Effect of [MnO₆] Octahedra to the Coloring Mechanism of (Li₃₋ₓNaₓ)₂MnO₃

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ABSTRACT: (Li₃₋ₓNaₓ)₂MnO₃ (0 ≤ x ≤ 0.10) solid solutions were synthesized by a conventional solid-state reaction technique to investigate the relationship between the steric structure of the [MnO₆] octahedra and coloration mechanisms. The color, optical properties, and crystal structure of the solid solutions were characterized. The (Li₁₋ₓNaₓ)₂MnO₃ (0 ≤ x ≤ 0.10) solid solutions absorbed the visible light at wavelengths shorter than 550 nm and around 680 nm. The former and latter optical absorption bands were attributed to the spin-allowed (4A₂g → 4T₁g, 4T₂g) and spin-forbidden (4A₂g → 2E₂g, 2T₁g) d–d transitions of tetravalent manganese ions, respectively. The absorption band assigned to the 4A₂g → 4T₂g transition shifted toward longer wavelengths with the enlargement of the average [Mn(2)O₆] bond distance by doping Na⁺. In contrast, the latter absorption bands did not shift but the absorption intensities increased due to the distortion of the [Mn(2)O₆] octahedra. Consequently, the red color purity of the sample gradually increased with the increase in the Na⁺ concentration. Among the (Li₁₋ₓNaₓ)₂MnO₃ (0 ≤ x ≤ 0.10) samples synthesized in this study, the highest red color purity was obtained in the (Li₀.93Na₀.07)₂MnO₃ (hue angle: h° = 39.1) sample. The results of this study provide important insights for the development of environment-friendly inorganic red pigments containing Mn⁴⁺ ions as a coloring source.

1. INTRODUCTION

Inorganic pigments consisting of metal oxides are applied in a wide range of fields, such as ceramics, paints, and plastics, because of their high hiding powers and fine coloring properties. In particular, red inorganic pigments are much in demand due to their high visibility. Some red pigments such as lead oxide red (Pb₃O₄), mercuric sulfide red (HgS), and cadmium red (CdS, CdSe) have been popularly used as industrial inorganic color materials. However, these pigments contain elements (e.g., Pb, Hg, Cd) that are toxic to the environment and the human body. Accordingly, the use of the conventional pigments composed of these harmful elements is considered to be regulated or banned on a global scale. In particular, many nontoxic red pigments have been developed by several researchers to replace the harmful pigments with the components are nontoxic elements. It has been reported that the color of this material is brick-red or orange-red due to the electronic transition between two 3d orbitals (t₂g and e_g) of Mn⁴⁺. The optical absorption band due to the d–d transition is influenced by the crystal field around the Mn⁴⁺ ions. The Mn⁴⁺ content is controlled approximately by 1 mol % to avoid concentration quenching in phosphors. However, it is considered that the visible light in the region from 350 to 550 nm is strongly absorbed by further increasing the Mn⁴⁺ concentration and coloring of the sample can be recognized. Since the visible light around 550 nm corresponds to green light, it is expected that a reddish color, which is a complementary color of green, will be obtained. For these reasons, Mn⁴⁺ is a promising coloring source to develop environment-friendly inorganic red pigments.

In this study, we focused on Li₂MnO₃ as a host material, and the components are nontoxic elements. It has been reported that the color of this material is brick-red or orange-red due to the optical absorption in the wavelength range between 350 and 550 nm, corresponding to the d–d transition of Mn⁴⁺ ions. However, the red color purity of pure Li₂MnO₃ is not enough, and it is necessary to enhance the red color purity to make it a red pigment. Because the d–d transitions in transition metal cations are strongly influenced by the crystal...
field around them, the control of the optical absorption due to the d–d transition is possible by adjusting the crystal field energy. The d–d transition band shifts to the lower energy (i.e., longer wavelength) side, when the crystal field around the chromophore ions becomes weak due to the introduction of larger cations into the host material. Therefore, a more reddish color than that of pure Li2MnO3 will be obtained by doping larger cations. To enhance the red color purity of Li2MnO3, we selected Na+ (ionic radius: 0.116 nm) as a dopant because this is a nontoxic element and has the same valence with Li+ (ionic radius: 0.090 nm). Namely, Na+-doped Li2MnO3 samples, (Li1−xNa)xMnO3 (0 ≤ x ≤ 0.10), were synthesized by a solid-state reaction technique and the influences of differences in the geometric structure around the Mn4+ ions on the color properties were investigated.

2. RESULTS AND DISCUSSION

2.1. X-ray Powder Diffraction (XRD) and Field Emission–Scanning Electron Microscopy (FE-SEM) Image. The XRD patterns of the synthesized (Li1−xNa)xMnO3 (0 ≤ x ≤ 0.10) samples are shown in Figure 1. The XRD pattern of Li2MnO3 (No. 01-073-0152) from the inorganic crystal structure database (ICSD) is also depicted as a reference on the bottom. A single-phase Li2MnO3 structure was observed for all samples, and no diffraction peaks of other phases or impurities were detected in the patterns. The diffraction patterns of the samples corresponded to that of the monoclinic Li2MnO3 from ICSD. The lattice volumes of the (Li1−xNa)xMnO3 (0 ≤ x ≤ 0.10) samples were calculated from the diffraction angles in the XRD patterns. The compositional dependence of the lattice volume for the (Li1−xNa)xMnO3 (0 ≤ x ≤ 0.10) solid solutions is shown in Figure 2. The cell volume increased with the increasing Na+ concentration, which indicated that some Li+ (ionic radius: 0.090 nm) ions in the Li2MnO3 structure were substituted with larger Na+ (ionic radius: 0.116 nm) ones. These results indicate that the solid solutions of the monoclinic Li2MnO3 phase were successfully formed.

The crystal structure of Li2MnO3 has been investigated using the Rietveld method by many researchers. Li2MnO3 has a layered rock-salt-type structure. It adopts a monoclinic unit cell with the C2/m (No. 12) space group. This layered structure is composed of Li+ (2c and 4h sites) and Li+/Mn4+ (2b and 4g sites) layers. These layers were alternately stacked via oxide anions. It has been reported by Boulineau et al. that Li+ and Mn4+ ions in the Li+/Mn4+ layer mainly occupy the 2b (Li-rich) and 4g (Mn-rich) sites, respectively, but the partial exchange between Li and Mn is possible on the 2b and 4g sites.

The Rietveld structure refinement of the (Li1−xNa)xMnO3 (x = 0 and 0.07) samples was carried out to investigate the geometric structure around the Mn4+ ions. Figure 3 shows the Rietveld refinement profiles of the Li2MnO3 and (Li0.93Na0.07)-MnO3 samples. The detailed crystallographic and structural parameters are tabulated in Tables 1 and 2, respectively. Figure 4 displays the crystal structure of Li2MnO3 depicted by the VESTA program on the basis of the crystallographic
parameters obtained from the Rietveld refinement.\textsuperscript{30} As shown in Figure 3, the broadening of the peaks consisting of reflections was observed in the range from $2\theta = 20$ to $25^\circ$, corresponding to the $[\sqrt{3}a_{\text{hex}} \times \sqrt{3}a_{\text{hex}}]$ superstructure caused by a Li(Na)/Mn ordering arrangement.\textsuperscript{24} Therefore, the refinement was conducted in the $2\theta$ ranges except in this region. The low $R$-factors were obtained for both $(\text{Li}_{1-x}\text{Na}_x)\text{MnO}_3$ ($x = 0$ and 0.07) samples. As shown in Table 2, almost all of the Na$^+$ ions doped into the host lattice were located at the Li(1) site, and this result was in good agreement with the structure of $(\text{Li}_{0.95}\text{Na}_{0.05})\text{MnO}_3$ reported by Dong et al.\textsuperscript{31}

The average Mn(2)−O bond distance and distortion index ($D$) of the $[\text{Mn(2)O}_6]$ octahedra in both $(\text{Li}_{1-x}\text{Na}_x)\text{MnO}_3$ ($x = 0$ and 0.07) samples are tabulated in Table 3. The numbers in parentheses indicate the standard deviation. A distortion index, $D$, based on bond lengths was calculated with the formula\textsuperscript{32}

Table 1. Crystallographic Parameters of $(\text{Li}_{1-x}\text{Na}_x)\text{MnO}_3$ ($x = 0$ and 0.07) Obtained by Rietveld Structural Refinement Analysis\textsuperscript{a}

| $x$ | Lattice Parameter | $R$-Factor |
|-----|------------------|------------|
|     | $a$ (nm)         | 0.49286(3) | 0.493658(12) |
|     | $b$ (nm)         | 0.83311(3) | 0.85404(2)   |
|     | $c$ (nm)         | 0.50222(2) | 0.503443(11)  |
|     | $\beta$ (deg)   | 109.236(4) | 109.4020(14) |
|     | $V$ (nm$^3$)     | 0.19938(2) | 0.200200(8)  |
| $x = 0$ | $R_w$ | 1.275     | 1.683 |
| $x = 0.07$ | $R_p$ | 0.873     | 1.061 |
| $x = 0.07$ | $R_e$ | 0.694     | 0.958 |
| $x = 0.07$ | $S$ | 1.837     | 1.757 |
| $x = 0.07$ | $R_F$ | 5.265     | 5.668 |

\textsuperscript{a}Crystal symmetry: monoclinic, space group: $C2/m$ (No. 12), number of formula units per unit cell: $Z = 4$.

Table 2. Structural Parameters of the $(\text{Li}_{1-x}\text{Na}_x)\text{MnO}_3$ ($x = 0$ and 0.07) Samples Refined by the Rietveld Method for the XRD Patterns Obtained at Room Temperature\textsuperscript{b}

| atom | site | occupancy ($g$) | multiplicity $\times g$ | $x$ | $y$ | $z$ | $B_{\text{iso}}$ (Å$^2$) |
|------|------|----------------|-------------------------|-----|----|----|---------------------|
| Li$_1$ | 2b  | 0.618$^b$ | 1.236 | 0 | 1/2 | 0 | 1.0 |
| Mn$_1$ | 2b  | 0.382(5) | 0.764(10) | 0 | 1/2 | 0 | 1.0 |
| Li$_2$ | 2c  | 0.264 | 2 | 0 | 0 | 1/2 | 1.0 |
| Li$_3$ | 4b  | 0.189$^b$ | 3.236 | 0 | 0.680(2) | 1/2 | 1.0 |
| Mn$_2$ | 4g  | 0.101$^b$ | 0.764 | 0 | 0.1642(4) | 0 | 0.5 |
| O$_1$ | 4i  | 0.215(2) | 0 | 0.2247(13) | 0.8 |
| O$_2$ | 8j  | 0.2471(14) | 0.3197(6) | 0.2188(7) | 0.8 |

$(\text{Li}_{0.93}\text{Na}_{0.07})\text{MnO}_3$ ($x = 0.07$)

| $x$ | average Mn(2)−O bond length (nm) | $D$ |
|-----|---------------------------------|-----|
| $x = 0$ | 0.1900(2) | 0.0068 |
| $x = 0.07$ | 0.1911(2) | 0.0154 |

The values of the isotropic atomic displacement parameter ($B_{\text{iso}}$) of the lithium, manganese, and oxygen sites were fixed at 1.0, 0.5, and 0.8 Å$^2$, respectively, with reference to the literature.\textsuperscript{24,25,29} The occupancies ($g$) of 2b and 4g sites in Li$_2$MnO$_3$ were linearly constrained to be the stoichiometric composition: $g$(Li$_1$) = 1 − $g$(Mn$_1$), $g$(Li$_4$) = 0.5 $g$(Mn$_1$), and $g$(Mn$_2$) = 1 − $g$(Li$_4$). The occupancy factors of 2b, 4h, and 4g sites in $(\text{Li}_{0.93}\text{Na}_{0.07})\text{MnO}_3$ were also linearly constrained: $g$(Li$_1$) = 0.72 − $g$(Mn$_1$) + 2 $g$(Na$_1$), $g$(Li$_4$) = 1 − $g$(Na$_1$), $g$(Li$_4$) = 0.5 $g$(Mn$_1$), $g$(Mn$_2$) = 1 − $g$(Li$_4$), and $g$(Na$_1$) = 0.28 − 2 $g$(Na$_1$).
where \( l_i \) is the distance between the central atom and the \( i \)th coordinating atom and \( l_{av} \) indicates the average bond length. The average bond distance between Mn(2) and O increased as the Na\(^+\) content increased. The increase in the \( D \) value indicates that the distortion of the octahedron has become larger. For the \([\text{Mn}(2)\text{O}_6]_{\text{octahedra}}\) in the \( \text{Li}_x\text{Na}_{1-x}\text{MnO}_3 \) \((x = 0 \text{ and } 0.07)\) samples, the \( D \) value increased twofold by Na\(^+\) doping, as shown in Table 3. These results indicate that the \([\text{Mn}(2)\text{O}_6]_{\text{octahedra}}\) were distorted by the introduction of Na\(^+\) into the lattice.

Figure 5 shows the FE-SEM photographs of the Li\(_2\)MnO\(_3\) and \((\text{Li}_{0.93}\text{Na}_{0.07})\text{MnO}_3\) samples. In the undoped Li\(_2\)MnO\(_3 \) sample, the primary particles aggregated and thermally fused to form the spherical secondary particles with lumpy surfaces. In contrast, the faceted primary particles, which had wide and flat surfaces, were observed for the \((\text{Li}_{0.93}\text{Na}_{0.07})\text{MnO}_3\) sample. In addition, the primary particle size for the sample with \( x = 0.07 \) was about 12 \( \mu \)m and almost equal to the secondary particle size of the undoped one.

### 2.2. Diffuse Reflectance Spectra.

The ultraviolet–visible (UV–vis) reflectance spectra for \((\text{Li}_{1-x}\text{Na}_x)\text{MnO}_3 \) \((0 \leq x \leq 0.10)\) samples are shown in Figure 6a. An enlarged view from 400 to 550 nm is also depicted in Figure 6b. Optical absorption at the wavelength shorter than 550 nm was observed for all samples. The absorption band around 400 nm was attributed to the \( d\text{–}d \) transition of Mn\(^{4+}\), which was assigned to the spin-allowed \( ^4\text{A}_2g \rightarrow ^4\text{T}_1g \) transition, according to the Tanabe–Sugano diagram.\( ^{33} \) The absorption in the wavelength range between 400 and 550 nm corresponded to the spin-allowed \( ^4\text{A}_2g \rightarrow ^4\text{T}_2g \) transition.\( ^{21} \) In addition to these optical absorptions, the absorption bands corresponding to the spin-forbidden \( ^4\text{A}_2g \rightarrow ^2\text{E}^{g,\text{t}}_g,^2\text{T}_{1g} \) transitions were observed in the range of 650–710 nm.

![Figure 6. UV–vis reflectance spectra (a) and enlarged spectra (b) of the \((\text{Li}_{1-x}\text{Na}_x)\text{MnO}_3 \) \((0 \leq x \leq 0.10)\) samples.](https://dx.doi.org/10.1021/acsomega.0c01071)

In the visible-light region from 400 to 700 nm, the light scattering capacity of a material tends to increase as the particle size decreases.\( ^{34} \) Accordingly, Li\(_2\)MnO\(_3\) is expected to scatter more visible light than \((\text{Li}_{0.93}\text{Na}_{0.07})\text{MnO}_3\) because the primary particle size of the former is smaller than that of the latter. Although such a result was obtained at wavelengths longer than 550 nm in the reflectance spectra, there was no significant change in the wavelength range from 400 to 550 nm, as shown in Figure 6b. Therefore, the effect of the particle morphology on the optical properties is quite small, and the change in the reflectance is due to the difference in the coordination environment around the Mn\(^{4+}\) ion caused by the substitution of Li\(^+\) with Na\(^+\) in the lattice.

As seen in Table 2, in both of Li\(_2\)MnO\(_3\) and \((\text{Li}_{0.93}\text{Na}_{0.07})\text{MnO}_3\), the amount \((= \text{multiplicity } \times \text{g})\) of Mn\(^2\) ions in the unit cell was significantly larger than that of Mn\(^1\) ions. Therefore, the absorption wavelength of the spin-forbidden \( ^4\text{A}_2g \rightarrow ^4\text{T}_2g \) transition predominantly depended on the coordination environment at the Mn\(^2\) site. The absorption band attributed to the \( ^4\text{A}_2g \rightarrow ^4\text{T}_2g \) transition shifted to the longer wavelength side with Na\(^+\) doping because the crystal field around the Mn\(^4+\) ion was weakened by the introduction of Na\(^+\), which was larger than Li\(^+\). In fact, the average Mn\(^2\)–O bond distance for the Na\(^+\)-doped sample at \( x = 0.07 \) was longer than that for the undoped sample \( (x = 0) \), as shown in Table 3.

In contrast, the optical absorption bands corresponding to the spin-forbidden \( ^4\text{A}_2g \rightarrow ^2\text{E}^{g,\text{t}}_g,^2\text{T}_{1g} \) transitions appeared more intensely with the increasing Na\(^+\) content, but no peak shift was observed. As already explained for the results in Table 3, the \([\text{Mn}(2)\text{O}_6]_{\text{octahedra}}\) in the lattice were more distorted when some Li\(^+\) ions were substituted with Na\(^+\) ions. Thus, the \( ^4\text{A}_2g \rightarrow ^2\text{E}^{g,\text{t}}_g,^2\text{T}_{1g} \) transitions were partially allowed because of the symmetry reduction caused by the enlargement of distortion. According to the Tanabe–Sugano diagram for d\(^3\) electron configuration, the energy levels of \( ^2\text{E}^{g,\text{t}}_g,^2\text{T}_{1g} \) are hardly affected by the crystal field strength. Therefore, the absorption intensity of the \( ^4\text{A}_2g \rightarrow ^2\text{E}^{g,\text{t}}_g,^2\text{T}_{1g} \) transitions of Mn\(^{4+}\) increased due to the loss of symmetry, but the absorption wavelength hardly depended on the crystal field energy around the Mn\(^{4+}\) ion.

### 2.3. Color Properties.

The \( L^*a^*b^*h^* \) chromatic parameters for the \((\text{Li}_{1-x}\text{Na}_x)\text{MnO}_3 \) \((0 \leq x \leq 0.10)\) samples are summarized in Table 4. The sample photographs are also summarized in Figure 7. The values of the brightness (\( L^* \)), redness (\( a^* \)), and yellowness (\( b^* \)) decreased as the concentration of Na\(^+\) increased. These relationships were attributed to the differences in the absorption wavelengths and the intensities of...
the d–d transitions. As already discussed with respect to the results in Figure 6, the yellow–orange light (580–605 nm) was absorbed because the optical absorption band around 550 nm was shifted to the longer wavelength side by Na+ doping. Additionally, the red-light reflection in the range from 605 to 700 nm was also reduced. As a result, all values of \(L^*\), \(a^*\), and \(b^*\) decreased. However, the hue angle (\(h^\circ\)) became smaller by Na+ doping and the color of the samples changed from orange to deep red.

Among the \((\text{Li}_{1-x}\text{Na}_x)\text{Mn}_2\text{O}_3\) (0 ≤ \(x\) ≤ 0.10) samples obtained in this work, \((\text{Li}_{0.93}\text{Na}_{0.07})\text{Mn}_2\text{O}_3\) exhibited the lowest \(h^\circ\) value, and the sample was, namely, reddish in color.

### 2.4. Chemical Stability and Humidity Resistance Tests

The chemical stability and humidity resistance of \((\text{Li}_{0.93}\text{Na}_{0.07})\text{Mn}_2\text{O}_3\) were also tested using a powder sample. To assess the chemical stability, the sample was soaked in 4% \(\text{CH}_3\text{COOH}\) and 4% \(\text{NH}_4\text{HCO}_3\) aqueous solutions. After leaving them at room temperature for 3 h, the samples were washed with deionized water and ethanol. Finally, the samples were dried at room temperature. The humidity resistance of the \((\text{Li}_{0.93}\text{Na}_{0.07})\text{Mn}_2\text{O}_3\) sample was tested in a thermohygrometer at 90% relative humidity (RH) and 80 °C for 24 h. The sample color after the leaching and humidity resistance tests was evaluated with a calorimeter. Unfortunately, a slight color deterioration was observed after the leaching and humidity resistance tests, as summarized in Table 5. To suppress the color degradation, therefore, it is necessary to cover the surface using an inert substance such as silica.

### 3. CONCLUSIONS

\((\text{Li}_{1-x}\text{Na}_x)\text{Mn}_2\text{O}_3\) (0 ≤ \(x\) ≤ 0.10) samples were synthesized by a solid-state reaction process. The Rietveld analysis of the \((\text{Li}_{1-x}\text{Na}_x)\text{Mn}_2\text{O}_3\) \((x = 0\) and 0.07) samples indicated that the average Mn(2)–O bond distance was increased, and the [Mn(2)O₆] octahedra were distorted by doping Na⁺ into the Li⁺ site. The spin-allowed \(^{4}\text{A}_{2g} \rightarrow ^{4}\text{T}_{2g}\) transition observed at the wavelength shorter than 550 nm shifted to the longer wavelength side due to the decrease of the crystal field strength around Mn⁴⁺. No shift was observed in the spin-forbidden \(^2\text{E}_{g} \rightarrow ^2\text{T}_{1g}\) transitions around 680 nm, but the absorption intensities increased with the increase in the distortion of the [Mn(2)O₆] octahedra. Consequently, the sample color gradually turned from orange to deep red with increasing Na⁺ concentration. This study proposes that the coordination environment around Mn⁴⁺ is one of the important factors to develop environmentally friendly inorganic red pigments containing Mn⁴⁺.

### 4. EXPERIMENTAL SECTION

#### 4.1. Materials and Methods

The \((\text{Li}_{1-x}\text{Na}_x)\text{Mn}_2\text{O}_3\) (0 ≤ \(x\) ≤ 0.10) samples were synthesized by a conventional solid-state reaction technique. Stoichiometric amounts of \(\text{Li}_2\text{CO}_3\), \(\text{Mn}_2\text{O}_3\), and \(\text{Na}_2\text{CO}_3\) were mixed with 5 cm³ of ethanol in an agate mortar to obtain 1 g of the final product. The mixtures were heated at an alumina crucible at 1050 °C for 6 h in the atmosphere. Before characterization, the sample was ground in an agate mortar.

#### 4.2. Characterization

The crystal structure of the samples was identified by X-ray powder diffraction (XRD; Rigaku, Ultima IV) with Cu Kα radiation (40 kV and 40 mA). The data were collected by scanning over the 2θ range of 20–80°, and the sampling width was 0.02°. The lattice volumes of the samples were calculated from the diffraction angles, which were refined using \(\alpha\)-alumina as a standard and CellCalc Ver. 2.20 software. Rietveld refinement of the resulting XRD patterns in the 2θ range of 10–120° was performed by the RIETAN-FP software package to determine the precise crystal structure and investigate the coordination environment around Mn⁴⁺ ions for the \((\text{Li}_{1-x}\text{Na}_x)\text{Mn}_2\text{O}_3\) \((x = 0\) and 0.07) samples. From the Rietveld refinement, the following final R-factors were obtained: weighted pattern R-factor (\(R_w\)), pattern R-factor (\(R_p\)), R-expected factor (\(R_e\)), R-structure factor (\(R_s\)), and goodness-of-fit indicator (\(S\)).

The particle size and morphology of the \(\text{Li}_2\text{Mn}_2\text{O}_3\) and \((\text{Li}_{0.93}\text{Na}_{0.07})\text{Mn}_2\text{O}_3\) samples were observed with a field emission–scanning electron microscope (FE-SEM; JEOL, JSM-6701F). The optical reflectance spectra were measured using an ultraviolet–visible–near-infrared (UV–vis–NIR) spectrometer (JASCO, V-770) with a standard white plate as a reference. The chromatic properties of the samples were estimated in terms of the Commission Internationale de l’Eclairage (CIE) \(L^*a^*b^*\) system using a colorimeter (Konica-Minolta, CR-300). The \(L^*\) parameter expresses the brightness or darkness of a color based on neutral grayscale, and the \(a^*\) (the red–green axis) and \(b^*\) (the yellow–blue axis) parameters indicate the color qualitatively. The value of \(h^\circ\) (hue angle) ranges from 0 to 360° and is calculated with the formula, \(h^\circ = \tan^{-1}(b^*/a^*)\). When \(h^\circ\) is in the region of 0 ≤ \(h^\circ\) ≤ 35, the color of the sample is red.

### Table 4. \(L^*a^*b^*h^\circ\) Chromatic Parameters for the \((\text{Li}_{1-x}\text{Na}_x)\text{Mn}_2\text{O}_3\) (0 ≤ \(x\) ≤ 0.10) Samples

| \(x\) | \(L^*\) | \(a^*\) | \(b^*\) | \(h^\circ\) |
|-------|---------|--------|--------|---------|
| 0.04  | 43.1    | +30.7  | +31.3  | 45.6    |
| 0.06  | 40.7    | +25.3  | +24.3  | 43.8    |
| 0.07  | 38.3    | +24.8  | +20.2  | 39.1    |
| 0.08  | 36.5    | +23.3  | +19.8  | 40.3    |
| 0.10  | 33.0    | +22.1  | +19.0  | 40.7    |

### Table 5. Color Coordinates of \((\text{Li}_{0.93}\text{Na}_{0.07})\text{Mn}_2\text{O}_3\) Before and After the Chemical Stability and the Humidity Resistance Tests

| Treatment | \(L^*\) | \(a^*\) | \(b^*\) | \(h^\circ\) |
|-----------|---------|--------|--------|---------|
| none      | 38.3    | +24.8  | +20.2  | 39.1    |
| 4% \(\text{CH}_3\text{COOH}\) | 35.2    | +21.8  | +16.5  | 37.1    |
| 4% \(\text{NH}_4\text{HCO}_3\) | 38.1    | +23.2  | +17.7  | 37.3    |
| 80 °C, 90%RH | 35.2    | +23.4  | +18.7  | 38.6    |

Figure 7. Photographs of the \((\text{Li}_{1-x}\text{Na}_x)\text{Mn}_2\text{O}_3\) (0 ≤ \(x\) ≤ 0.10) samples.
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Notes
The authors declare no competing financial interest.

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