Sodium Ion Ordering of $Na_{0.77}CoO_2$ under Competing Multivacancy Cluster, Superlattice, and Domain Formation

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Phase-separation phenomenon has been observed in thenarrow ranges of ~0.77–0.82 and 0.83–0.86,[4] where detailed phase diagram has been mapped and interpreted as a result of Na ordering within each layer as well as staging along the c direction. The superstructure of $Na_{0.77}CoO_2$ that sits near the lower end of the 0.77–0.82 miscibility gap has not been reported in detail so far, especially it shows the largest simple hexagonal superlattice size of $\sqrt{19}a$ in comparing with the rest compositions of $x \geqq 0.82$ with $\sqrt{13}a$ and x=0.71 with $\sqrt{12}a$. Combining independently obtained Na content from electron probe microanalysis (EPMA) and Laue-diffraction study using synchrotron x-ray source, we propose Na ordering for x~0.77 is composed of average 4.5 vacancies out of 19 filled Na sites per $\sqrt{19}a$ superlattice unit.

Crystal growth of the original high Na-content sample and the additional electrochemical deintercalation procedures have been reported in detail previously.[2,3] Since we need to construct our superstructure model based on independently obtained Na content and diffraction pattern, the Na content has been carefully characterized to be 0.768±0.004 using both EPMA and its linear *c*-axis lattice parameter versus *x* relationship, which was constructed from combined inductively-coupled plasma and EPMA.[1,3] Unlike the treated low *x* Na_xCoO_2 crystals of wavy surface and easily to be hydrated in the air, for $x \geqq 0.71$, on the other hand, large, flat, and shinny crystal surface can be prepared easily through cleaving, which significantly reduces the standard deviation from multiple EPMA scans. The typical sample used on for EPMA study is freshly scanned piece of ~1×1 mm^2 in size, five ten-point line scans are taken both horizontally and vertically and the atomic percentage is calculated

We are able to solve the 2D superlattice of 0.77 using synchrotron Laue diffraction on single crystal along the (001) direction. Similar to that found in 0.71 and 0.84, The 12-spot ring that is a result of superstructure diffraction and surrounds the low-indexing primitive $(100)_p$ planes for 0.77 is shown in the inset of Fig.1. *x*=0.77 pattern shows two setsof simple hexagonal lattice of $a^{*\prime} \sim 1/\sqrt{19}a$ in the reciprocal space with an angle of 46.8° in between. These two sets of *a**' in the reciprocal space correspond to two simple hexagonal lattices in real space of $\sqrt{19}a$ with an angle of 13.2° in between, which turns out to be two equivalent choices of simple hexagonal superlattices of **a**'=5**a**+2**b**. This two domain interpretation has also been verified by electron diffraction from the observed untwinned region (not shown). The found superlattice of $\sqrt{19}a$ for *x*=0.77 is the largest for $x \geqq 0.71$, where $\sqrt{12}a$ superlattice for 0.71 is composed of trivacancy and quadrivacancy clusters and $\sqrt{13}a$ superlattice for 0.84 is composed of divacancy clusters.[3,5]

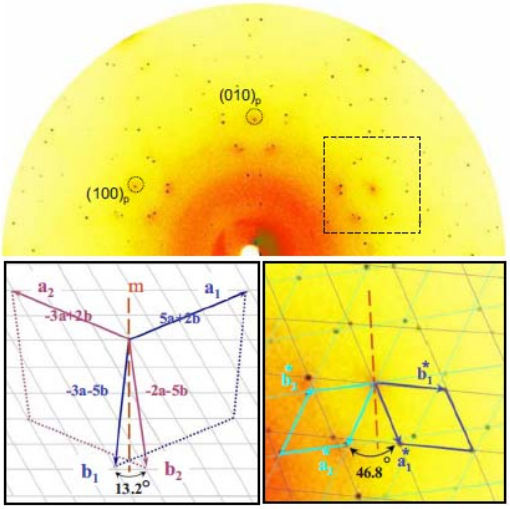

Fig. 1: (Color online) Laue-diffraction pattern of *x*=0.77.

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