1   **Investigation of the NaNi$_x$Mn$_{1-x}$O$_2$ (0 ≤ x ≤ 1) System for Na-ion Battery Cathode Materials**

2

3   R. Fielden and M.N. Obrovac*

4

5   Department of Chemistry, Dalhousie University, Halifax, N.S., B3H 4R2 Canada

6
7   * - corresponding author: mnobrovac@dal.ca

8

9   **Abstract**

10   Layered NaNi$_x$Mn$_{1-x}$O$_2$ (0 ≤ x ≤ 1) oxides were prepared via solid state reactions.

11   Different reaction conditions were required to obtain phase pure samples, depending on the value

12   of x. The 0 ≤ x ≤ 0.1 compositions were prepared in an inert argon atmosphere at 700 °C and

13   had a monoclinically distorted O'3 type structure. The 0.25 ≤ x ≤ 0.33 compositions were

14   prepared in air at 850 °C and had a P2-type structure. Compositions in the range of 0.5 ≤ x ≤

15   0.66 were synthesized in air at 850 °C and had an O3-type structure. Lastly, compositions with

16   0.9 ≤ x ≤ 1 were prepared in an oxygen atmosphere at 700 °C and had a monoclinically distorted

17   O'3 type structure. Electrochemical experiments were performed on pure phase samples. All

18   showed reversibility of sodium ions and high capacities. The highest reversible capacity was

19   achieved for x = 0.66, with a capacity of ~ 190 mAh/g and an average discharge voltage of 3.07

20   V, corresponding to a high energy density of 2705 Wh/L. This is among the highest reported

21   volumetric energy densities for Na-ion battery electrodes.

22

23   **Introduction**

24   Sodium-ion batteries that comprise electrode materials derived from low cost and earth

25   abundant raw materials have been proposed as an alternative to Lithium-ion batteries.[1,2] Layered

26   oxides derived from the rock salt structure are often amenable towards reversible intercalation

27   and have garnered interest in recent years for their application as cathode intercalation materials

28   for sodium-ion batteries.[3–6] Structures of layered AMO_2 oxides (A is an alkali metal and M is a

29   transition metal or a mixture of transition metals) have been categorized according to their

30   layered stacking sequence and the geometry of the alkali metal ion site by Delmas.[7] This

31   notation is followed here. Common layered AMO_2 oxides have a rhombohedral O3 type,

32   monoclinic O'3 type, or hexagonal P2 type structure. These common structure types are shown

33   in Figure 1.

34   The $NaMO_2$ oxides generally form layered structures quite easily due to the large ionic

35   size of Na^+, which reduces electrostatic repulsion between the oxide layers.[8] This is not always

36   true in the case of $LiMO_2$ oxides, which can be susceptible to cation mixing or conversion to

37   spinel structures. For example, layered $LiNi_{0.5}Mn_{0.5}O_2$ has been studied as a cathode material for

38   lithium-ion batteries, however it suffers from cation mixing.[9–11] This is due to the similarity of

39   ionic size of Li^+ and Ni^{2+}.[12] However, in $NaNi_xMn_{1-x}O_2$ cation mixing between sodium and the

40   transition metals does not occur, as sodium has a significantly larger ionic radius than the

41   transition metal ions. Because of the extra stability of layered AMO_2 oxides with large alkali

42   metal cations (A), they can often accommodate significantly more deficiency in the alkali metal

43   layer, when A is not lithium.[8] This allows such materials to have high capacity while still

44   maintaining their structural integrity.

45   A number of studies have investigated compositions that fall within the $NaNi_xMn_{1-x}O_2$

46   series and their use as cathodes in sodium ion batteries, however no systematic study of this

47   system has been reported. Parant et al. studied the structures of Na_xMnO_2 (x = 0.2, 0.40, 0.44,

48   0.70, 1) made by solid state methods.[13] $NaMnO_2$ was found to form a low temperature

49   monoclinic α-$NaMnO_2$ phase (which is denoted here as O'3 $NaMnO_2$), and a high temperature

50   orthorhombic phase (β-$NaMnO_2$). Mendiboure et al. investigated the structural transitions

51   induced by electrochemical desodiation of $NaMnO_2$ bronzes in 1M $NaClO_4$ in PC electrolyte.[14]

52   They found that for $Na_{0.70}MnO_2$ the P2 structure is maintained from $0.45 \leq x \leq 0.85$, while both

53   the O'3 α-$NaMnO_2$ and β-$NaMnO_2$ show two structural transitions during cycling. Ma et al.

54   measured the electrochemical performance of O'3 $NaMnO_2$ in 1M $NaPF_6$ in EC:DMC

55   electrolyte[15] and obtained significantly higher capacities compared to Mendiboure et al. They

56   claimed that this improved result was due to the difference in electrolyte used. The voltage

57   curve of O'3 $NaMnO_2$ was found to comprise many pronounced features with strong voltage

58   steps and plateaus indicative of phase transitions. The sequence of phase transitions during

59   charge and discharge were found not to be the same, indicating that the charge and discharge

60   processes go through different reaction paths. However, this hysteresis was found to be

61   reversible. After 20 charge/discharge cycles 132 mAh/g capacity was retained from a 185

62   mAh/g first discharge capacity.[15]

63   The electrochemistry of O'3 $NaNiO_2$ has been studied by Braconnier et al. in 1M $NaClO_4$

64   in PC electrolyte.[16] Only 0.2 Na could be removed during electrochemical desodiation.

65   Recently Vassilaras et al. reinvestigated the electrochemistry of O'3 $NaNiO_2$ in 1M $NaPF_6$ in

66   EC:DMC electrolyte and achieved a reversible discharge capacity of 120 mAh/g (corresponding

67   to the removal of about 0.5 Na).[17] The voltage curve of O'3 $NaNiO_2$ was found to comprise a

68   number of plateaus which are completely reversible.

69   Paulsen and Dahn studied the layered manganese bronzes, $Na_{2/3}[Mn_{1-x}M_x]O_2$ with the P2-

70   structure.[18] $Na_{2/3}[Mn_{1-x}Ni_x]O_2$ could be made phase pure at compositions up to x = ⅓. Higher

71   nickel contents resulted in phases coexisting with NiO. It was reasoned that this behavior could

72   be understood if Ni^{2+} replaces Mn^{3+} to make $Na^{+}_{2/3}[Mn^{3+}_{1-3x}Mn^{4+}_{2x}Ni^{2+}_x]O_2$, then the composition

73   limit is reached at x = ⅓. For compositions with x < 1/5, the oxidation state of Mn is less than

74   3.5, which results in an orthorhombic distortion of the P2 structure due to the co-operative Jahn-

75   Teller effect. At compositions with x > 1/5, an undistorted P2 structure was obtained.

76   Lu and Dahn studied the electrochemical extraction and insertion of sodium in P2-

77    $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ by in situ x-ray diffraction.[19] They found that the Na can be completely

78   extracted from this material and reversibly inserted again. When x > 1/3 the structure is P2. At x

79   = 1/3 a small amount of O2 structure is observed. For x < 1/3 the structure adopts the P2

80   structure, with some minor O2 and $Ni_{1/3}Mn_{2/3}O_2$ phases also present. O3 $NaNi_{1/2}Mn_{1/2}O_2$ has

81   been studied extensively by Komaba et al..[20–22] This material has a first discharge capacity of

82   185 mAh/g, between 2.2 – 4.5 V and a density of 4.59 g/mL. This corresponds to a volumetric

83   energy density of 2700 Wh/L vs Na, which is similar to the energy density of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

84   vs Li. However, the reversibility of O3 $NaNi_{1/2}Mn_{1/2}O_2$ cycled in this voltage range is poor. If

85   the upper voltage window is narrowed to 3.8 V then 125 mAh/g is achieved with good capacity

86   retention. During cycling the O3 starting material changes to the O'3, P3, P'3, and then P3"

87   structures.

88   The high capacities and stable cycling obtained in cathodes containing Ni and Mn make

89   such electrodes attractive for use in commercial applications. To more fully explore the

90   properties of these materials a synthetic, structural and electrochemical study of the entire

91    $NaNi_xMn_{1-x}O_2$ (0 ≤ x ≤1) system is needed, and was undertaken herein. Using a number of

92   synthetic conditions, it was found that phase pure materials could only be obtained for x = 0,

93    $0.25 \leq x \leq 0.66$ and x = 1. The phases obtained during synthesis depended strongly on the

94   precursor materials and the oxygen partial pressure during their heating. To our knowledge this

95   is first report of the single-phase oxides with x = 0.25 and x = 0.66. The electrochemical

96   performance of phase pure materials was evaluated in sodium cells. These materials were found

97   to reversibly intercalate sodium and have a high tolerance towards sodium vacancies, leading to

98   high gravimetric capacities and energy densities.

99

100   **Experimental**

101       $NaNi_xMn_{1-x}O_2$ materials were prepared via solid-state reactions. Phase pure samples

102   proved difficult to produce. Upwards of 300 samples were synthesized in order to determine

103   synthesis conditions that would give phase pure samples, as synthesis was not trivial. It was

104   found that the synthesis conditions strongly affected the phases obtained, including the precursor

105   material composition, the mixing and/or grinding method, powder preparation (pelletization),

106   heating temperature, heating atmosphere, and quenching rate. The precursors used in the

107   syntheses were: Na_2CO_3 (BioXtra, $\geq$ 99.0% Sigma Aldrich), NiO (-325 mesh, 99 % Alfa Aesar),

108   Mn_2O_3 (-325 mesh, 99 %, Sigma Aldrich), MnO_2 (*ReagentPlus*®, 60 - 230 mesh, $\geq$ 99%, Sigma

109   Aldrich), and Na_2O_2 (granular, + 140 mesh particle size, 97 %, Sigma-Aldrich). This method

110   differs from previous reports, which used mixed transition metal hydroxides as precursors.[19,20]

111   An excess amount of the sodium containing precursors (usually 10 % weight) was added to

112   compensate for the loss of sodium due to its volatility at the high reaction temperatures. For this

113   reason the stated sodium compositions of these samples are nominal.

114   Different precursor combinations and heating conditions were found to be the most

115   effective for obtaining phase pure samples, depending on the composition range in $NaNi_xMn_{1-}$

116        $_xO_2$. For $0 \leq x \leq 0.05$, Na_2CO_3, NiO, and MnO_2 were ball milled for a half hour and the powder

117   was then fired at 800 °C in argon for 10 hours. For $0.25 \leq x \leq 0.66$, Na_2CO_3, NiO and Mn_2O_3

118   were ball milled for one hour and pelletized before heating in air at 850 °C for 24 hours,

119   followed by quenching in liquid nitrogen. Samples with compositions in the range of $0.95 \leq x \leq$

120   1 used Na_2O_2, NiO and Mn_2O_3 as precursors that were ball milled for a half hour and then fired

121   in oxygen at 700 °C for 12 hours. Minimal iron contamination is expected to be present in these

122   samples due to milling in a hardened steel vessel, however this was not assessed.   Table 1

123   summarizes the three synthesis methods that resulted in phase pure products for the various

124   composition ranges. These synthesis methods will be referred to as Method A, B and C, as

125   denoted in Table 1. After synthesis the samples were transferred directly in an argon filled

126   glovebox to avoid air exposure, as the samples were found to be hygroscopic. All subsequent

127   powder handling (X-ray measurement, electrode and coin cell preparation) was performed under

128   an inert atmosphere.

129   X-ray powder diffraction (XRD) measurements were made with a Siemens D500 powder

130   diffractometer equipped with a Cu target X-ray tube and a diffracted beam monochromator.

131   Powder samples were measured in a gas tight X-ray sample holder (DPM Solutions, Hebbville

132   NS), shown in Figure 2. The sample holder had an aluminized Mylar window mounted in an arc

133   such that it was perpendicular to the incident and scattered x-ray beam and did not contribute to

134   the measured XRD patterns. A continuous flow of helium gas was provided through the sample

135   holder diffraction measurements to maintain an inert atmosphere and increase counts. Rietveld

136   refinement and profile matching of the powder diffraction data were performed using the

137   computer program Rietica.   A Phenom G2-pro scanning electron microscope (SEM,

138   Nanoscience, Arizona) was used to determine particle size and morphology of the powder

139   samples.

140   Electrodes for electrochemical measurements consisted of $NaNi_xMn_{1-x}O_2$ powder, carbon

141   black (Super P, Erachem Europe), and PVdF (polyvinylidene fluoride, Kynar HSV 900) in an

142   8:1:1 weight ratio. These components were thoroughly mixed in N-methyl-2-pyrrolidone (Sigma

143   Aldrich, anhydrous 99.5%) with two tungsten carbide balls in a Retsch PM200 rotary mill (200

144   rpm, 1 hour) to create uniform black slurries. The slurries were then coated onto aluminum foil

145   and dried under vacuum at 120 °C for 2 hours. 2 cm^2 circular electrodes were punched from the

146   resulting coatings and incorporated into 2325 type coin cells. Circular Na foil counter/reference

147   electrode disks were punched from thin foil (0.015 inch) that was rolled from sodium ingot

148   (Sigma Aldrich, ACS reagent grade). 1 M $NaPF_6$ (Sigma Aldrich 98%) dissolved in propylene

149   carbonate (Novolyte Technologies) was used as electrolyte. Two Celgard 3501 and one BMF

150   (blown microfiber separator, 3M Company) were used as separators. Cells were tested with a

151   Maccor Series 4000 Automated cycler and were typically cycled between 2.0 V and 4.3 V at a

152   constant current of C/10, calculated based on the theoretical capacity corresponding to the

153   desodiation of all of the sodium from the positive electrode.

154   Samples were dissolved in aqua regia acid in order to perform Inductively coupled

155   plasma (ICP) analysis using a Varian Vista Pro (radial view) ICP OES instrument located in the

156   Materials Engineering Centre at Dalhousie University.   This analysis allowed the accurate

157   determination of atomic ratios within the powder samples.

158   **Results and Discussion**

159   **Phase Behavior in the $NaNi_xMn_{1-x}O_2$ System**

160   Figure 3 shows an SEM image of $NaNi_xMn_{1-x}O_2$ with x = 2/3, which is typical of the

161   samples made here. The particles have a thin hexagonal plate like morphology and are about 1 -

162   2 μm in size. Figures 4 - 6 show the XRD patterns of samples prepared by methods A, B and C,

163   respectively.   All diffraction patterns of layered phases could be refined using either a

164   monoclinic (O'3 type, C2/m), rhombohedral (O3 type, R3m) or hexagonal (P2 type, $P6_3/mmc$)

165   space group. In some cases a NiO impurity was detected as peaks near 43°. XRD patterns

166   indicative of phase pure samples are highlighted in Figures 4 - 6. Figure 7 summarizes the

167   phases observed for samples prepared by methods A, B and C as a function of x in $NaNi_xMn_{1-}$

168    $_xO_2$. The phase boundaries were drawn to roughly correspond to the phase behavior considering

169   the limited of number of sample compositions analyzed.

170   Method A was the only method used that resulted in phase pure O'3 $NaMnO_2$, as shown

171   in Figure 4. However, this method did not result in phase pure samples for x > 0. Instead,

172   increasing the nickel content in the range of $0.05 \leq x \leq 0.25$, led to a monoclinic structure mixed

173   with a distorted P2 structure.

174   Method B resulted in phase pure samples having the P2 structure for $0.25 \leq x \leq 0.33$, as

175   shown in Figure 5. In addition, phase pure samples having the O3 structure were obtained for x

176   = 0.5 and 0.66. Samples with higher nickel content contained increasing amounts of NiO in

177   addition to the O3 phase.   When x = 1 only a NiO phase was present.   This is likely a

178   consequence of significant sodium evaporation, in the form of sodium oxide, from the sample /

179   precursors during the heating step in air. This is directly related to the synthesis temperature and

180   length of heating time. Higher synthesis temperatures are needed for product formation, however

181   when temperatures of 900 °C or above are used significant sodium evaporation occurs and a NiO

182   phase is observed. If longer heating times (> 24 hours) are used sodium evaporation is also

183   increased and in many cases no ordered layered phases are formed.

184   When samples were prepared using method C, phase pure samples having the P2

185   structure were obtained for $0.25 \leq x \leq 0.33$, as shown in Figure 6. Phase pure O'3 $NaNiO_2$ of the

186   O'3 type was also obtained when $x = 1$. Method C was the only method used that resulted in

187   phase pure O'3 $NaNiO_2$. Outside these composition ranges, method C did not result in phase

188   pure samples. Samples with $0.33 < x < 0.66$ consisted of a mixture of O3 $NaNi_xMn_{1-x}O_2$ and

189   NiO, while samples with $0.66 < x < 1$ consisted of O'3 $NaNi_xMn_{1-x}O_2$ and NiO. The phase

190   boundary at $x = 0.66$ is bothersome as NiO is observed on either side of the boundary. This

191   appears to violate the Gibbs phase rule for a binary system, but sodium evaporation adds another

192   degree of freedom to the system.

193   By selecting one of the methods, A, B, or C, phase pure $NaNi_xMn_{1-x}O_2$ could be made for

194    $x = 0$, $0.25 \leq x \leq 0.66$, and $x = 1$. A 2-phase region exists between O'3 $NaMnO_2$ and P2

195    $NaNi_{0.25}Mn_{0.75}O_2$, while the $0.66 < x < 1$ composition range seems to lie in a 3-phase

196    $NaNi_{0.66}Mn_{0.33}O_2$ - NiO - NaNiO2 coexistence region in our synthesis conditions. We believe

197   the co-operative Jahn Teller distortion in the O'3 $NaMnO_2$ and O'3 $NaNiO_2$ end members of this

198   composition series induces phase separations with non-distorted phases, rather than forming

199   intermediate phases with internal stresses.

200   Figure 8 shows the structural relationship between the O'3 and O3 unit cells. The

201   monoclinic distortion of the O3 occurs due to the presence of Jahn-Teller ions. Rietveld

202   refinements were performed on all samples to obtain lattice constants. Examples of these

203   refinements are shown in Figures 9 and 10 for the compositions with $x = 0.66$ and 0.25,

204   respectively. The crystallographic data for these compositions are summarized in Tables 2 and

205   3, respectively. For x = 0.66 the O3 α-NaFeO$_2$ (space group R$\overline{3}$m) structure type was used to

206   refine the XRD pattern. In initial refinements Na and Ni were allowed to mix, however the

207   degree of cation mixing was found to be only 0.7 %. This indicates that there was relatively little

208   cation mixing, which is typical of NaMO$_2$ materials. This can be attributed to the difference in

209   ionic radius of Na$^+$ (1.02 Å) and Ni^{2+} (0.69 Å), which would tend to make cation mixing

210   unfavorable.[12] Therefore cation mixing was not considered in the final refinements. For x =

211   0.25, the P2 β-RbScO$_2$ structure type (space group P6$_3$/mmc) was used to refine the XRD

212   measurements. The lattice parameters and site occupancies agree with what has been reported

213   by Delmas and Werner.[23] A relatively high R-factor was obtained for this P2 structure which is

214   attributed to the presence of unrefined peaks at low angles, which likely arise from superlattice

215   ordering.

216   Due to the high volatility of Na at the high reaction temperatures employed here the

217   atomic ratios of the products found from XRD refinement were verified via ICP analysis. The

218   ICP results show good agreement with the anticipated atomic ratios for all pure phase samples,

219   with the Na and TM atomic ratios only varying from the anticipated ratios at most ±3 %.

220   When the monoclinic structures with x = 0 and 1 were refined, two separate M-O bond

221   lengths in the MO$_6$ octahedra were observed, which is characteristic of the Mn^{3+} (d^4 high-spin)

222   and Ni^{3+} (d^7 low-spin) Jahn-Teller ions. NaMnO$_2$ has Mn-O bond lengths of 1.93 Å (x4) and

223   2.40 Å (x2). NaNiO$_2$ has Ni-O bond lengths of 2.02 Å (x4) and 2.22 Å (x2). These distortions

224   will result in variation from the ideal hexagonal a/b ratio of $\sqrt{3}$ (1.732) and β angle of 109.11°,

225   leading to a monoclinic distortion of the layered structure. This is seen clearly from the lattice

226   parameters of the NaMnO$_2$; a = 5.67 Å, b = 2.86 Å and β angle = 113.2, where a/b = 1.98.

227   These are similar to results reported by the Ceder group.[15,17] Table 4 summarizes the cell

228   parameters that were used to fit all of the as prepared single phase samples. Values from past

229   studies are also included and they are in close approximation to those found in this work.
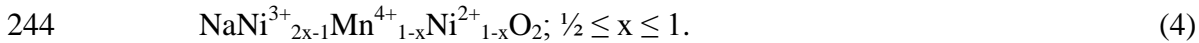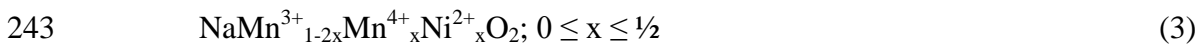
230   Figure 11 shows the lattice parameters of the phase pure $NaNi_xMn_{1-x}O_2$ compositions

231   obtained as a function of x. In order to make comparisons all structures were indexed according

232   to the hexagonal O3 lattice using the following relations:

233        $O'3 \rightarrow O3: \quad a_1 = \sqrt{\left(\frac{a_m}{2}\right)^2 + \left(\frac{b_m}{2}\right)^2}; \ a_2 = b_m; \ c = 3c_m \sin\beta$ (1)

234        $P2 \rightarrow O3: \quad a = b = a_{P2}; \ c = \frac{3}{2}c_{P2}$ (2)

235   where a, b, and c are lattice constants with respect to the O3 unit cell, a_m, b_m, c_m and β are the O'3

236   unit cell parameters and a_{P2}, b_{P2}, c_{P2} are the P2 unit cell parameters. Using this formalism, the

237   O'3 lattice will have two non-equivalent a lattice constants, denoted as a_1 and a_2. Lattice

238   constants from previous studies are also plotted on Figure 11, and are in good agreement with

239   results herein. Generally, as x increases a increases and c decreases. Some discontinuities in

240   these parameters are present at the structural phase boundaries.

241   To understand the trends in the lattice constants and structural changes it is first

242   convenient to assume the transition metal oxidation states are as follows:

243        $NaMn^{3+}_{1-2x}Mn^{4+}_xNi^{2+}_xO_2; \ 0 \le x \le ½$ (3)

244        $NaNi^{3+}_{2x-1}Mn^{4+}_{1-x}Ni^{2+}_{1-x}O_2; \ ½ \le x \le 1.$ (4)

245   This formulism can explain the different phases observed, as shown in Figure 7. When x = 0, all

246   the manganese is present as Mn^{3+}, resulting in a co-operative Jahn-Teller distortion and $NaMnO_2$

247   having a monoclinic phase. Typically such a distortion persists while the average oxidation state

248   remains below 3.5, as it does in $Na_{⅔}[Mn_{1-y}Ni_y]O_2$ for $0 < y < 1/6$, in which a distorted P'2

249   structure is formed.[18] Such a distorted P'2 phase was not observed here. Although the average

250 oxidation state of Mn is below 3.5 for $x < \frac{1}{3}$, the system prefers to form a 2-phase region

251 between monoclinic $NaMnO_2$ and an ideal P2 structure for $0 < x < \frac{1}{4}$. For $\frac{1}{3} < x < \frac{2}{3}$ the lattice

252 remains fully symmetric as the O3 phase. For $\frac{2}{3} < x < 1$ the system again prefers adopting a 2-

253 phase state as a response to increasing amounts of the Ni^{3+} Jahn-Teller ion, instead of adopting a

254 distorted structure.

255   The change in the a lattice constant is typically attributed to the difference in radii of the

256 different ions in the transition metal layer. In this case where a increases with increasing Ni

257 content this argument cannot be made because as x increases each Mn^{3+} (0.645 Å) is replaced by

258 a Ni^{2+} (0.69 Å) and a Mn^{4+} (0.53 Å), which have a lower average ionic radius.[12] The variation in

259 the c lattice constant with x is likely due to the packing efficiency between the different

260 structures. The O'3 and O3 all have similar c values while the less efficient packing of the P2

261 structures cause them to have much higher c lattice constants. Overall the changes in lattice the

262 constants result in the little changes in the density for the P2 and O3 compositions ($0.2 \leq x \leq$

263 0.67), which is about 4.63 g/mL in this range of x. The density of $NaMnO_2$ is much less than

264 this, presumably due to the large monoclinic distortion in the structure.

265 **Electrochemical Characteristics**

266   Figure 12 shows the voltage curves of the phase pure $NaNi_xMn_{1-x}O_2$ materials that were

267 prepared. There are several plateaus which appear for each composition and they are similar for

268 both charge and discharge (except for the first charge in some compositions), indicating

269 reversible processes. The step like character of the many plateaus is expected for these sodium

270 containing materials.[24] In general sodium intercalation materials tend to have more phase

271 transitions than the lithium containing ones. This is likely due to the strain effects of the larger

272 Na^+ ions which produce ordering interactions.

273   Many of the compositions in the $NaNi_xMn_{1-x}O_2$ series display a high first discharge

274   capacity. The highest first discharge capacity was for x = 0.66, with a capacity of ~ 190 mAh/g.

275   It should be noted that all of these materials have high first cycle irreversible capacities, except

276   for x = 0.33 and 0.5.   Electrolyte decomposition above 4 V could contribute to these high

277   irreversible capacities, which can be somewhat supressed when the upper voltage limit is

278   lowered.   NMR studies could be performed after cycling to determine whether electrolyte

279   decomposition has occurred. It is anticipated that other factors could contribute to these high

280   irreversible capacities, such as irreversible material changes during cycling.

281   Figure 13 shows the specific discharge capacities with cycle number for $NaNi_xMn_{1-x}O_2$

282   cycled between 2.0 to 4.3 V. All compositions, except x = 1, had capacities greater than 100

283   mAh/g over for 20 cycles, but had severe capacity fade. The reversibility of these materials

284   could be improved by optimization of the electrolyte formulation, as additives such as FEC have

285   shown to improve cycling.[22] For compositions where there exist results in the literature these

286   findings show good agreement.[15,17,20] When cycled in this voltage range, the volumetric energy

287   densities of $NaNi_xMn_{1-x}O_2$ ranged from 1650 − 2705 Wh/L. The highest volumetric energy

288   density of 2705 Wh/L was achieved for x = 0.66, with 190 mAh/g capacity and an average

289   discharge voltage of 3.07 V. This approaches the energy density of Li-ion cathodes (e.g. ~2900

290   Wh/L for $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$) and is among the highest reported volumetric energy densities for

291   Na-ion battery electrodes. For example, one of the best known and highest energy density Na-

292   ion cathode materials, $P2\text{-}Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$, has a volumetric energy density of 2132 Wh/L.[4]

293

294

295   **Conclusions**

296   Phase pure layered $NaNi_xMn_{1-x}O_2$ (where x = 0, 0.25, 0.33, 0.5, 0.66, and 1) were

297   synthesized via solid state reactions. Different synthesis conditions were required, depending on

298   the composition. These materials have a monoclinically distorted O'3 structure (x = 0, 1), P2

299   structure ($0.25 \leq x \leq 0.33$) or an O3 structure ($0.5 \leq x \leq 0.66$). Excepting for x = 0, all

300   compositions have high densities, above 4.6 g/mL. All compositions have high reversible

301   capacities when cycled between 2.0 to 4.3 V. The x = 0.66 composition had the highest first

302   discharge capacity of ~ 190 mAhr/g and highest volumetric energy density of 2705 Wh/L. This

303   is one of the highest energy densities reported for Na-ion cathode materials. However, all

304   compositions had poor cycling performance. Further improvements are required for materials in

305   this series to be utilized in practical cells.

306

307   **Acknowledgements**

References

311   1.   S.-W. Kim, D.-H. Seo, X. Ma, G. Ceder, K. Kang, *Advanced Energy Materials*, **2** (7) , 710
312   (2012).

313   2.   A.Y. Tsivadze, T.L. Kulova, A.M. Skundin, *Protection of Metals and Physical Chemistry*
314   *of Surfaces*, **49** (2) , 145 (2013).

315   3.   S. Komaba, C. Takei, T. Nakayama, A. Ogata, N. Yabuuchi, *Electrochemistry*
316   *Communications*, **12** (3) , 355 (2010).

317   4.   N. Yabuuchi, M. Kajiyama, J. Iwatate, H. Nishikawa, S. Hitomi, R. Okuyama, R. Usui, Y.
318   Yamada, S. Komaba, *Nature Materials*, **11** (6) , 512 (2012).

319   5.   R. Berthelot, D. Carlier, C. Delmas, *Nature Materials*, **10** (1) , 74 (2011).

320   6.   Y. Takeda, K. Nakahara, M. Nishijima, N. Imanishi, O. Yamamoto, *Materials Research*
321   *Bulletin*, **29** (6) , 659 (1994).

322   7.   C. Delmas, C. Fouassier, P. Hagenmuller, *Physica*, **99B** , 81 (1980).

323   8.   C. Delmas, J.J. Braconnier, A. Maazaz, P. Hagenmuller, *Revue de Chimie Minerale*, **1**
324   (19) , 343 (1982).

325   9.   J. Reed, G. Ceder, *Electrochemical and Solid-State Letters*, **5** (7) , A145 (2002).

326   10. T. Ohzuku, Y. Makimura, *Chemistry Letters*, **2** , 744 (2001).

327   11. E. Rossen, C.D.W. Jones, J.R. Dahn, *Solid State Ionics*, **57** , 311 (1992).

328   12. R.D. Shannon, *Acta Cryst.*, **A32** , 752 (1976).

329   13. J.-P. Parant, R. Olazcuaga, M. Devalette, C. Fouassier, P. Hagenmuller, *Journal of Solid*
330   *State Chemistry*, **3** (1) , 1 (1971).

331   14. A. Mendiboure, C. Delmas, P. Hagenmuller, *Journal of Solid State Chemistry*, **57** , 323
332   (1985).

333   15. X. Ma, H. Chen, G. Ceder, *Journal of The Electrochemical Society*, **158** (12) , A1307
334   (2011).

335   16. J.-J. Braconnier, C. Delmas, P. Hagenmuller, *Materials Research Bulletin*, **17** (8) , 993
336   (1982).

337   17. P. Vassilaras, X. Ma, X. Li, G. Ceder, *Journal of the Electrochemical Society*, **160** (2) ,
338   A207 (2012).

339   18.   J.M. Paulsen, J.R. Dahn, *Solid State Ionics*, **126** , 3 (1999).

340   19.   Z. Lu, J.R. Dahn, *Journal of The Electrochemical Society*, **148** (11) , A1225 (2001).

341   20.   S. Komaba, T. Nakayama, A. Ogata, T. Shimizu, C. Takei, S. Takada, A. Hokura, I.
342   Nakai, *ECS Transactions*, **16** (42) , 43 (2009).

343   21.   S. Komaba, N. Yabuuchi, T. Nakayama, A. Ogata, T. Ishikawa, I. Nakai, *Inorganic
344   Chemistry*, **51** (11) , 6211 (2012).

345   22.   S. Komaba, T. Ishikawa, N. Yabuuchi, W. Murata, A. Ito, Y. Ohsawa, *ACS Applied
346   Materials and Interfaces*, **3** , 4165 (2011).

347   23.   C. Delmas, P. Werner, *Acta Chemica Scandinavica*, **A32** , 329 (1978).

348   24.   J. Molenda, *Solid State Ionics*, **21** (4) , 263 (1986).

349

350 **Table 1**

351

Method	precursors	atmosphere	Annealing temperature (°C)	Annealing time (hours)
A	Na_2CO_3, NiO, MnO_2	Argon	800	10
B	Na_2CO_3, NiO, Mn_2O_3	Air	850	24
C	Na_2O_2, NiO, Mn_2O_3	Oxygen	700	12

352

353   Table 1 Synthesis conditions that were utilized to produce pure phase $NaNi_xMn_{1-x}O_2$ samples.

354

355 **Table 2**

NaNi$_{0.66}$Mn$_{0.33}$O$_2$ (R$\bar{3}$m)

atom	site	x	y	z	occupancy
Na	3b	0	0	0.5	0.988(7)
Ni	3a	0	0	0	0.66
Mn	3a	0	0	0	0.34
O	6c	0	0	0.268(4)	1.0

Cell parameters	a	b	c			
	2.964(5)	2.964(5)	15.810(7)		R-factor	1.99
	α	β	γ		R$_p$	10.4
	90	90	120		R$_{wp}$	16.2

356

357 Table 2 Rietveld refinement results for the NaNi$_{0.66}$Mn$_{0.33}$O$_2$ phase.

358

359 **Table 3**

NaNi$_{0.25}$Mn$_{0.75}$O$_2$ (P6$_3$/mmc)

atom	site	x	y	z	occupancy
Na$_f$	2b	0	0	0.25	0.331(5)
Na$_e$	2d	0.33	0.67	0.75	0.66
Ni	2a	0	0	0	0.25
Mn	2a	0	0	0	0.75
O	4f	0.33	0.67	0.098(2)	1.0

Cell parameters	a	b	c		
	2.887(8)	2.887(8)	11.142(8)	R-factor	4.60
	α	β	γ	R$_p$	19.38
	90	90	120	R$_{wp}$	29.52

360

361 Table 3 Rietveld refinement results for the NaNi$_{0.25}$Mn$_{0.75}$O$_2$ phase.

362

363 **Table 4**

x	Space group	a	b	c	β	M-O bond distance
0	C2/m	5.67, 5.672 [1]	2.86, 2.856 [1]	5.80, 5.807 [1]	113.2, 113.2 [1]	1.93, 2.40 1.94[1], 2.39[1]
0.25	P6$_3$/mmc	2.89	-	11.15	-	1.96
0.33	P6$_3$/mmc	2.89	-	11.07	-	2.002
0.5	R$\overline{3}$m	2.94, 2.968 [2]	-	15.99, 15.909 [2]	-	2.159
0.66	R$\overline{3}$m	2.96	-	15.81	-	2.00
1	C2/m	5.34, 5.322 [3]	2.85, 2.845 [3]	5.62, 5.584 [3]	110.5, 110.467 [3]	2.02, 2.22 1.932 [3], 2.177 [3]

364

365 Table 4 Rietveld refinement results for NaNi$_x$Mn$_{1-x}$O$_2$ samples, with literature results, where

366 available, for comparison.

367

368 **Figure Captions**

369

370 Figure 1 P2 (a), O3 (b), and O'3 (monoclinic) (c) structures of ABO_2 layered type oxides. The

371 unit cell in each diagram is indicated by solid lines. The figures are drawn from the 110

372 perspective.

373

374 Figure 2 Sample holder used for XRD measurements of air sensitive samples. Holder base (a)

375 and holder top (b).

376

377 Figure 3 SEM image of $NaNi_{2/3}Mn_{1/3}O_2$, showing particle size and morphology.

378

379 Figure 4 X-ray diffraction patterns for samples prepared by method A. The red box highlights

380 phase-pure samples.

381

382 Figure 5 X-ray diffraction patterns for samples prepared by method B. The red box highlights

383 phase-pure samples.

384

385 Figure 6 X-ray diffraction patterns for samples prepared by method C. The red box highlights

386 phase-pure samples.

387

388 Figure 7 A pseudo-binary phase diagram of the $NaNi_xMn_{1-x}O_2$ system, for samples prepared by

389 the three synthesis methods as indicated in Table 1.

390

391   Figure 8 An O3 unit cell illustrating the structural relationship between the lattice constants of

392   the O3 and O'3 phases.

393

394   Figure 9 XRD pattern and Rietveld refinement of phase pure $NaNi_{0.66}Mn_{0.33}O_2$. The refined

395   parameters are summarized in Table 2.

396

397   Figure 10 XRD pattern and Rietveld refinement of the phase pure $NaNi_{0.25}Mn_{0.75}O_2$. The refined

398   parameters are summarized in Table 3.

399

400   Figure 11 Evolution of the lattice parameters a and c, as well as the density of $NaNi_xMn_{1-x}O_2$ as

401   a function of x. All lattice parameters are expressed in terms of the O3 structure, as described in

402   the text.

403

404   Figure 12 Voltage curves of $NaNi_xMn_{1-x}O_2$ at C/10 cycling rate and 30°C. The voltage curves of

405   the 10th cycle are shown as dotted lines.

406

407   Figure 13 The discharge capacities versus cycle number for $NaNi_xMn_{1-x}O_2$. Cells were cycled at

408   C/10 at 30°C between 2 and 4.3 V.

409

410

411 **Figure 1**

412

(a)   (b)   (c)

413

414   **Figure 2**

415

Top View — Sample Stage, Gas Inlets, O-ring Groove

Side View

(a)

Aluminized Mylar, 1.75"

(b)

416

417　**Figure 3**

30 μm
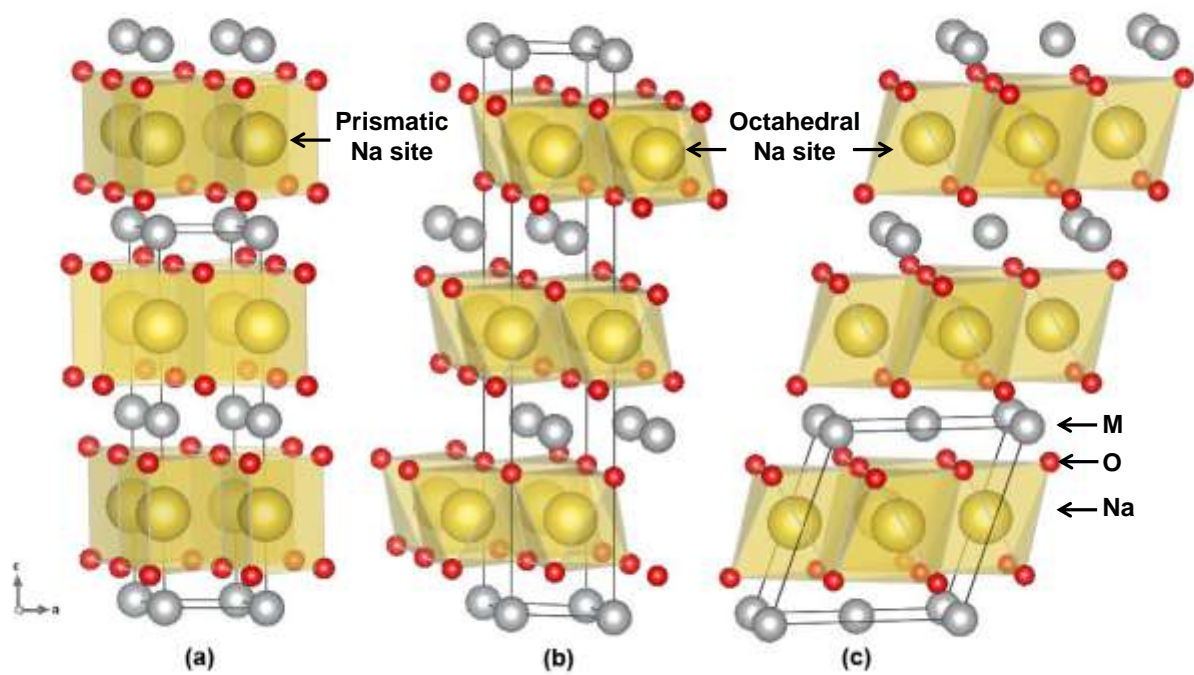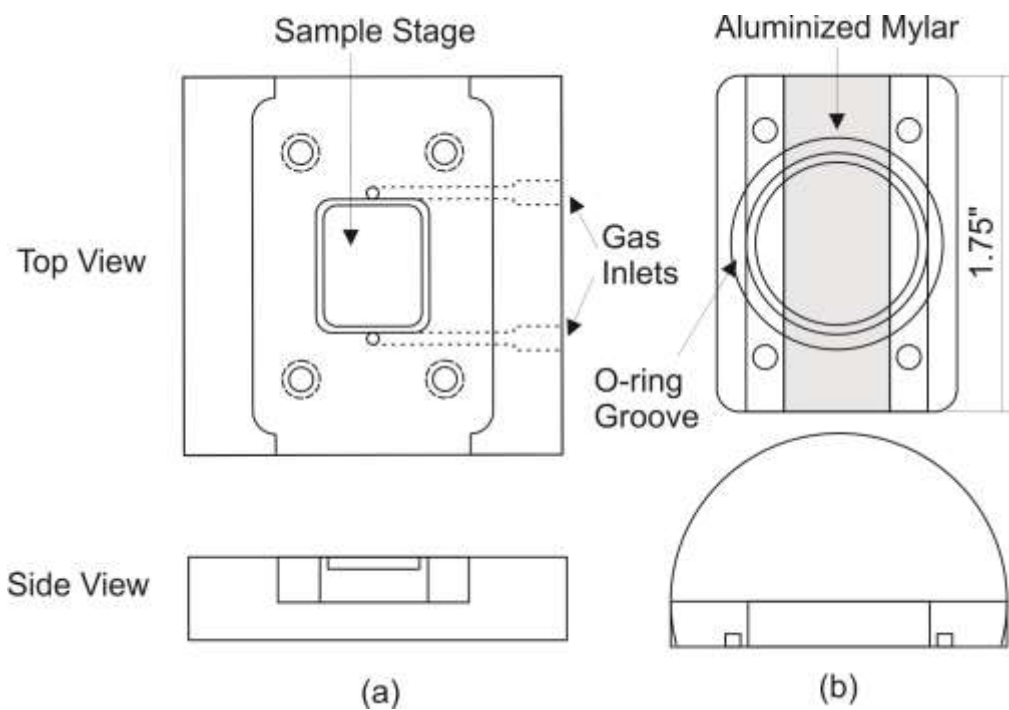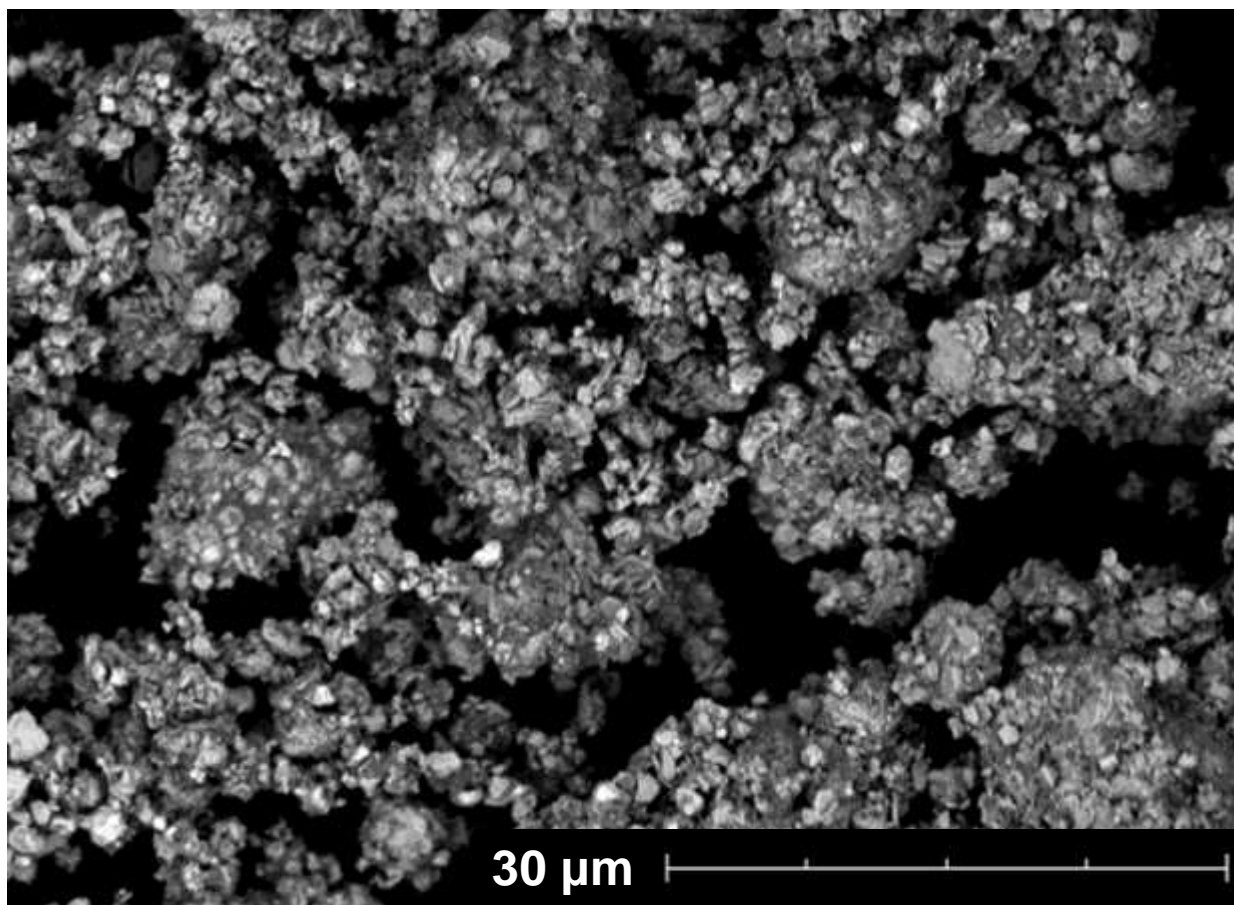
418

419

420   **Figure 4**

421

422

423   **Figure 5**

424

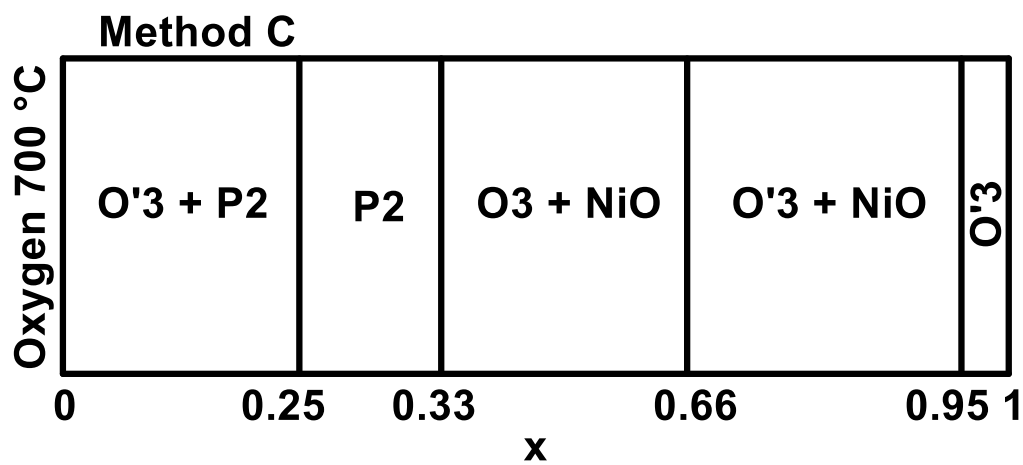425   **Figure 6**

428   **Figure 7**

Method A

Argon 800 °C

| O'3 | O'3 + P'2 |

0 0.05   0.33

x

Method B

Air 850 °C

| O'3 + P2 | P2 | O3 | O3 + NiO | NiO |

0   0.25 0.33   0.66   0.95 1

x

Method C

Oxygen 700 °C

| O'3 + P2 | P2 | O3 + NiO | O'3 + NiO | O'3 |

0   0.25 0.33   0.66   0.95 1

x

429

430
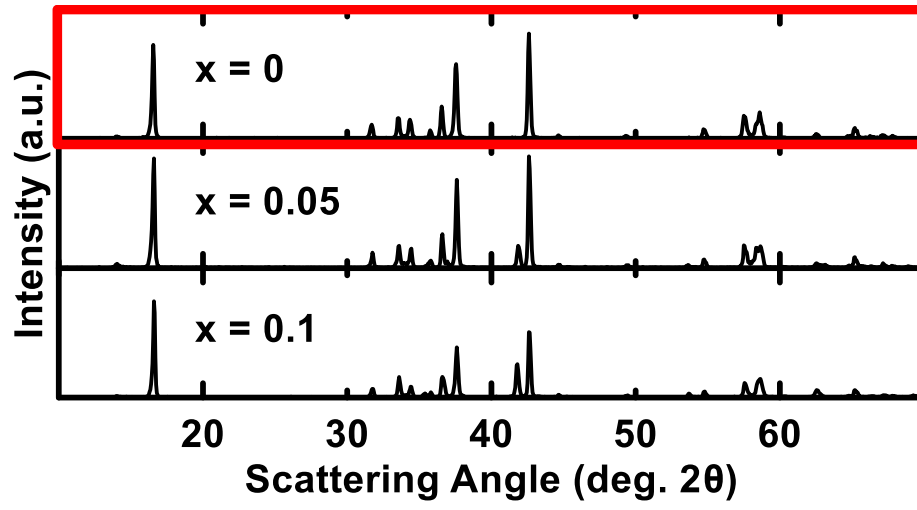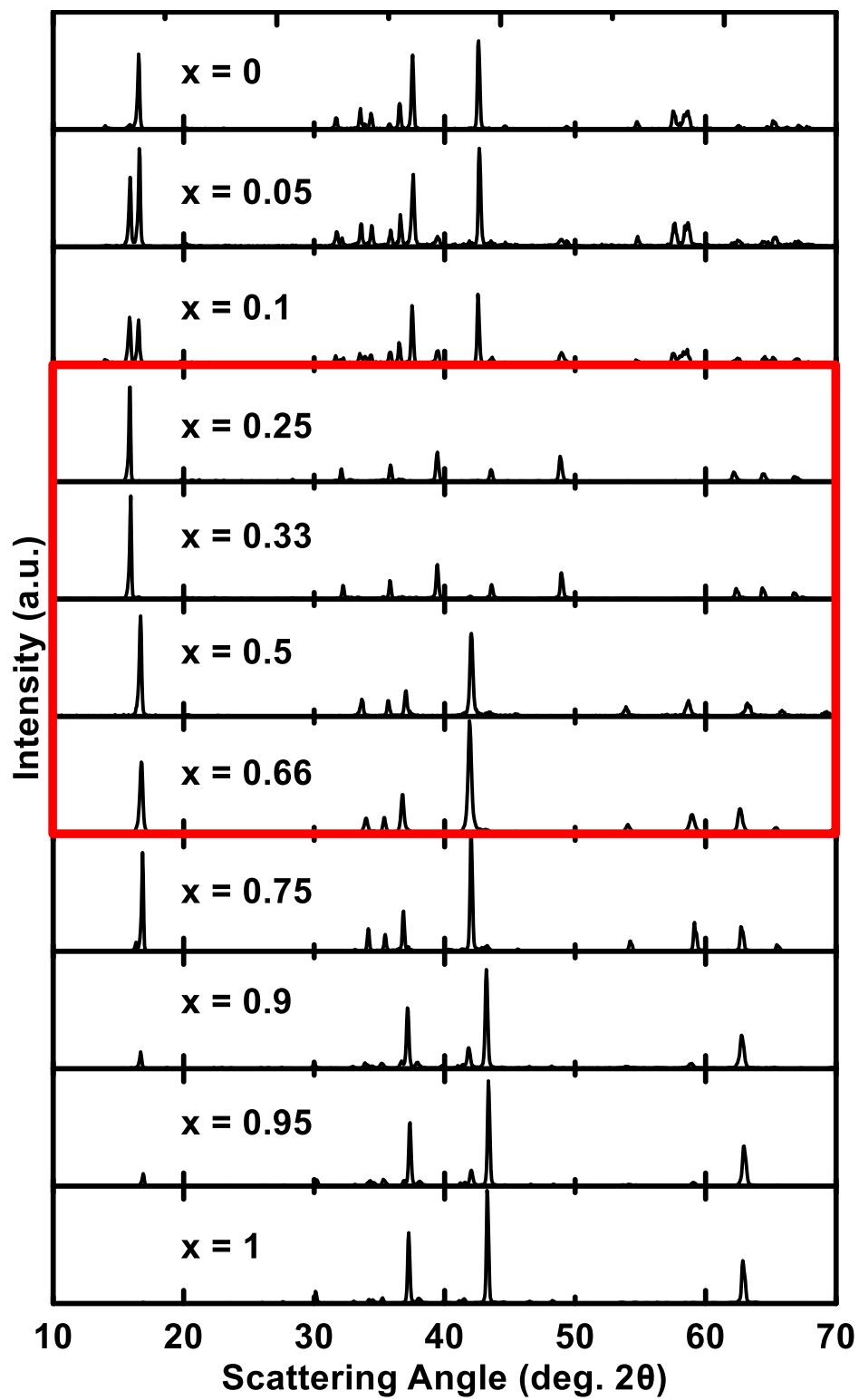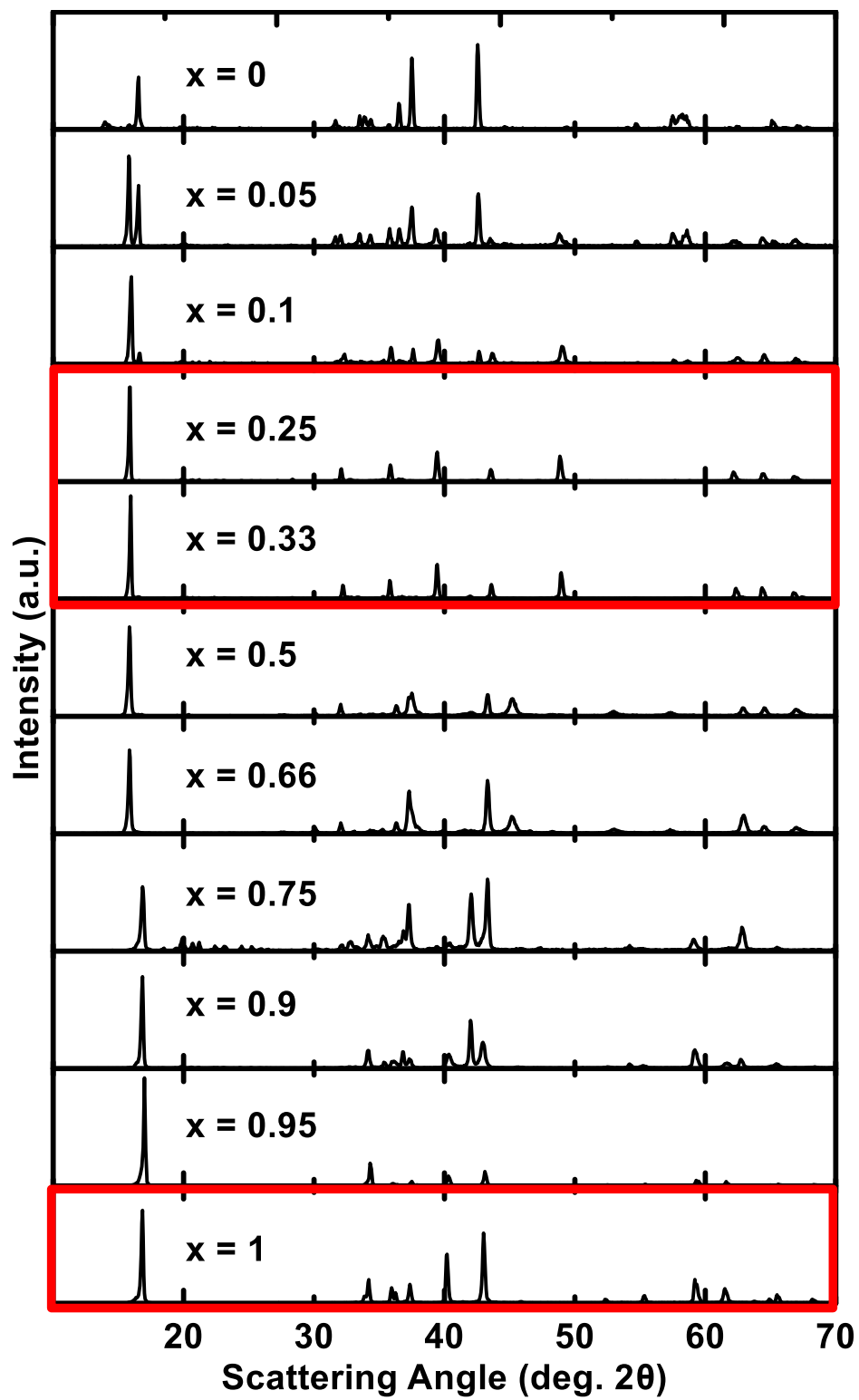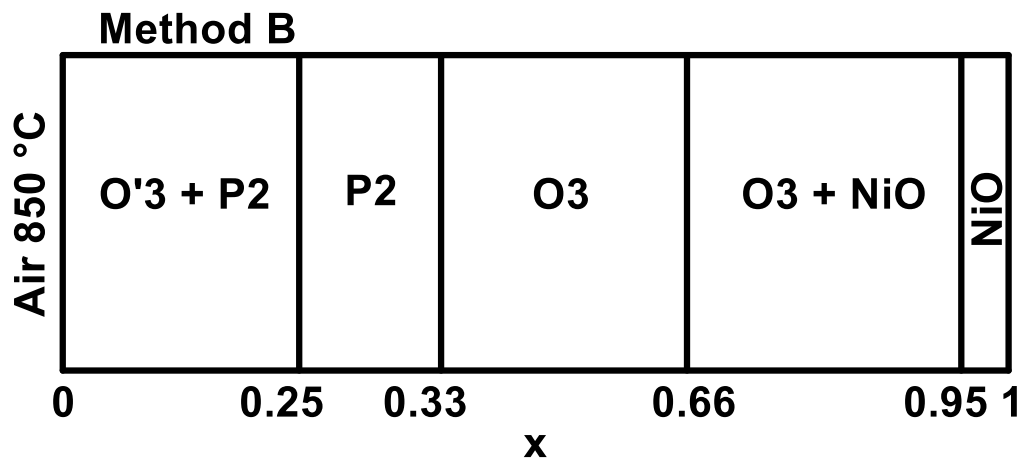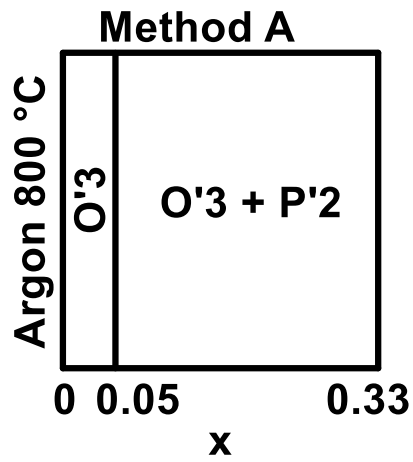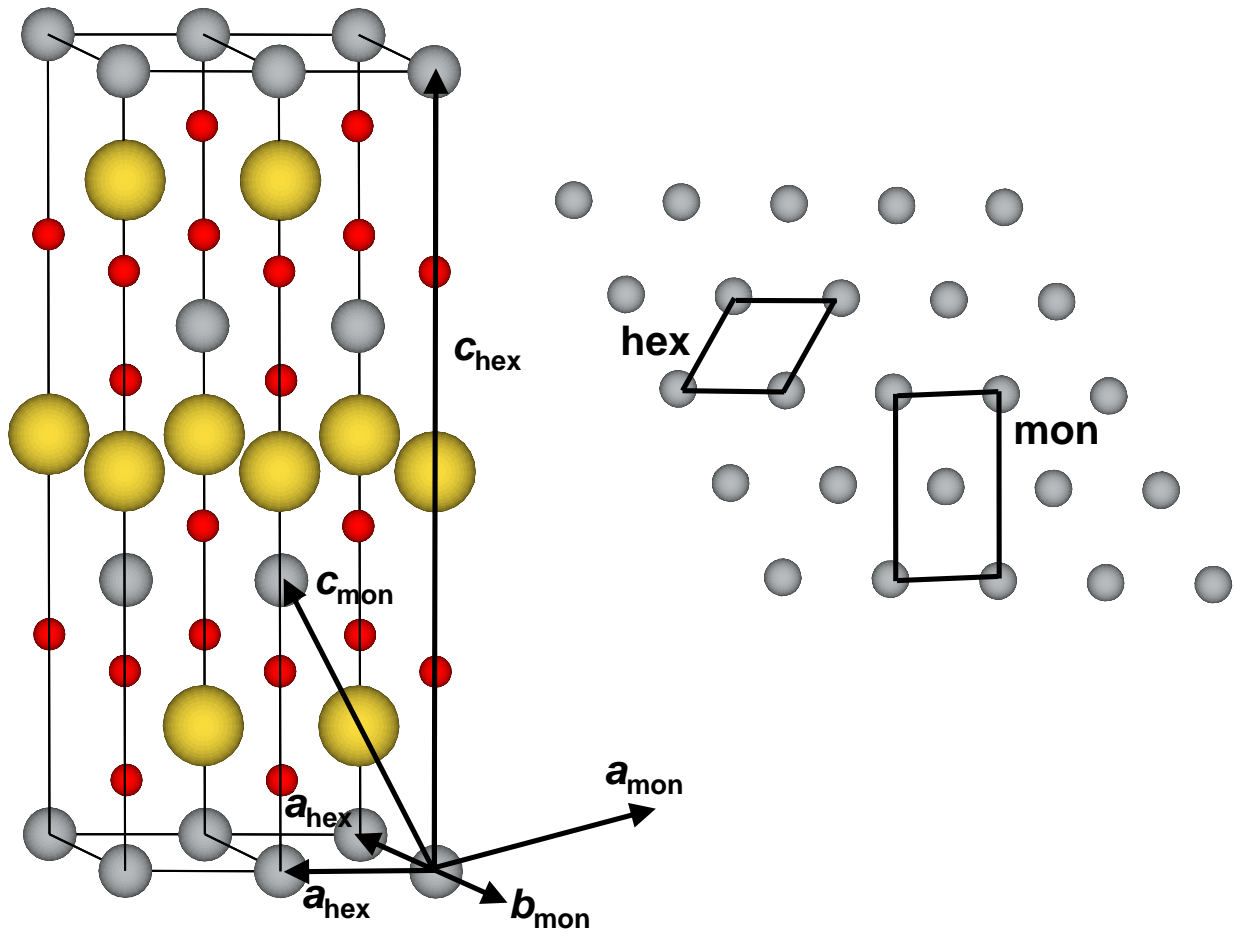
Figure 8

434   **Figure 9**
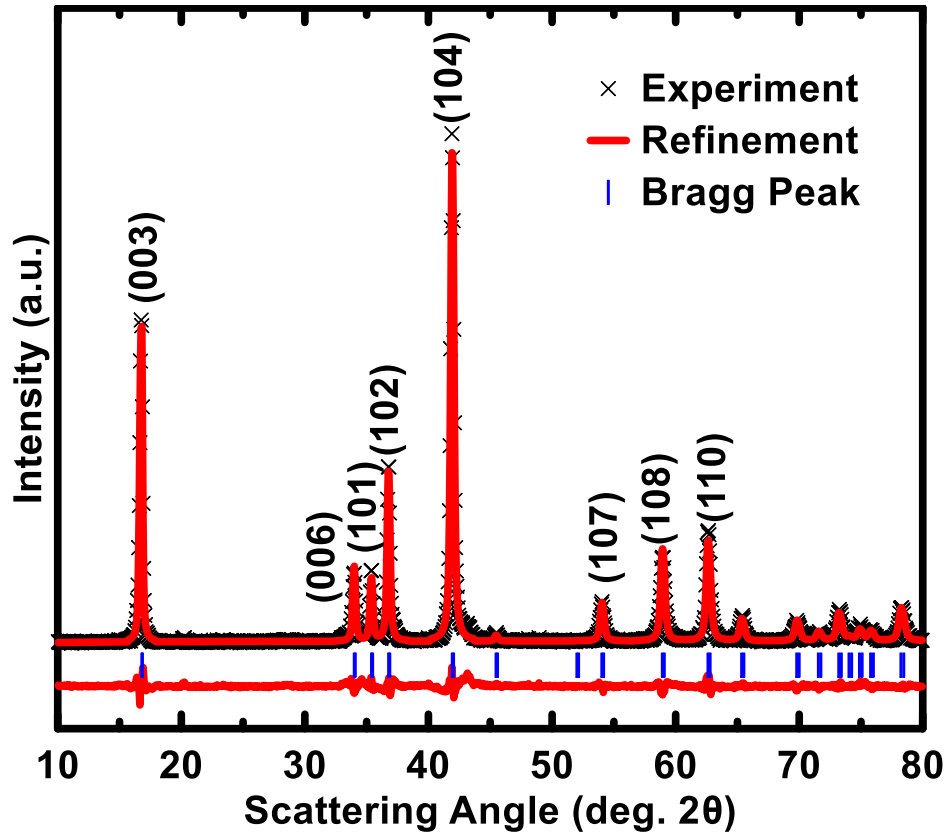
438   **Figure 10**

439

440
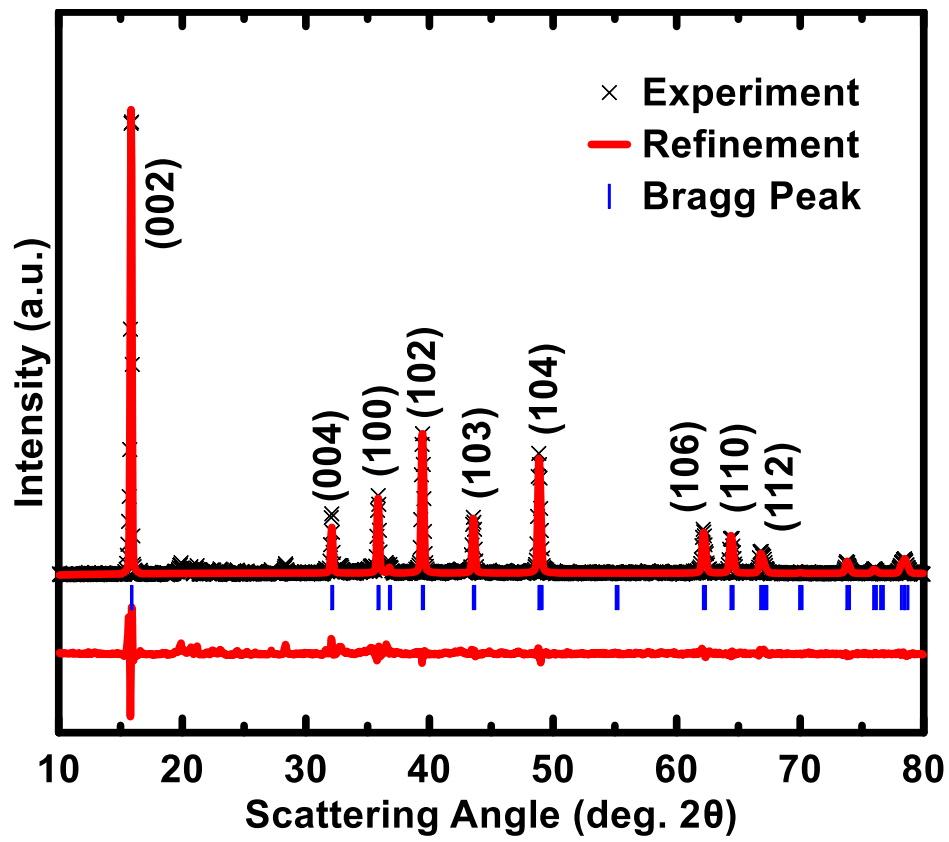
Figure 11

443   **Figure 12**

447 **Figure 13**

448
449

450