Floating zone growth of $\alpha$-Na$_{0.90}$MnO$_2$ single crystals

Rebecca Dally$^{a,b}$, Raphaële J. Clément$^c$, Robin Chisnell$^d$, Stephanie Taylor$^b$, Megan Butala$^b$, Vicky Doan-Nguyen$^{b,\dagger}$, Mahalingam Balasubramanian$^a$, Jeffrey W. Lynn$^d$, Clare P. Grey$^e$, Stephen D. Wilson$^{b,\ddagger}$

$^a$ Department of Physics, Boston College, Chestnut Hill, MA 02467, USA
$^b$ Materials Department, University of California, Santa Barbara, CA 93106-5050, USA
$^c$ Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom
$^d$ NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
$^e$ California NanoSystems Institute, University of California, Santa Barbara, CA 93106, USA
$^f$ Advanced Photon Source, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439, USA

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ABSTRACT

Single crystal growth of $\alpha$-Na$_{0.90}$MnO$_2$ (x=0.90) is reported via the floating zone technique. The conditions required for stable growth and intergrowth-free crystals are described along with the results of trials under alternate growth atmospheres. Chemical and structural characterizations of the resulting $\alpha$-Na$_{0.90}$MnO$_2$ crystals are performed using ICP-AES NMR, XANES, XPS, and neutron diffraction measurements. As a layered transition metal oxide with large ionic mobility and strong correlation effects, $\alpha$-Na$_{0.90}$MnO$_2$ is of interest to many communities, and the implications of large volume, high purity, single crystal growth are discussed.

1. Introduction

Two-dimensional layered transition metal oxides of the form ABO$_2$ (A=alkali metal, B=transition metal) have drawn the attention of scientists from a variety of backgrounds due to their wide array of novel electronic and functional properties. For instance, in the realm of novel cathode materials, $\alpha$-Na$_{0.90}$MnO$_2$ ($\alpha$-NMO) with the monoclinic NaNiO$_2$ structure type is widely studied as a potential Na-based cathode platform due to its superior cycling performance and operating potential [1,2]. At the same time, $\alpha$-NMO also holds interest for researchers in the area of fundamental condensed matter physics due to its underlying anisotropic triangular lattice of Mn$^{3+}$ moments and its rich electronic phase diagram accessible via deintercalation [3]. While small volume crystals of the $\alpha$-NMO system have been produced via hydrothermal and sealed crucible techniques [4,5], high purity floating zone (FZ) growth of large volume crystals has remained elusive. This is primarily due to the challenge of dual Na and Mn volatility during growth as well as two competing polymorphic forms for NMO, namely $\alpha$-NMO and $\beta$-NaMnO$_2$ ($\beta$-NMO), with very close energetics [6-9]. The successful synthesis of large volume FZ grown crystals of the form ABO$_2$, such as Na$_x$CoO$_2$ [10-13], have historically provided access to deeper experimental insights. The current absence of high purity, large volume FZ crystals of $\alpha$-NMO presents an impasse to the community’s understanding of this system’s rich phase behavior, where recent studies have been limited to polycrystalline specimens [3,7,14-17].

$\alpha$-NMO is composed of alternating layers of two-dimensional manganese oxide and sodium sheets as shown in Fig. 1. It crystallizes in the monoclinic C2/m spacegroup with an O3 layering sequence where Na ions occupy octahedrally coordinated sites between the MnO$_2$ layers. MnO$_2$ octahedra within these layers form an edge sharing triangular lattice where the Mn$^{3+}$ cations undergo a large, cooperative Jahn-Teller distortion [14]. This results in an anisotropic triangular lattice of manganese cations in the high-spin S=2 state and a (d$_x^2$y$_2$) electronic configuration. In contrast, the $\beta$ polymorph is made up of alternating zigzag-like layers of Na and MO$_2$ sheets and has orthorhombic symmetry (Pnma space group). The removal of Na from the $\alpha$ polymorph provides a means of hole doping, which introduces Mn$^{4+}$ cations and locally relaxes the Jahn-Teller distortion in the manganese oxide planes. This can lead to a rich interplay between Na ion/vacancy ordering, charge ordering, magnetic correlations, and Jahn-Teller lattice distortions as the Na-site occupancy is tuned [3]. While studies of this interplay in $\alpha$-NMO are just beginning, detailed investigations of single crystal specimens are notably lacking. Successful FZ crystal growth was previously harnessed to explore and gain considerable physical insight into the structurally related Na$_x$CoO$_2$ system [18], suggesting a similar approach for the crystal growth of $\alpha$-NMO.

$\dagger$ Corresponding author at: Materials Department, University of California, Santa Barbara, CA 93106-5050, USA.
E-mail address: stephendwilson@engineering.ucsb.edu (S.D. Wilson).

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Here we report the FZ growth of single crystals of α-NMO with x=0.90. While α-NMO is prone to disorder from stacking faults (SF) and intergrowths of the competing polymorph β-NMO—both of which originate from the tendency of the structure to twin (6–8)—by tailoring the crystal growth speed we were able to mitigate this intergrowth contamination. Specifically, $^{23}$Na nuclear magnetic resonance (NMR) measurements characterize the degree of structural faulting demonstrate that the growth rate correlates to the relative phase fractions of α- and β- polymorphs and the number of stacking faults within the resulting crystals. This fact, along with neutron powder and single crystal diffraction data, show that the optimized, large volume α-NMO crystals are free of both local and long-range β-phase intergrowths with a good quality mosaic. Combined x-ray absorption near edge spectroscopy (XANES), x-ray photoelectron spectroscopy (XPS), and inductively coupled plasma atomic emission spectroscopy (ICP-AES) data determine the stoichiometry of crystals grown under optimal conditions to be $\text{Na}_{0.90}\text{MnO}_2$. Our work opens the α-NMO system to new avenues of investigation via single crystal studies harnessing a variety of experimental techniques, such as neutron scattering where large volume single crystals are required.

2. Experimental details

2.1. Powder synthesis and crystal growth

Starting powders were prepared from $\text{Na}_2\text{CO}_3$ and $\text{MnCO}_3$ powders (Alfa Aesar, Puratronic® 99.997% and 99.985%, respectively). The powders were mixed with a 1:1 molar ratio, plus 10% weight excess of $\text{Na}_2\text{CO}_3$ to account for sodium loss during synthesis. The mixed powder was sintered in an alumina crucible at 350 °C for 15 h, reground and then sintered at 750 °C for 15 h. The powder was then reground, formed into a rod with a diameter of 5 mm, and pressed at 50,000 psi in an isostatic press. The pressed rod was then sintered in a vertical furnace at 1000 °C for 15 h and then quenched in air. At this point in the synthesis process, the polycrystalline rod is comprised of a majority of β-NMO. We note here that quenching was used as a preventative measure to avoid decomposition of the rod into mixed phases, and the effect of alternatively slow cooling the sintered feed rod is not explored here. The polycrystalline sintered β-rod was then cut and used as both the feed rod and as a polycrystalline seed for floating zone growth in a four mirror optical floating zone furnace with 500 W halogen lamps (Crystal Systems Corp. Model FZ-T-10000-H-V1-VPO-I-HR-PC). A 4.1 ratio of Ar:O$_2$ was used to pressurize the chamber to 0.15 MPa in order to help mitigate Na volatility, and gases were flowed through the growth chamber at rates of 80 SCCM and 20 SCCM for Ar and O$_2$, respectively. Once grown and cooled, crystals were immediately transferred to an Ar-filled glovebox for storage and further analysis.

2.2. Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

To determine sodium and manganese concentrations in α-NMO crystals and polycrystalline samples, ICP-AES measurements were performed in a Thermo iCap 6300. Samples for analysis were prepared by first massing the starting materials on a 0.01 mg resolution balance and then dissolving the crystals in concentrated trace metals grade hydrochloric acid (High-Purity Standards). Heat was applied via a hot water bath over a hotplate to the samples in a closed container containing HCl until no particulates could be seen and the solution became clear. This reduced the room temperature dissolution time in HCl from 4 to 10 days to only 1–3 h. Upon cooling, the dissolved sodium manganese oxide was diluted with deionized water to obtain a 5% HCl matrix. Instrument calibrations for Na and Mn were done using blank, low, and high PPM solutions within a 5% HCl matrix, which were prepared using standard analysis grade solutions of Na (1000 pg/mL in 1% HCl) and Mn (1000 pg/mL in 2% HCl) from High-Purity Standards.

2.3. $^{23}$Na solid-state NMR (ssNMR)

$^{23}$Na ssNMR spectra were acquired at room temperature on a Bruker Advance III 200 wide-bore spectrometer (4.7 T external magnetic field) at a Larmor frequency of ~53.0 MHz. All NMR experiments were performed under 60 kHz magic angle spinning (MAS) using a 1.3 mm double-resonance HX probe and a recycle delay of 30 ms. $^{23}$Na NMR data were acquired on finely ground samples of single crystal NMO. $^{23}$Na NMR chemical shifts were referenced against solid $^{23}$NaCl at 7.21 ppm. $^{23}$Na spin echo NMR spectra were acquired using a 90° radiofrequency (RF) pulse of 1.03 μs and a 180° RF pulse of 2.06 μs at 25.04 W. Transverse (T$_2$) relaxation times were obtained from an exponential fit of the decay of the signal intensity obtained as the echo delay was increased in an NMR spin echo pulse sequence.

2.4. X-Ray absorption near edge spectroscopy (XANES)

XANES data were taken at beamline 20-BM-B at the Advanced Photon Source at Argonne National Laboratory with an incident energy tuned to the Mn K-edge. Single crystals of NMO were finely ground and a thin, uniform layer of powder was sealed between pieces of kapton tape under an inert environment. The standards used, LiMn$_2$O$_4$ and Mn$_2$O$_3$, were prepared in a similar manner. Data were deglitched, calibrated, and normalized using the software Athena [19]. Mn foil was used as a reference, and a simultaneous spectrum of the foil was collected in transmission mode during each run of the sample and standards. Calibrations to each data set were made by matching the absorption edge of the Mn foil to 6539 eV and then shifting the data set by that amount [20].

2.5. X-ray photoelectron spectroscopy (XPS)

Data were taken using a Kratos Axis Ultra X-ray Photoelectron Spectroscopy system with a pass energy of 40 eV and step size of 0.1 eV. Data were analyzed using the splitting of the Mn 3s peak, which...
is a result of the exchange coupling between 3s holes and 3d electrons. The NMO spectrum was corrected using a Shirley background and peaks were fit to a Gaussian-Lorentzian line shape.

2.6. Neutron diffraction measurements

Neutron powder diffraction data were collected using the BT-1 neutron powder diffractometer at the NIST Center for Neutron Research (NCNR). A Cu(311) monochromator with a 90° take-off angle, \( \lambda = 1.5397(2) \text{ Å} \), and in-pile collimation of 60°–60° were used. Data were collected over the 20 range of 3–168° with a step size of 0.05°. About 3 g of crystal from a single growth run was ground and sealed in a vanadium container of length 50 mm and diameter 9.2 mm inside a dry He-filled glovebox. A fit to the data was calculated using the Le Bail refinement [21] option in FullProf [22].

The triple-axis instrument BT-7 [23] at NCNR was used to demonstrate the mosaic of the typical crystals using a vertically focused PG(002) monochromator and an incident energy of 14.7 meV. A single crystal of \( \alpha-NM\) was aligned in the HK0 plane using \( \pm 25° \)–\( \pm 120° \) collimators placed before the monochromator, before the sample, after the sample, and before the detector, respectively. Uncertainties where indicated represent one standard deviation.

3. Results and discussion

A number of varying growth speeds and translation rates were attempted with key results summarized in Table 1. The optimal growth conditions for phase pure \( \alpha-NM\) were found to be a 20 mm/h mirror translation rate, 2 mm/h feed rod translation rate, 30 rpm feed rod rotation, and 20 rpm feed rod rotation. Under these conditions, attempts to seed from a previously grown \( \alpha-NM\) crystal were unsuccessful, likely due to substantial decomposition (i.e. Na loss) of the seed crystal during the initial heating process. However, seeding from a polycrystalline rod was able to repeatedly nucleate a single grain crystal after \( \approx 4\) cm of growth. Facets form readily after the start of growth leading to the formation of a single domain within 4 cm, negating the need for a seed crystal. Specifically, a stable molten zone which leads to \( \alpha\)-phase growth with minimal stacking faults (the determination of which is discussed later) was achieved by starting mirror translation at 50 mm/h from the initial polycrystalline seed and then stepping it down gradually toward 20 mm/h, where steady state growth was performed. We note that our attempts at seeding growth at this eventual lower growth rate failed to maintain a stable molten zone. This is illustrated in Fig. 2, where the boule’s cross section becomes more elliptical in shape with flat facets forming perpendicular to the direction of seed translation at the point where a stable molten zone was achieved at 20 mm/h. These perpendicularly faceted are oriented along the (\( \alpha\)-101) lattice plane, and the crystal growth direction is along the short b-axis. Substantial evaporation of both Na and Mn occurred during FZ growth, and depositions composed of a mixture of Na and Mn oxides built up on the inner quartz walls of the growth chamber. We found it necessary to increase the power of the lamps slightly over the course of growth (\( \approx 1\)–\( \approx 2\))% to compensate for the decreasing transparency of the tube.

Table 1

Summary of growth trials using varying crystal pull rates and growth environments. Compositional analyses of crystals grown under each condition as well as the polycrystalline feed material are also summarized.

| Sample          | Na:Mn (molar ratio) | \( \alpha/SF/\beta \) (%) | Growth Rate | Atmosphere | Pressure |
|-----------------|---------------------|--------------------------|-------------|------------|----------|
| starting powder | 1:1+10 wt% excess Na\(_2\)CO\(_3\) | –                        | n/a         | n/a        | n/a      |
| \( \beta \)-rod | 1.04:1              | 6/37                     | n/a         | ambient    | ambient  |
| crystral 1      | 0.90:1              | 96/4                     | 20 mm/h     | 4:1 Ar/O\(_2\) | 0.15 MPa |
| crystal 2       | 0.94:1              | 15/10                    | 50 mm/h     | 4:1 Ar/O\(_2\) | 0.15 MPa |
| crystal 3       | 0.75:1              | –                        | 20 mm/h     | 1:1 Ar/O\(_2\) | 0.15 MPa |
crystal neutron diffraction measurements on a crystal observed only a single grain with an observed full-width-at-half-maximum (FWHM) of 0.41° ± 0.01° as plotted in Fig. 4(b), which after correction for the instrumental resolution indicates a mosaic spread of 0.35°. Together these measurements establish the long-range ordered lattice structure of crystals grown under optimal conditions to phase pure α-NMO single crystals; however, they are not directly sensitive to local intergrowths of β-NMO which may arise as a series of stacking faults within the O3 layered structure.

To investigate the presence of local intergrowths of β-NMO and stacking faults within the lattice of α-NMO crystals, 23Na solid-state NMR (ssNMR) data were collected with results plotted in Fig. 5. If a number of 23Na resonant frequencies are resolved in the NMR spectra collected on crushed α-NMO crystals, it suggests the presence of multiple chemical environments reflective of the formation of stacking faults (twin planes) between nanodomains of the α and β polymorphs of NMO. While structural intergrowths and the formation of stacking faults between the α- and β-polymorphs of NMO have been reported previously [6–8], quantifying their relative abundance across a macroscopic sample presents a challenge. Recently, a 23Na NMR study of β-NMO identified three resonances with isotropic shifts of ca. 750, 530 and 320 ppm and assigned them to Na nuclei in α-NaNMO domains (Naα), in β-NaNMO domains (Naβ), and in the vicinity of a stacking fault (NaSF), are shown on the figure. Spinning sidebands due to fast sample rotation are indicated by (*).

Relative fractions of Na site occupations were determined by integration of spin echo spectra shown in Fig. 5, and contributions from individual Na sites were scaled by a transverse relaxation factor accounting for the loss of NMR signal intensity over the signal acquisition time. Fig. 5(b) was collected on a crystal grown at 20 mm/h and indicates the dominance of a single Na crystallographic
where environment where ca. 96% of Na in the sample resides in an α-NMO environment with a small percentage (ca. 4%) of Na near stacking faults. A nearly negligible fraction (<1%) of Na in β-like environments indicates local β-NMO regions. This demonstrates that the lattice structure of crystals grown at the lowest rate of 20 mm/h is largely free of faulting and that the local structure is consistent with the long-range α-NMO crystal structure determined via neutron diffraction. The fraction of Na⁺ ions in an α-like environment can be further broken down into Na⁺ ions close to a Mn⁴⁺ ion (ca. 6% of all Na) and into Na⁺ ions surrounded by Mn³⁺ ions only (ca. 90% of all Na). The former environment is indicated by a Na resonance at 950 ppm (see small peak on the left of the alpha peak in Fig. 5(b)) which determines the proportion of Mn⁴⁺/Na vacancies to be in relatively good agreement with the total Na content obtained with XPS/ICP-AES. At this time, control over the sodium content is limited to x=0.90 for quality, phase-pure samples.

Having established that phase pure α-NMO single crystals can be grown via FZ, one further question explored was the degree through which the NMO polymorphs can be selected via the crystal growth rate. While the β-phase of NMO is nominally the higher temperature structure [1,2,29], β-NMO is known to persist at ambient conditions as the optimal α – Na₉₀M₉₀₂ crystals. To investigate this, crystals were grown under identical conditions as the optimal α – Na₉₀M₉₀₂ crystals discussed previously with the exception of an increase in the sustained mirror translation rate to 50 mm/h. The ²⁵Na ssNMR spectrum collected on crystals grown under this increased rate is plotted in Fig. 5(a) and is dominated by the characteristic signal from Na ions in β-NMO type local environments; specifically, the majority phase fraction of the more rapidly grown sample is 66% β-NMO, which far exceeds the relative fractions of 15% α-NMO and 19% of Na near locally faulted regions. This demonstrates that the dominant growth mode has switched to the metastable β-NMO polymorph. We note that this local phase mixture between α-NMO, β-NMO, and faulted regions is consistent with the composition of powders whose long-range lattice structure is β-NMO – a lattice known to be highly defect prone [8,9] and intermixed with regions of the competing α-phase. Due to the defect prone lattice of β-NMO, it is currently unclear whether even higher growth rates (>50 mm/hr) would result in more locally phase pure β-NMO crystals.

4. Conclusions

Floating zone crystal growth in an optical image furnace was utilized to produce large volume, single crystals of α-phase Na₉₀M₉₀₂ with minimal stacking faults. ICP-AES, XANES, and XPS measurements determined that crystals grown via the parameters reported here possess a 10% Na deficiency and a final stoichiometry of Na₉₀M₉₀₂. Further characterization of crystals grown at slower growth rates via combined neutron diffraction and ssNMR studies determined both the long-range and local structure of these crystals to be single-phase α-NMO. By varying the crystal growth rate (i.e. the mirror translation rate), the mixture of polymorphs present in Na₉₀M₉₀₂ crystals can be selected/tuned—a finding of potential interest for the creation of tailored cathode materials with a tunable intermixure of α- and β-phases. Furthermore, the large volume growth of high purity α-NMO crystals opens the compound to detailed exploration via a new array of probes such as single crystal neutron scattering and single crystal muon spin relaxation.

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