus, the magnetic moment will also change.

Although previous powder neutron measurements have not detected any long-range order in $LiNiO_2$ [4,5], a semi-disordered cluster model has been proposed based on high-field magnetisation measurements [6]. Despite the peaks, they do not fit a simple propagation vector, so full 3D information from single crystals is required. Although there have been several studies on the powder form, there has yet to be a report on the bulk crystal growth and its property studies of $LiNiO_2$. In the present study, we report the first successful growth of neutron-size $LiNiO_2$ single-crystal by employing the optical floating-zone technique. We underwent a study by using the as-grown $LiNiO_2$ single crystals using the high flux of synchrotron x-rays to determine the ionic superstructure and magnetic ordering. This measurement has provided important new information on the superstructure. Our study demonstrates the optimization of $LiNiO_2$ growth parameters and provides vital insights into desirable material properties for developing cathode materials with better performance.

References

[1]Andre et al. Future generations of cathode materials: an automotive industry perspective. J.Mater.Chem.A.2015;3:6709-6732.
[2] Kleiner et al.Challenges Considering the Degradation of Cell Components in Commercial Lithium-Ion Cells: A Review and Evaluation of Present Systems.Top Curr. Chem.(Z).2017;375:1-45.
[3] Frank de Groot et al.Core Level Spectroscopy of Solids.1st Edition.(CRC Press.2008).
[4] K.Hirakawa et al.Experimental Studies of Triangular Lattice Antiferromagnets with S=1/2:NaTiO2 and $LiNiO_2$.1985;54:3526-3536.
[5] Hideki Yoshizawa et al.Ferromagnetic Short-Range Correlations in a Two-Dimensional Triangular Lattice Antiferromagnet with S=1/2 $LiNiO_2$.J. Phys.Soc.Jpn.1990;59:2631-2634.
[6] Chappel et al.Interlayer magnetic frustration in quasistoichiometric $Li_{1-x}Ni_{1+x}O_2$ Phys.Rev.B.2002;66:132412-4.