



High-temperature X-ray diffraction study of crystallization and phase segregation on spinel-type lithium manganese oxides

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ABSTRACT

To study crystallization process of spinel-type $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$, in-situ high-temperature X-ray diffraction technique (HT-XRD) was utilized for the mixture consisting of Li_2CO_3 and Mn_2O_3 as starting material in the temperature range of 25–700 °C. In-situ HT-XRD analysis directly revealed that crystallization process of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ was significantly affected by the difference in the Li/Mn molar ratio in the precursor. Single phase of stoichiometric LiMn_2O_4 formed at 700 °C. The formation of single phase of spinel was achieved at the lower temperature than the stoichiometric sample as Li/Mn molar ratio in the precursor increased. Lattice parameter of the stoichiometric LiMn_2O_4 at 25 °C was 8.24 Å and expanded to 8.31 Å at 700 °C, which corresponds to the approximately 3% expansion in the unit cell volume. From the slope of the lattice parameter change as a function of temperatures, linear thermal expansion coefficient of the stoichiometric LiMn_2O_4 was calculated to be $1.2 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$ in this temperature range. When the Li/Mn molar ratio in $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ increased ($x > 0.1$), the spinel phase segregated into the $\text{Li}_{1+y}\text{Mn}_{2-y}\text{O}_4$ ($x > y$) and Li_2MnO_3 during heating, which involved the oxygen loss from the materials. During the cooling process from 700 °C, and the segregated phase merged into $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ with oxygen incorporation. Such trend directly observed by in-situ HT-XRD was supported by thermal gravimetric analysis as reversible weight (oxygen) loss/gain at higher temperature (500–700 °C).

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1. Introduction

The demand for large-scale lithium-ion batteries for electric vehicles is rapidly grown. As one of the most promising positive electrode materials for the large-scale batteries, spinel-type lithium manganese oxides [1] and its derivatives have been extensively studied. The non-stoichiometric spinel can be obtained over a wide compositional range including the Li-rich or -deficient spinel and oxygen-rich or -deficient spinel, which is modulated by controlling Li/Mn molar ratio, synthesis temperature, and oxygen partial pressure [2–5]. Depending on the synthesis conditions, such non-stoichiometric character of the spinel phase results in the difficulty to synthesis electrochemically reactive LiMn_2O_4 with high reproducibility. Various synthesis methods of the spinels have been reported by many researchers so far, such as solid-state reaction [1–7], oxidation reaction [8], melt-impregnation [9], emulsion drying [10], sol-gel [8] etc. Among these synthesis methods of the spinel oxides, the solid-state reaction is most commonly used for manufacturing

electrode materials for the lithium-ion batteries. In the case of the solid-state reaction, the physical properties and electrochemical performances of the synthesized spinels depend on the difference in the synthetic conditions [11]. Recently, we have systematically examined that relation between the synthesis conditions, especially for selection of the starting materials, and electrochemical properties by applying the in-situ high-temperature X-ray diffraction technique (in-situ HT-XRD) [12,13]. In general, a high-temperature phase is observed at the room temperature after the quenching. However, the possibility of deviation from the equilibrium condition, including partial phase transitions and oxidation, cannot be eliminated during the quenching process from the high-temperature conditions. Moreover, the thermal expansion of the lattice can be observed only by the in-situ HT-XRD method, which gives additional insight into the mechanism underlying the crystallization process. It has been reported that the crystallization process of the spinel-type LiMn_2O_4 is highly influenced by the starting materials. Among the precursors we examined, it has been found that combination of Mn_2O_3 and Li_2CO_3 enables formation of the highly crystallized and single phase of LiMn_2O_4 even at 700 °C for 12 h, and thus prepared material shows the excellent electrochemical reversibility.

In this work, we investigate crystallization process of the spinel-type lithium-manganese oxides from the mixture of Mn_2O_3

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and Li_2CO_3 with different Li/Mn stoichiometry by in-situ HT-XRD together with thermal gravimetric (TG) analysis. We have first succeeded by in-situ HT-XRD method that direct observation of the phase segregation of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ at the elevated temperatures, from which segregation trend of the $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ phase will be discussed.

2. Experimental

$\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ samples ($0.33 \geq x \geq 0.0$) were prepared by a solid-state reaction from a mixture of Li_2CO_3 and Mn_2O_3 . The mixtures of Li_2CO_3 and Mn_2O_3 (Li/Mn molar ratio: 1.00/2.00, 1.05/1.95, 1.10/1.90, 1.15/1.85, 1.20/1.80, 1.25/1.75, or 1.33/1.67) were ground by using a planetary ball mill. The mixtures were pelletized, and then heated at 700°C for 12 h in air at heating and cooling rates of 1°C min^{-1} . Thermal gravimetric analysis (TG, DTG-60, Shimadzu Co. Ltd., Japan) was also performed on these starting mixtures with the same heating condition. An alumina crucible was used for the TG measurements. Structural evolution during the heating was examined by using X-ray diffractometer (HT-XRD, MultiFlex, SHT-1500 and PTC-30, Rigaku Co. Ltd., Japan) equipped with a heating stage for the in-situ measurements. The powder X-ray diffraction (XRD) data were collected at 25°C and each targeted temperature ranged from 50 to 700°C with a step of 50°C . After reaching the targeted temperatures at a heating/cooling rate of 1°C min^{-1} , the temperature was held for 5 min prior to the data collection, and then the XRD data were collected for 60 min in the 2θ range of 10 – 80° at each temperature. The lattice parameters of the samples were calculated by a least-square method from at least eight individual Bragg reflections.

3. Results and discussion

Crystal structures of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ($0.33 \geq x \geq 0.0$) at room temperature: Fig. 1 shows X-ray diffraction (XRD) patterns of

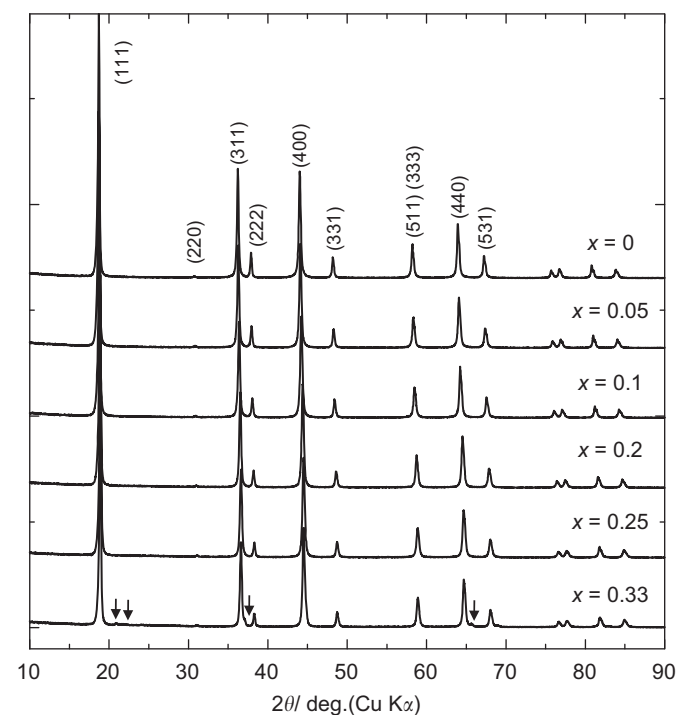


Fig. 1. XRD patterns of a series of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ($0.33 \geq x \geq 0.0$) spinel samples. Arrows indicate Li_2MnO_3 phase as impurity phase.

$\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ samples ($0.33 \geq x \geq 0.0$) collected at 25°C , which are obtained by calcination of the mixture consisting of Li_2CO_3 and Mn_2O_3 at 700°C for 12 h in air. The variation of the lattice parameters for the spinel phase with a space group symmetry of $Fd\bar{3}m$ is shown in the Fig. 2. Lattice parameter of the stoichiometric LiMn_2O_4 is calculated to be $a=8.239\text{ \AA}$, which is in good agreement with the literature [1,2]. Lattice parameters of the $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ samples almost linearly decreased from $a=8.239\text{ \AA}$ ($x=0$) to 8.154 \AA ($x=0.25$), which suggests the formation of the solid-solution system in this region, i.e., LiMn_2O_4 – $\text{Li}_{1.25}\text{Mn}_{1.75}\text{O}_4$. Similar trend can be found in the literature [5–7,14,15]. In this system, manganese ions residing at $16d$ octahedral sites are substituted by the same amount of lithium-ions, resulting in the oxidation of manganese ions from trivalent state to the tetravalent state for the charge compensation. Thus, the lattice parameters are reduced because of the difference in the ionic radii ($\text{Mn}^{3+}=0.645\text{ \AA}$ (HS) and $\text{Mn}^{4+}=0.53\text{ \AA}$ in the octahedral environment) [16]. For $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ (as nominal composition), the lattice parameter of the sample is calculated to be $a=8.147\text{ \AA}$. The value is slightly deviated from the extrapolated value based on the linear relation for the LiMn_2O_4 – $\text{Li}_{1.25}\text{Mn}_{1.75}\text{O}_4$ system as shown in Fig. 2. This is consistent with the fact that diffraction lines assigned into the Li_2MnO_3 is found by XRD for $x=0.33$. $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ is thermodynamically stable below 400°C , [2,5] which decomposes into the $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ($x < 0.33$) and Li_2MnO_3 at higher temperature. The formation of the Li_2MnO_3 reduces the molar fraction of lithium-ion in the spinel phase $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ and reduces oxidation state of manganese in average, leading the increased lattice parameters for the main phase in Fig. 2. For the decomposed $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ phase, the value of x is estimated to be approximately 0.27–0.28 by assuming the linear relation on the lattice parameters in LiMn_2O_4 – $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ solid-solution system.

Thermal gravimetric study on the $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ($0.33 \geq x \geq 0.0$): To study the crystallization process of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ during the heating and cooling process in detail, firstly thermal gravimetric (TG) measurements were carried out on the mixtures consisting of different molar ratio of $\text{Li}_2\text{CO}_3/\text{Mn}_2\text{O}_3$. Fig. 3 shows TG curves of the mixtures measured at a rate of 1°C min^{-1} . Three characteristic features are summarized as follows: (1) steep decline in weight from $\sim 340^\circ\text{C}$, (2) gentle gain in weight after

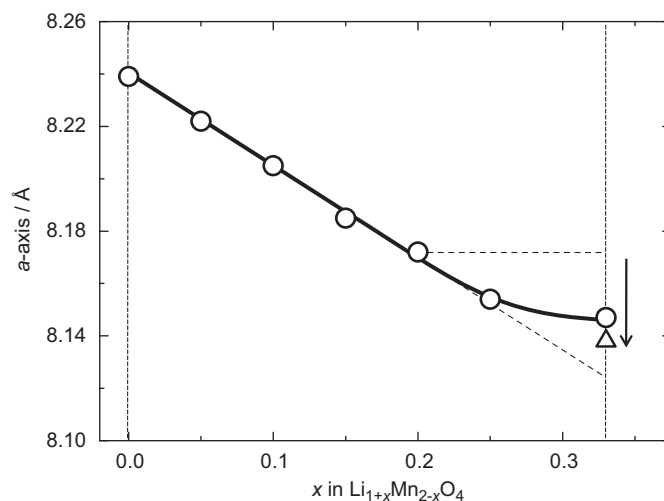


Fig. 2. The change in lattice parameters of a series of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ($0.33 \geq x \geq 0.0$) spinel samples. Open triangle indicates lattice parameter of the spinel phase prepared from the mixture of $\text{Li}_{1.25}\text{Mn}_{1.75}\text{O}_4$ and Li_2MnO_3 at 450°C for 50 h (See text in detail).

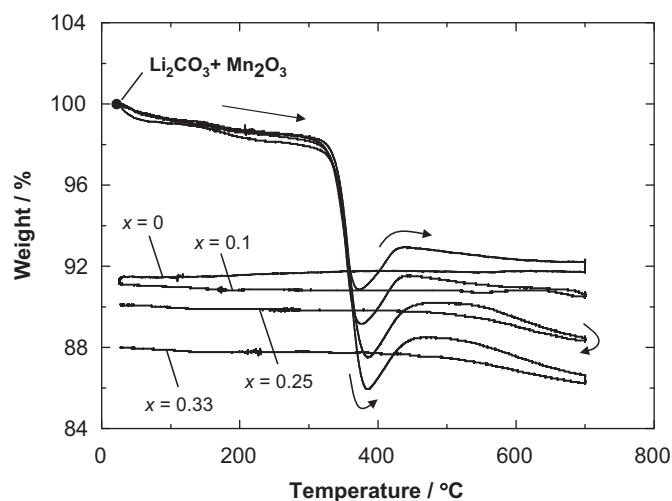
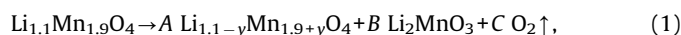


Fig. 3. TG curves of the starting materials consisting of Li_2CO_3 and Mn_2O_3 with different lithium/manganese molar ratio: $\text{Li}/\text{Mn}=1/2, 1.1/1.9, 1.25/1.75,$ and $1.33/1.67$.

the decline from $\sim 400^\circ\text{C}$, and (3) reversible weight loss/gain above $500\text{--}650^\circ\text{C}$, depending on the molar ratio of Li/Mn in the precursors. The onset temperature for the steep weight loss around 340°C is independent of the molar ratio of Li/Mn , whereas the percentage of weight loss depends on it. This clearly indicates that the weight loss originated from the decomposition of Li_2CO_3 into Li_2O and CO_2 . Subsequently, the formed Li_2O , which is chemically reactive, could react with $\text{Mn}_2^{3+}\text{O}_3$ to form the spinel $\text{Li}_{1+x}\text{Mn}^{3+.4+}_{2-x}\text{O}_4$, leading to the weight gain with incorporation of the oxygen ions to the lattice as observed around $400\text{--}500^\circ\text{C}$. The reversible weight loss/gain above 500°C for the Li -rich samples will be further discussed in the next section.

Structural evolution on the $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ by in-situ high-temperature X-ray diffraction method: To further study the structural evolution of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ during the heating process, in-situ high-temperature X-ray diffraction (HT-XRD) analysis was conducted on the mixtures of $\text{Li}_2\text{CO}_3/\text{Mn}_2\text{O}_3$. We have already reported the study on the crystallization process on the stoichiometric LiMn_2O_4 from $\text{Li}_2\text{CO}_3/\text{Mn}_2\text{O}_3$ by in-situ HT-XRD and its electrochemical reactivity [12,13]. The crystallization of the spinel phase starts from 400°C without the formation of the intermediate phase. The spinel phase coexists with Mn_2O_3 below 700°C , and formation of single phase LiMn_2O_4 was achieved at 700°C . Once the stoichiometric spinel phase is formed, the sample is thermodynamically stable in air during the subsequent heating process at 700°C and cooling down to 25°C . Thus prepared stoichiometric LiMn_2O_4 from Li_2CO_3 and Mn_2O_3 can deliver the rechargeable capacity of 130 mAh/g in the voltage ranged from 3.0 to 4.3 V at a rate of 20 mA g^{-1} , which is the highest value among the LiMn_2O_4 samples prepared from different precursors, e.g., MnCO_3 , EMD, and Mn_3O_4 [12,13]. Fig. 4 shows in-situ HT-XRD patterns of the mixture consisting of Li_2CO_3 and Mn_2O_3 with the molar ratio of $\text{Li}/\text{Mn}=1.1/1.9$ during heating process up to 700°C . No difference in the peak intensity for Mn_2O_3 is found from $25\text{--}300^\circ\text{C}$, but shift of the diffraction angle to the lower angle is noted, indicating thermal expansion of the Mn_2O_3 lattice below 300°C . The (111) Bragg reflection of the spinel phase, locating at $18\text{--}19^\circ$ in 2θ , appears at 350°C . These observations are consistent with the results observed by TG at 350°C in Fig. 3, i.e., releasing CO_2 gas and manganese oxidation by Li_2O . The spinel phase coexists with Mn_2O_3 from 350 to 500°C , and then the single phase of $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ is confirmed at 550°C . During the heating from 550 to 700°C , peak width of each Bragg reflection is sharpened as the heating temperature increases up to 700°C .

Structural evolution observed during subsequent heating at 700°C for 12 h is shown in Fig. 4b. New peaks appear during the continuous heating at 700°C . These Bragg peaks become clearly visible as the heating time at 700°C is elongated. These peaks can be assigned into the Li_2MnO_3 as a second phase. This indicates that $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ segregates into the Li_2MnO_3 and $\text{Li}_{1+y}\text{Mn}_{2-y}\text{O}_4$ ($y < 0.1$) at the elevated temperatures. According to the literature [5], the segregation reaction is formulated as



where y changes as a function of the temperature. This segregation reaction involves the oxygen loss from the system, which is supported by the weight loss observed above 650°C by TG (Fig. 3). Moreover, by in-situ HT-XRD study, we have first demonstrated in the direct manner that the reaction shown in Eq. (1) proceeds in partly reversible manner. The structural evolution of the sample observed by XRD during the cooling process after the holding at 700°C for 12 h is shown in Fig. 4c. The XRD patterns of the sample were collected from 700 to 25°C . Intensity of Bragg reflections contributed by the Li_2MnO_3 segregated phase becomes weak from 700 to 550°C . Finally, Li_2MnO_3 disappears at 500°C . These results indicate that the segregation reaction for $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$ shown in Eq. (1) is reversible process associated with oxygen loss/gain in this experimental condition.

In-situ HT XRD patterns of the mixture consisting of Li_2CO_3 and Mn_2O_3 with $\text{Li}/\text{Mn}=1.2/1.8$ during heating process from 25 to 700°C are shown in Fig. 5a. The spinel phase appears at 350°C , which is the same temperature with $\text{Li}/\text{Mn}=1.1/1.9$. In contrast, it is found that the spinel phase and Mn_2O_3 coexist only below 450°C , which is approximately 100°C lower than that of $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$. Li_2MnO_3 phase is also confirmed at 700°C , and the intensity during the subsequent heating at 700°C (Fig. 5b) is relatively stronger than that of $\text{Li}/\text{Mn}=1.1/1.9$. When the sample is cooled from 700 to 25°C , the segregated Li_2MnO_3 phase is merged into the major spinel phase (Fig. 5c). Although the intensity originated from Li_2MnO_3 is considerably reduced during the cooling, it is noted that trace of the segregated phase is still observed at 25°C .

The trend of the phase segregation and crystallization of the $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ at the elevated temperatures: The variation in the lattice parameters of the $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ($x=0.0, 0.05, 0.10,$ and 0.20) obtained by the in-situ HT-XRD study, during the cooling process from 700°C after holding for 12 h, is shown in the Fig. 6. For the samples of $x=0.0$, the lattice parameters linearly decrease from $a=8.31\text{ \AA}$ at 700°C to $a=8.24\text{ \AA}$ at 25°C . Since the noticeable weight gain was not observed in this temperature range by TG, the increased lattice parameters are due to thermal expansion of the lattice. From the slopes of the lattice parameters as a function of the temperature, linear and volume thermal expansion coefficients are calculated to be $\alpha_L=1.2 \times 10^{-5}\text{ }^\circ\text{C}^{-1}$ and $\alpha_V=3.8 \times 10^{-5}\text{ }^\circ\text{C}^{-1}$, respectively. The obtained volume thermal expansion coefficient is similar to that of MnO with a rocksalt-type structure ($\alpha_V=3.4\text{--}4.7 \times 10^{-5}\text{ }^\circ\text{C}^{-1}$) [17] and slightly smaller than that of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ with a layered structure ($\alpha_V=5.64 \times 10^{-5}\text{ }^\circ\text{C}^{-1}$) [18].

For the samples of $x=0.10$ and 0.20 , two distinct regions for the lattice parameter change are observed with different slopes. The slope from 400 to 25°C for both samples is calculated to be $1.1 \times 10^{-5}\text{ }^\circ\text{C}^{-1}$, which is comparable with that of the stoichiometric sample [12]. In contrast, the slope is considerably steeper from 700 to 500°C ($x=0.10$) or 400°C ($x=0.20$). If apparent linear thermal expansion coefficient is estimated from the slope, the value of $2\text{--}3 \times 10^{-5}\text{ }^\circ\text{C}^{-1}$ can be obtained. These values are two times larger than that of the stoichiometric phase

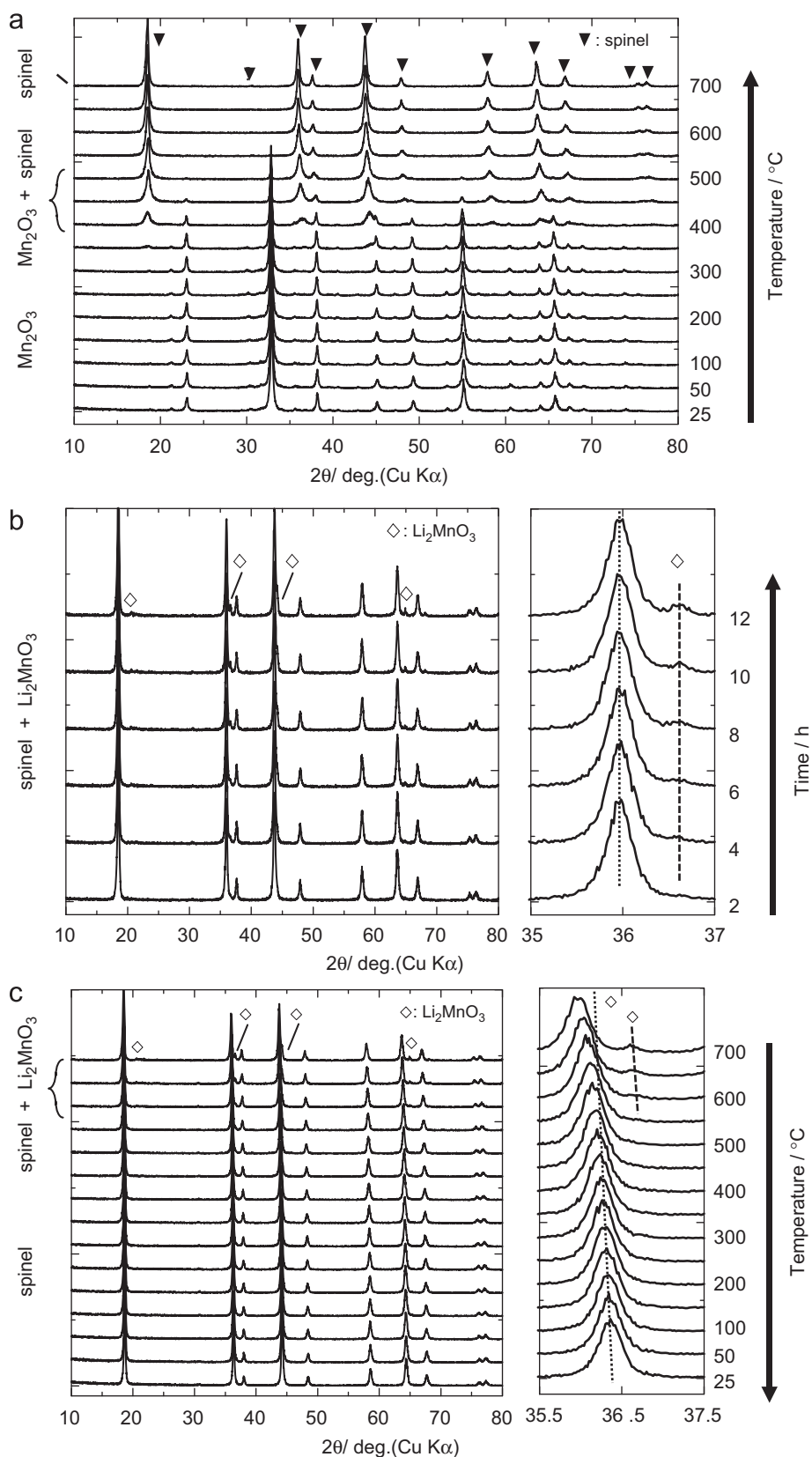


Fig. 4. In-situ HT-XRD patterns for the sample with Li/Mn ratio of 1.1/1.9; (a) heating process from 25 to 700 °C, (b) temperature holding at 700 °C for 12 h, and (c) cooling process from 700 to 25 °C. Dotted and dashed lines are guide for eyes, indicating shift of the reflection lines and existence of the Li₂MnO₃ phase, respectively.

($\alpha_L = 1.2 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$), and considerably larger as the linear thermal expansion coefficients. Hence, it is concluded that this could involve the oxidation/reduction process of manganese ions, i.e.,

chemical expansion [19]. As shown in Figs. 3–5, the phase segregation occurs together with oxygen loss (Eq. (1)) for both samples in these temperature ranges. Therefore, it is in good

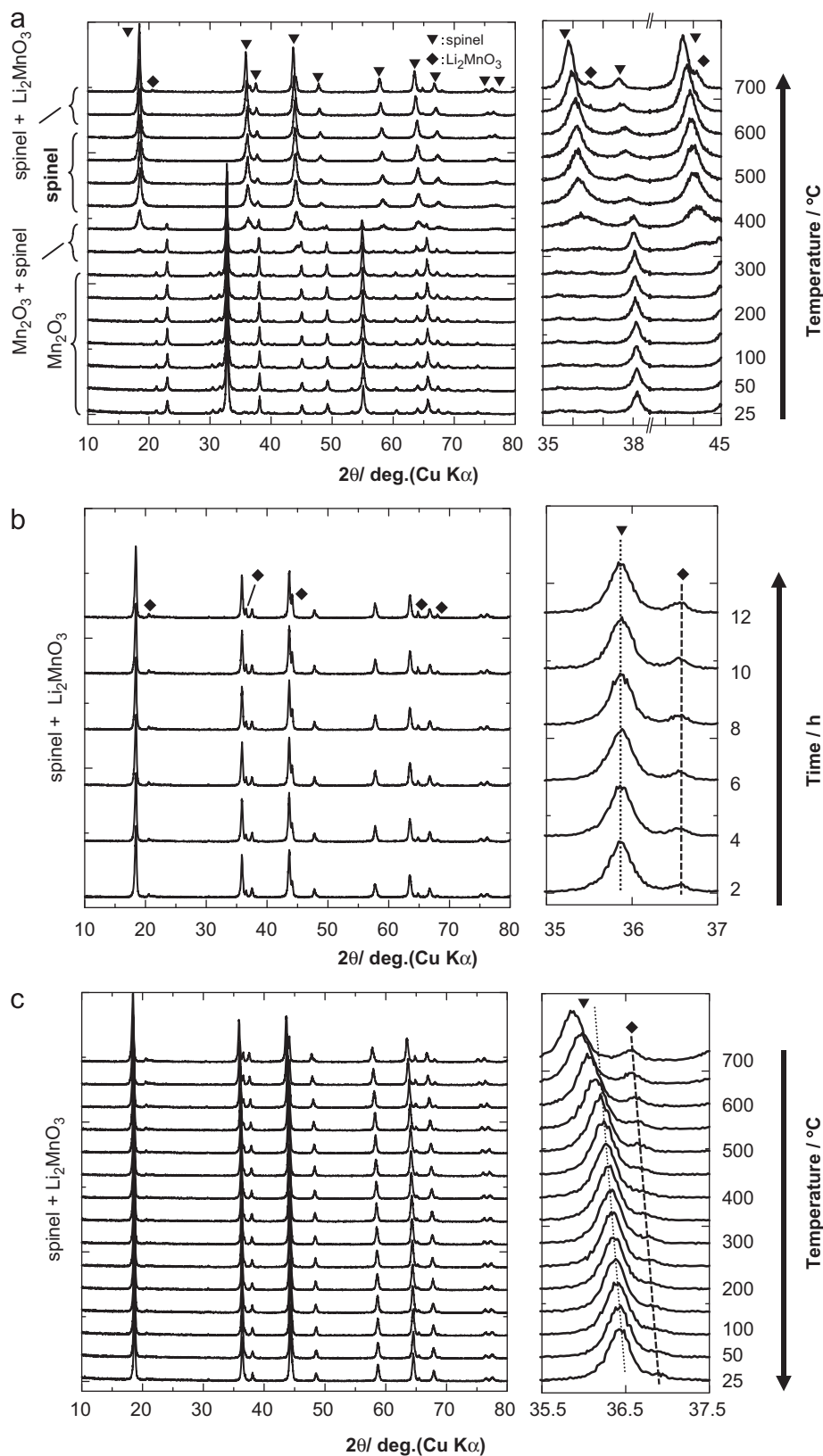


Fig. 5. In-situ HT-XRD patterns for the sample with Li/Mn ratio of 1.2/1.8; (a) heating process from 25 to 700 °C, (b) temperature holding at 700 °C for 12 h, and (c) cooling process from 700 to 25 °C.

agreement with the fact that apparent thermal expansion coefficient increased as were discussed above. From the inflection temperatures on the lattice parameter variations (Fig. 6), it can be

estimated that oxidation of manganese ions (crystallization of $Li_{1+x}Mn_{2-x}O_4$) takes place during cooling process until ca. 500 °C for $x=0.1$ and 400 °C for $x=0.2$, associated with merging Li_2MnO_3

segregate phase with oxygen into the spinel phase. This is also supported by the results of TG during cooling process (Fig. 3), in which weight gain was observed in similar temperatures for these samples. Moreover disappeared or weakened intensity of the reflections originated from Li_2MnO_3 (Figs. 4 and 5) was directly confirmed during the cooling process by in-situ HT-XRD.

On the other hand, for the $x=0.1$ and 0.2 , during the temperature holding at 700°C for 12 h, the lattice parameter stays constant value without peak shift (Figs. 4b and 5b). This indicates that no oxygen loss including the phase segregation occurs during the subsequent heating process at 700°C for both samples, which is also consistent with the fact that the sample weight stays constant value during the temperature holding at 700°C for $x=0.1$ – 0.25 from the TG observation. For $x=0.1$, the intensity of the Li_2MnO_3 became visible during the continuous heating for 12 h by in-situ HT-XRD, suggesting that the Li_2MnO_3 crystallites grow, rather than continuous decomposition of the spinel phase associated with the oxygen loss.

The structural evolution and phase segregation for the $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ synthesized from Li_2CO_3 and Mn_2O_3 are summar-

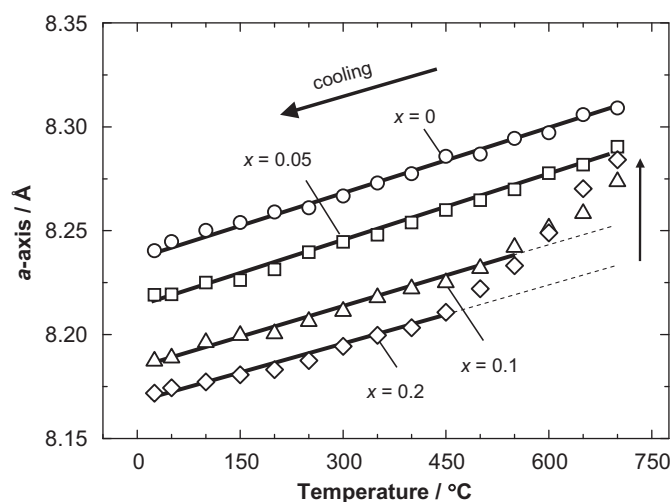


Fig. 6. The variation of the lattice parameters of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ spinel samples during cooling process from 700 to 25°C .

ized in Fig. 7. The reactions proceed as follows: (1) the spinel phases appear from 350 – 400°C , which was not influenced by the difference in the Li/Mn molar ratio in the starting materials, and depended on only the temperature. This is consistent with the observation by TG (Fig. 3) as discussed in the previous section. (2) The region, in which two-phase (Mn_2O_3 and spinel phase) coexists, shifts to the lower temperature limit from 650°C at the stoichiometric sample ($x=0.00$) to 450°C at $x=0.20$. In contrast to the decomposition temperature of Li_2CO_3 , two-phase region is highly influenced by the Li/Mn molar ratio in the starting material. The single phase formation of spinel-type structure was achieved at the lower temperature as the Li/Mn ratio increased. (3) Phase segregation associated with oxygen loss during the heating, and recrystallization with oxygen gain during cooling, are evident when the value of x is greater than 0.1 for $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$. The lattice parameters of the spinel phase are similar ($a=8.28\text{Å}$) at the 700°C (Fig. 7) for $x > 0.05$ in $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ samples. These results suggest that the $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ samples segregates into the $\text{Li}_{1+y}\text{Mn}_{2-y}\text{O}_4$ ($x > y$) phases, which have the similar stoichiometry as the spinel phase at 700°C , and Li_2MnO_3 was formed complementarily, i.e., $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ with small portion of Li_2MnO_3 . When the heating temperature is further raised above 700°C , the phase segregation would further progress even for the stoichiometric LiMn_2O_4 . For example, the thermal gravimetric study on $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ showed that weight loss associated with oxygen loss started from ca. 720°C for $x=0.095$ and ca. 850°C for the stoichiometric sample ($x=0$) [14]. When the heating temperature is increased above 850°C , the stoichiometric spinel LiMn_2O_4 also segregates into the Li deficient (Mn-rich) tetragonal spinel, $\text{Li}_{1-x}\text{Mn}_{2+x}\text{O}_4$ ($I4_1/amd$), and Li_2MnO_3 [3]. As shown in Figs. 3–5, the segregation reaction shown in this paper is reversible process in air condition. During the cooling process from 700 to 25°C , the segregated Li_2MnO_3 merged into the spinel phase again. By in-situ HT XRD study, the trace of Li_2MnO_3 is confirmed for $x=0.2$ after the cooling process. This segregated phase was not able to be detected for the XRD pattern in Fig. 1. It is speculated that this is originated from the difference in the cooling condition used for both study. For in-situ HT XRD, the temperature is ramped down from 700 and 25°C at a rate of 1°C min^{-1} with the holding for 60 min at each step (50°C) for the XRD data collection. Such minor difference observed in this

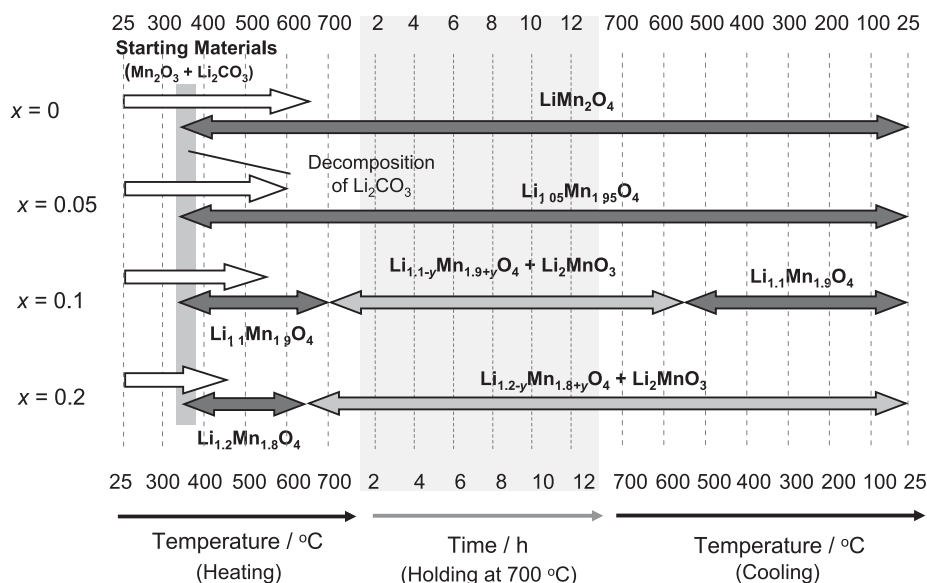


Fig. 7. A scheme of the phase evolution from starting materials consisting of Li_2CO_3 and Mn_2O_3 for the calcination process observed by in-situ HT-XRD.

study can be minimized by using a bright X-ray source, e.g., synchrotron X-ray, to reduce data acquisition time at each step [18].

Trial on the synthesis of highly crystallized $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$: The trend of the phase segregation of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ at elevated temperature prevents synthesis of the highly crystallized $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$, especially for the $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$, which consists of only tetravalent manganese ion, as an end member of the solid solution $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ system ($0.33 \geq x \geq 0.0$). Single phase of $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ can be prepared at lower temperature of 400 °C from lithium salt and manganese oxides [5,6]. Synthesis at lower temperature, however, results in lower crystallinity with broadened diffraction lines [5,6]. In this paper, we have described that the recrystallization process from the segregated phases during the cooling by in-situ HT-XRD. Therefore, it is expected that highly crystallized $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ could be obtained from Li-rich spinel and Li_2MnO_3 under the optimum post-heating condition.

To test this hypothesis, $\text{Li}_{1.2}\text{Mn}_{1.8}\text{O}_4$ and Li_2MnO_3 were prepared by a conventional solid-state method, and were used as the starting material instead of Li_2CO_3 and Mn_2O_3 . Powders of $\text{Li}_{1.2}\text{Mn}_{1.8}\text{O}_4$ and Li_2MnO_3 were mixed well by a mortar and pestle, and then pressed into a pellet. The pellet was heated at 450 °C for 50 h. XRD patterns of the mixture consisting of $\text{Li}_{1.2}\text{Mn}_{1.8}\text{O}_4$ and Li_2MnO_3 before and after the heating are shown

in Fig. 8. After the heating at 450 °C, clear change in the XRD patterns is confirmed. As shown in the inset of Fig. 8, the intensity of the diffraction lines originated from Li_2MnO_3 is clearly weakened after the heating, and then the diffraction lines of the spinel phase shifts toward higher diffraction angle without peak broadening. The lattice parameter is shortened from $a=8.172$ to 8.138 Å after the heating process, indicating that Li content is further enriched based on the $\text{Li}_{1.2}\text{Mn}_{1.8}\text{O}_4$. The lattice parameter of the spinel phase after the heating is plotted in Fig. 2 for comparison. The observed lattice parameter ($a=8.138$ Å) is smaller than the sample prepared by the direct solid-state method at 700 °C ($a=8.147$ Å). Although the value of x seems to be slightly smaller than that of $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$, the highly crystallized phase is successfully obtained from the mixture of $\text{Li}_{1.2}\text{Mn}_{1.8}\text{O}_4$ and Li_2MnO_3 .

The Li enrichment process for the $\text{Li}_{1.2}\text{Mn}_{1.8}\text{O}_4$ during the heating at 450 °C was further examined by in-situ HT-XRD. The variation in the lattice parameter for the mixture of $\text{Li}_{1.2}\text{Mn}_{1.8}\text{O}_4$ and Li_2MnO_3 during the heating at 450 °C is shown in Fig. 8c. The lattice parameter of the spinel phase is shortened as a function of holding time at 450 °C, which indicates that the Li enrichment process continues for 20 h in this experimental condition. From these results, it is believed that highly crystallized $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ could be prepared by controlling post-heating temperature and holding time together with proper precursors.

4. Conclusion

Crystallization process of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ from the precursor consisting of Li_2CO_3 and Mn_2O_3 was examined in detail by in-situ high-temperature X-ray diffraction method (HT-XRD) in the temperature range of 25–700 °C. It was found that crystallization process was highly influenced by the difference in the molar ratio between Li_2CO_3 and Mn_2O_3 in the precursor. Crystallization of the single phase of spinel was also achieved at the lower temperature as molar fraction of Li ion in the precursor increased. The stoichiometric LiMn_2O_4 and Li-rich $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ samples are thermodynamically stable below 700 °C, and only thermal expansion of the lattice is observed (linear thermal expansion coefficient; $1.2\text{--}1.3 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$). When the molar fraction of Li ions versus Mn ions became larger ($x > 0.1$ in $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$), apparent thermal expansion coefficient of the spinel phase clearly increased with appearance of the Li_2MnO_3 phase at the elevated temperatures. It was directly confirmed by in-situ HT XRD that oxygen loss from the spinel phase and phase segregation into the Li_2MnO_3 and $\text{Li}_{1+y}\text{Mn}_{2-y}\text{O}_4$ ($x > y$) take place during heating for these samples, which were consistent results with the observation by thermal gravimetric analysis as the reversible weight loss/gain. Such oxygen release from the spinel phase is partly reversible process and the segregated phase were merged and crystallized again into the $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ during cooling. In this paper, we have clearly demonstrated that in-situ HT-XRD is powerful tool to study the crystallization process during the heating/cooling, and then it has been directly proven that the phase segregation and re-crystallization of $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ at the elevated temperatures by the in-situ HT-XRD method. We believe that further systematic study on the spinel and spinel-related lithium insertion materials would be beneficial for the development of the large-scale lithium-ion batteries.

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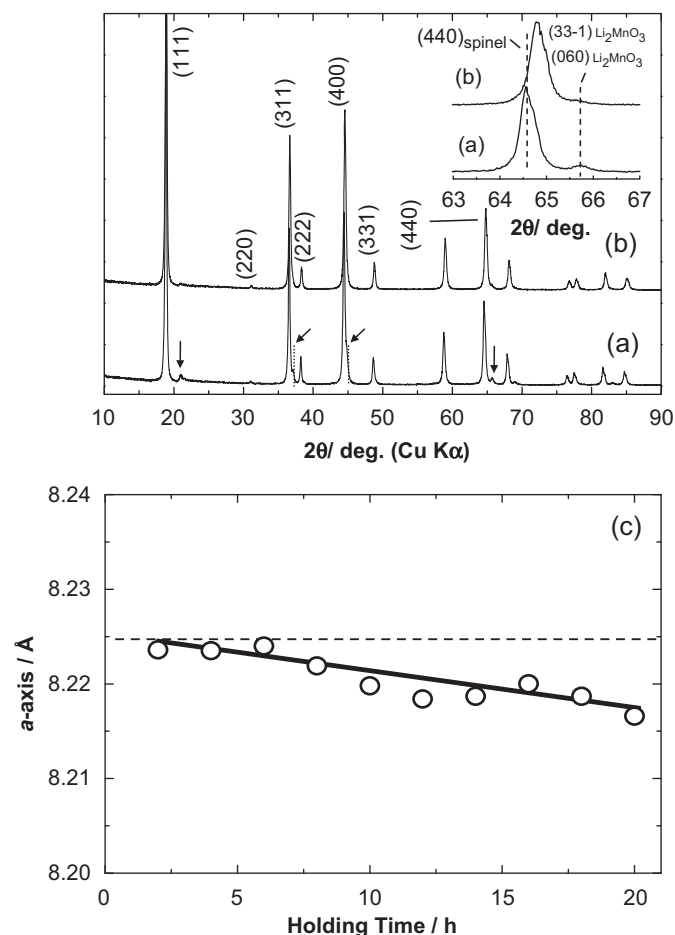


Fig. 8. XRD patterns of spinel phase $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ prepared from the mixture consisting of $\text{Li}_{1.2}\text{Mn}_{1.8}\text{O}_4$ and Li_2MnO_3 : (a) before and (b) after heating at 450 °C for 50 h. Bragg reflections from Li_2MnO_3 are marked by arrows. The lattice parameter of the spinel phase is shortened from $a=8.172$ to 8.138 Å at 25 °C after the heating process at 450 °C for 50 h. Change in the lattice parameter of the spinel phase at 450 °C for 20 h are shown in (c), which was obtained by the in-situ HT-XRD for the mixture of $\text{Li}_{1.2}\text{Mn}_{1.8}\text{O}_4$ and Li_2MnO_3 .

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