

Article

Physicochemical Characteristics of the Birnessite and Todorokite Synthesized Using Various Methods

Soyoung Min and Yeongkyoo Kim *

School of Earth System Sciences, Kyungpook National University, Daegu 41566, Korea; soyoung9207@knu.ac.kr

* Correspondence: ygkim@knu.ac.kr; Tel.: +82-53-950-5360

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Abstract: The synthesis methods used to produce todorokite (10 Å manganate, OMS-1) and birnessite (7 Å manganate), which are abundant in marine manganese nodules, have been studied to confirm whether pure mineral phases can be obtained and to compare their physicochemical characteristics. The physicochemical characteristics of todorokite and its precursor Na–birnessite can vary widely based on the precursors used during their synthesis. Birnessite can be synthesized via three mechanisms, i.e., the oxidation of Mn^{2+} , a redox reaction between Mn^{2+} and MnO_4^- , or the reduction of MnO_4^- . Herein, four precursors are used to synthesize birnessite using different methods before being transformed into todorokite. The characteristics of the birnessite and todorokite synthesized using different methods are investigated via X-ray diffraction (XRD), chemical analysis, Brunauer–Emmett–Teller (BET), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), and field emission scanning electron microscopy (SEM). Based on the method used, birnessite and todorokite exhibit distinct physicochemical features, including crystallinity, crystal structure, specific surface area, oxidation state of manganese, thermal stability, and morphology. Thus, the characteristics of birnessite and todorokite are closely correlated, indicating the importance of designing suitable methods to synthesize them for specific applications.

Keywords: manganese oxides; birnessite; todorokite; synthesis mechanism; characterization

1. Introduction

Manganese oxides can be observed in different natural forms, including manganese nodules, layers in sediments [1–3], hydrothermal alteration products [4], or rock varnish forms [5,6]. These minerals have also been observed abundantly in engineered systems and polluted environments worldwide, including the acid-mine-drainage (AMD)-polluted streams [7–9]. Majority of the manganese oxide minerals are brown–black and typically occur as intimately intermixed, fine-grained, poorly crystalline masses or coatings [10]. According to Burns and Burns [11], the marine manganese nodules primarily comprise manganese oxides such as birnessite (7 Å manganate), todorokite (10 Å manganate, octahedral molecular sieve (OMS)-1), and vernadite. Birnessite is abundant in soil and an important precursor of todorokite [12–18]. The MnO_6 octahedrons with manganese ions in the $\text{Mn}^{3+,4+}$ oxidation state (Figure 1) share edges and form layers in birnessite [10]. Birnessite is a layered structural mineral with hydrated cations between the layers [19–23]. The hydrated cations between the layers compensate for the layer charges of the low-oxidation-state manganese ions and the octahedral-layer vacancies [11,24–26]. Hydrated Na^+ exists as a single layer between the manganese octahedron layers in birnessite with a d-spacing of ~ 7 Å. Buserite is a layered manganese oxide with hydrated Mg^{2+} between the layers; this is obtained by an ion exchange reaction that increases the d-spacing to 10 Å. Todorokite can be obtained via low-temperature heat treatment of buserite. Todorokite is a microporous material with a one-dimensional tunnel structure, having 3×3 ($6.9 \text{ Å} \times 6.9 \text{ Å}$) arrays of edge-shared MnO_6 octahedra (Figure 1) [12–14,27].

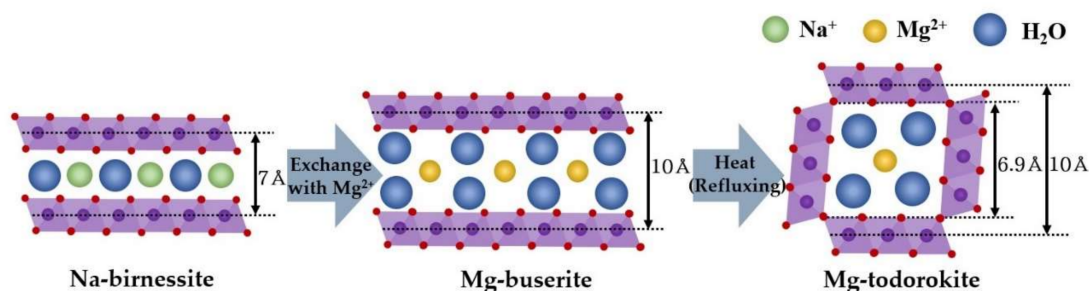


Figure 1. Synthesis procedure of Mg-todorokite and its structure.

Birnessite and todorokite have various industrial and commercial applications. Birnessite is a good ion exchanger and can play an important role in controlling heavy metals and other trace metals in soil and groundwater [10,28]. Several heavy metals and toxic trace elements from the AMD-affected streams and soils can be observed in birnessite and todorokite [9]. In addition, ion-trapping properties of birnessite make it a potential negative electrode material for rechargeable lithium batteries [29–31]; further, it can be used as a heterogeneous catalyst [32–34]. Todorokite has the same ion exchange properties as those of zeolite with a molecular sieve because of its large tunnel size [13,35]. Therefore, todorokite has been used as an ion exchanger [14,36–38], electrode material for rechargeable batteries [20–22,39–42], and oxidation–reduction catalyst [13,14,32,43–47].

In nature, birnessite exhibits low crystallinity and contains considerable amounts of other mineral phases as impurities. Therefore, several synthesis methods have been explored to obtain pure-phase minerals. Birnessite can be synthesized via three mechanisms in highly basic media for obtaining high-crystallinity products in a laboratory: oxidation of Mn^{2+} , redox reactions between Mn^{2+} and MnO_4^- , and the reduction of MnO_4^- [48]. These mechanisms have been used to study the impact of various synthesis conditions, such as the type of oxidant (O_2 gas, H_2O_2) [19,24,49–51], reductant (HCl, alcohol, glucose, glycol, maleic acid, etc.) [19,52–55], base concentration [56], and temperature [56,57], on the physical properties of birnessite. Other synthesis methods have also been reported including sol-gel and electrochemical processes [20,23,58–61]. However, single-phase manganese oxides are difficult to obtain because of their nonstoichiometric compositions [62].

Therefore, the crystalline quality of synthetic todorokite is considerably dependent on that of the original birnessite [57]. The different physicochemical properties of birnessite are highly related to the specific surface area and average oxidation number, both of which vary based on the synthesis conditions [63]. The various methods used to synthesize single-phase high-purity manganese oxide have been studied to understand the natural formation process, crystal structure, and chemical composition of todorokite and its suitability for various applications [49–51,64–73].

The physicochemical properties of the produced todorokite are dependent on the heat treatment method used during the synthesis, i.e., autoclave, microwave, or refluxing. Todorokite was initially synthesized by Golden et al. [12] by autoclaving birnessite with a Mg^{2+} -exchanged precursor. The todorokite synthesized by microwave heating is more stable and exhibits superior crystallinity and catalytic properties when compared with those exhibited by the autoclave-synthesized todorokite [73,74]. Feng et al. [68,75] synthesized todorokite under refluxing conditions at atmospheric pressure, resulting in a material with characteristics considerably similar to those of the natural samples formed by hydrothermal processes. In this study, we select the refluxing process as the heat treatment because it is the most similar condition when compared with the natural formation conditions of todorokite.

Manganese oxide exhibits high adsorption and scavenging capacity with respect to heavy metals and other trace elements in soil and hydrological environments [76,77]. Clearfield [78] determined that the microporous inorganic compound crystals with a layered and tunnel structure, including birnessite and todorokite, exhibited excellent selectivity and capacity as an adsorbent for specific monovalent and divalent cations. Several studies have investigated the utility of birnessite and todorokite as adsorbents for geochemically hazardous materials [50,62,79–93].

Various studies have investigated the adsorption characteristics of birnessite and todorokite synthesized via conventional synthetic means. However, none of these studies have systematically focused on their physical properties and the differences in birnessite formed using different synthetic methods as well as todorokite based on the different properties of birnessite. In this study, birnessite is synthesized via four types of previously reported methods: oxidation reaction (Oxi-BIR), redox reaction (Rdx-BIR), redox reaction with Mg^{2+} doped (Rdx_{Mg} -BIR), and reduction reaction (Red-BIR). Each sample was compared based on X-ray diffraction (XRD), chemical analysis, Brunauer–Emmett–Teller (BET), thermogravimetric analysis (TGA), infrared (IR) spectroscopy, field emission scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS). Furthermore, the physicochemical characteristics of the todorokite synthesized from the investigated birnessite are studied and compared using the same analysis methods. The two sets of results are correlated to obtain design principles for various mineral applications.

2. Materials and Methods

2.1. Na–Birnessite Synthesis (Precursor Preparation)

2.1.1. Oxidation Method

It is difficult to control the purging velocity of gaseous oxygen, which is a critical parameter associated with the synthesis of a pure product [94,95]. Herein, a relatively easy-to-control hydrogen peroxide oxidant, i.e., (Oxi-BIR), was used to obtain pure birnessite. We added 1000 mL of a mixed solution containing 3% hydrogen peroxide (Sigma-Aldrich, Darmstadt, Germany) and 0.6 M NaOH (Duksan, Seoul, Korea) to 500 mL of 0.3 M MnCl_2 (Sigma-Aldrich) and stirred it using a magnetic stir bar. After stirring for 1 h, the solution was aged at room temperature for 24 h (Oxi-BIR) [51].

2.1.2. Redox Reaction Method

Two of the previously reported synthesis methods that use a redox mechanism were selected to investigate the dependence of the birnessite on Mg^{2+} doping. (Rdx-BIR) and (Rdx_{Mg} -BIR) are birnessites produced via redox reactions occurring between Mn^{2+} and MnO_4^- .

- Mg-free Na–birnessite

A 125 mL aqueous solution with 44 g NaOH (Duksan) was poured into a 125 mL solution of 9.516 g MnCl_2 (Sigma-Aldrich) under magnetic stirring to precipitate $\text{Mn}(\text{OH})_2$ (pyrochroite) as a pale-pink gel. Then, KMnO_4 aqueous solution prepared by dissolving 3.982 g of KMnO_4 (Sigma-Aldrich) in 250 mL of distilled water, and this solution was gradually and entirely added to the above suspension. This final suspension was stirred for 30 min and maintained at 60 °C for 12 h. A dark-gray precipitate was obtained using this method (Rdx-BIR) [68].

- Mg-doped Na–birnessite

A solution was prepared by adding 13.5 g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (Sinyo Pure Chemicals, Tokyo, Japan) and 1.926 g of MgSO_4 (Sigma-Aldrich) to 160 mL of distilled water. This solution was gradually added into 180 mL of distilled water and 40 g of NaOH (Duksan) under vigorous stirring, and a pink gel-based precipitate of $\text{Mn}(\text{OH})_2$ was obtained. An aqueous solution containing 5.1 g KMnO_4 (Sigma-Aldrich) dissolved in 160 mL of distilled deionized water was slowly added to the gel-form mixed solution under fast stirring conditions. The resulting black MnO suspension was aged at 65 °C for 100 h (Rdx_{Mg} -BIR) [57].

2.1.3. Reduction Method

This differs from the previously reported K–birnessite synthesis method. In this study, NaMnO_4 (Sigma-Aldrich) was replaced with KMnO_4 to prepare Na–birnessite. Then, 300 mL of a 0.316 M

NaMnO₄ aqueous solution was mixed with 300 mL of 0.3 M of NaOH (Duksan), 100 mL of ethanol (Samchun, Seoul, Korea), and 100 mL of distilled water. The mixture was stirred for an additional 30 min and aged at 60 °C for 20 days (Red-BIR) [55].

2.2. Na–Birnessite to Mg–Buserite via the Ion Exchange Process

A buserite structure with double water layers is required to achieve hydrothermal transformation of birnessite to todorokite. It can be obtained via ion exchange for divalent cations and birnessite intercalation. Therefore, after synthesis and vacuum filtration, the Na–birnessite in the wet-state cake was dispersed in 1 L of an aqueous 1 M MgCl₂·6H₂O (Sigma-Aldrich) solution and stirred at 300 rpm for 24 h. After the ion exchange process, the supernatant was separated via vacuum membrane filtration. This ion exchange treatment was repeated thrice to ensure complete exchange of Mg²⁺. Thus, birnessite with a single water layer was converted to a buserite structure with double water layers and used as a todorokite precursor.

2.3. Todorokite Synthesis (Hydrothermal Treatment)

After the ion exchange process, the samples were dispersed in 1 L of tertiary distilled water and subjected to vacuum filtration thrice to eliminate the unnecessary Mg²⁺. Buserite was dispersed in 300 mL of distilled water, transferred to a 500-mL flask for reflux, and heated to 100 °C on a heating plate for 72 h while stirring. After hydrothermal treatment, manganese oxide was cooled to room temperature and lyophilized for at least three days after vacuum filtration with a 0.2-μm membrane filter to completely eliminate moisture. In this study, the dried sample was powdered using an agate mortar, and a standard sieve No. 45 (355 μm) was used to ensure uniform particle size. Furthermore, the four samples are referred to as (Oxi-TOD), (Rdx-TOD), (Rdx_{Mg}-TOD), and (Red-TOD).

2.4. Characterization

Powder XRD (D/Max-2500, Rigaku, Tokyo, Japan) analysis was used to characterize the synthesis products based on the data obtained when $2\theta = 5^\circ$ to 90° with steps of $2\theta = 0.02^\circ$, counting time of 1 s per step, and Ni-filtered Cu-K α radiation at 40 kV and 30 mA.

The powdered sample (50 mg) was added to 20 mL of tertiary distilled water, in which 1 mL of concentrated HNO₃ and 2 mL of 30% H₂O₂ were added, to obtain chemical compositions of the synthesized manganese oxides. The solution was boiled for 2–5 min, the remaining hydrogen peroxide evaporated, and the final sample was diluted to 100 mL. The concentrations of Mn, Na, K, and Mg were measured using an inductively coupled plasma-atomic emission spectrometer (Optima 7300DV, Perkin Elmer, Waltham, MA, USA). The content of water molecules was estimated based on the mass loss at temperatures of 30–400 °C via thermogravimetric analysis.

The specific surface area of the synthesized samples was measured via BET method using Autosorb iQ and Quadrasorb SI (Quantachrome, Boynton Beach, FL, USA). The pretreatment temperature was 77 K, and N₂ degassing was performed at 150 °C at a pressure of 10^{−5} Torr for 12 h.

The oxidation state of manganese with respect to the samples was determined via XPS (NEXSA, ThermoFisher, Waltham, MA, USA) using the monochromatic X-ray source of Al-K α (1486.6 eV), and vacuum was maintained at a pressure of 5×10^{-9} mbar or less. The survey scans were recorded using a spot size of 400 μm and an energy resolution of 0.1 eV. The oxidation state of manganese was identified based on the binding energy spectra of Mn3s and Mn2p_{3/2} compared with those reported previously [96–101].

The thermal behavior of the synthesized manganese oxides was investigated using thermogravimetric scanning calorimetry (Thermal Analyzer System, TGA-DSC, Q600, TA Instruments, New Castle, DE, USA). The samples were heated under an airflow rate of 20 mL/min and a heating rate of 10 °C/min. The measurement temperature ranged from room temperature to 800 °C.

The difference in molecular vibration or rotation because of the irradiation observed on various products using infrared rays was investigated using infrared spectroscopy (FT-IR/NIR

Spectrophotometer, Frontier, Perkin Elmer, Waltham, MA, USA). The analysis was conducted using KBr as the beamsplitter at wavelengths of 4000–500 cm^{-1} , and the differences in the Mn–O bonds, H_2O bending, and H_2O stretching bonds were observed.

Further, the morphological features of birnessite and todorokite were investigated using SEM (SU8220, Hitachi, Tokyo, Japan). The powdered sample was fixed to a holder with a carbon tape. Then, the sample was coated with platinum, and photographs were taken at an acceleration voltage of 5 kV.

3. Results and Discussion

3.1. XRD Features

The XRD patterns of the four birnessite samples synthesized through different methods are presented in Figure 2a. All samples contained birnessite (001) and (002) peaks, indicating that birnessite was formed using all methods used herein. However, birnessite synthesized by the previous redox methods, (Rdx-BIR) and (Rdx_{Mg} -BIR), contained an intermediate feitknechtite phase known as $\beta\text{-MnOOH}$ at $\sim 19.5^\circ$ [57]. Birnessite is stable under the synthesis conditions, whereas feitknechtite is only metastable [57]. In our experiment, the other two samples did not exhibit feitknechtite peak, indicating that pure-phase birnessite was synthesized for (Oxi-BIR) and (Red-BIR) and their XRD peaks indexed well with reference spectrum (Table 1).

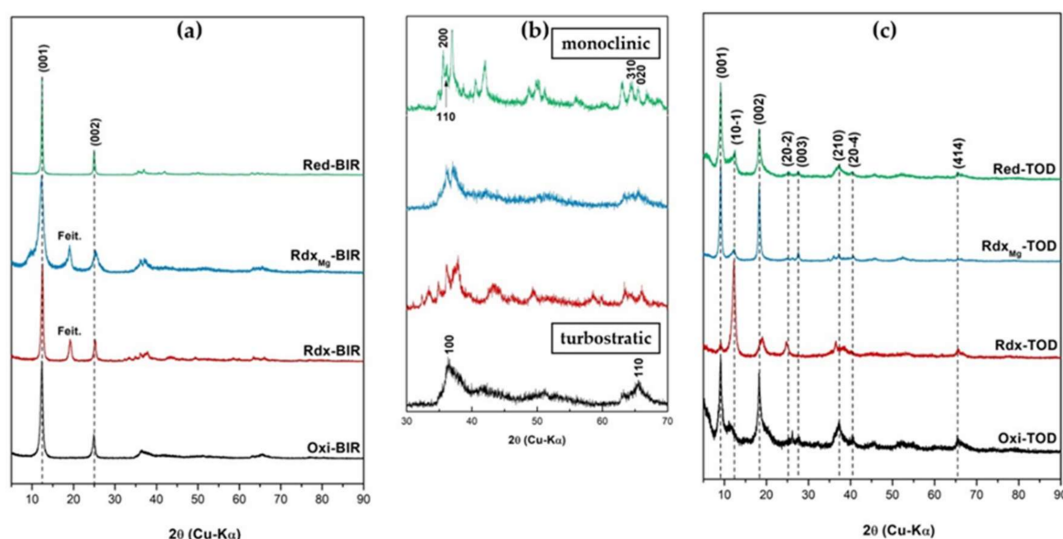


Figure 2. X-ray diffraction (XRD) patterns of birnessite (a) synthesized through the oxidation ((Oxi-BIR)), redox ((Rdx-BIR), (Rdx_{Mg} -BIR)), and reduction ((Red-BIR)) methods. The peaks of birnessite between 30° and 70° are separately shown (b). The todorokite (c) synthesized using each precursor ((Oxi-TOD), (Rdx-TOD), (Rdx_{Mg} -TOD), and (Red-TOD)). The XRD patterns (a,c) are scaled by converting to the highest intensity value of 100.

A wide peak can be observed at $\sim 9.5^\circ$ in the XRD patterns of (Rdx_{Mg} -BIR), which likely originated from the partially present busenite structure; in this case, the Mg^{2+} ions were incorporated from the reaction solution. The XRD patterns of (Rdx-BIR) showed narrow and sharp peaks, whereas those of (Rdx_{Mg} -BIR) showed wider peaks, potentially because of the disorder observed in case of the displaced layered structure due to the substantial size difference of the hydrated Mg^{2+} and Na^+ ions bound between the birnessite layers.

The (Oxi-BIR) synthesized at room temperature showed a single wide peak between 35° and 40° ; however, the remaining samples, (Rdx-BIR), (Rdx_{Mg} -BIR), and (Red-BIR), aged at higher temperatures clearly had two or more peaks (Figure 2b). (Red-BIR), which had the longest aging period of 20 days,

showed several peaks even at angles greater than 40° . Further, the crystal structure of birnessite can be determined based on the pairs of XRD peaks shown in Figure 2b. Drits et al. [102] explained the crystal structure of birnessite based on the XRD analysis conducted when $2\theta = 30\text{--}70^\circ$. The birnessite with a turbostratic structure shows (00 l) reflections and only two 2D diffraction patterns corresponding to the (100) and (110) planes with $d_{100} = 2.42 \text{ \AA}$ and $d_{110} = 1.42 \text{ \AA}$, respectively [102]. The described diffraction features were confirmed using the pattern of (Oxi-BIR) observed in this study. The monoclinic structure showed diffraction pairs of (200), (110) and (310), (020) with d-spacing values of 2.52 ± 0.01 , 2.48 ± 0.01 , 1.445 ± 0.005 , and $1.423 \pm 0.005 \text{ \AA}$, respectively [102], which was confirmed using (Red-BIR) in this study. (Rdx-BIR) and (Rdx_{Mg}-BIR) did not completely match with any previously reported structure; the former showed an approximately monoclinic structure, whereas the latter showed XRD features associated with the turbostratic structure. Our XRD results showed that birnessite samples with different subcell structure characteristics were obtained using different synthesis methods.

Table 1. XRD data for the synthesized birnessite and todorokite with respect to the reference data.

Oxi-BIR			Rdx-BIR			Rdx _{Mg} -BIR			Red-BIR			Birnessite [103]		
2 θ	d/ $\text{\AA}$	I (%)	2 θ	d/ $\text{\AA}$	I (%)	2 θ	d/ $\text{\AA}$	I (%)	2 θ	d/ $\text{\AA}$	I (%)	hkl	d/ $\text{\AA}$	I (%)
12.4	7.14	100.0	12.4	7.12	100.0	12.3	7.18	100.0	12.4	7.14	100.0	001	7.14	100.0
24.9	3.57	24.5	19.2	4.62	21.5	19.0	4.67	22.6	24.9	3.57	25.2	002	3.57	25.3
36.2	2.48	3.41	25.0	3.55	23.1	25.2	3.54	15.5	35.6	2.52	3.52	011	2.52	9.0
51.2	1.78	0.77	33.4	2.68	2.01	36.1	2.48	9.56	36.2	2.48	2.03	100	2.48	1.5
63.1	1.47	1.19	36.1	2.49	7.27	37.0	2.43	8.95	36.9	2.43	4.75	110	2.43	6.7
65.5	1.42	2.67	37.9	2.37	5.78	63.3	1.47	2.91	42.0	2.15	2.18	003	2.37	0.5
80.6	1.20	0.32	42.0	2.15	1.72	65.6	1.42	3.50	62.9	1.47	1.69	102	2.14	5.9
			49.6	1.84	2.48	76.9	1.24	0.83	64.5	1.44	1.47	121	1.47	1.8
Oxi-TOD			Rdx-TOD			Rdx _{Mg} -TOD			Red-TOD			Natural Todorokite [35]		
2 θ	d/ $\text{\AA}$	I (%)	2 θ	d/ $\text{\AA}$	I (%)	2 θ	d/ $\text{\AA}$	I (%)	2 θ	d/ $\text{\AA}$	I (%)	hkl *	d/ $\text{\AA}$	I (%)
9.12	9.69	100.0	9.08	9.73	8.03	9.15	9.66	100.0	9.08	9.73	100.0	001	9.76	100.0
18.25	4.86	77.26	12.23	7.23	100.0	12.38	7.14	8.16	12.52	7.06	17.42	10 $\bar{1}$	7.05	29.9
26.17	3.40	14.41	19.07	4.65	16.78	18.29	4.85	81.01	18.26	4.86	52.80	002	4.88	9.4
27.57	3.23	7.69	24.74	3.59	13.31	27.49	3.24	7.93	25.30	3.52	4.25	20 $\bar{2}$	3.52	3.2
37.19	2.42	24.44	36.51	2.46	11.83	36.00	2.49	4.13	36.43	2.46	6.71	003	3.25	0.8
40.66	2.22	6.20	38.40	2.34	5.09	37.20	2.41	4.56	37.26	2.41	10.30	210	2.43	7.3
45.55	1.99	4.20	65.69	1.42	5.77	40.63	2.22	3.37	40.44	2.23	3.10	20 $\bar{4}$	2.23	0.0
65.48	1.42	9.48	77.56	1.23	0.93	65.55	1.42	1.96	65.46	1.42	3.81	414	1.42	0.0

* Miller index.

The XRD patterns in Figure 2c are the products of thermal treatment of (Oxi-BIR), (Rdx-BIR), (Rdx_{Mg}-BIR), and (Red-BIR), which contained primary XRD peaks similar to those of the two natural samples obtained from Cuba and South Africa, characterized via Rietveld refinement of the X-ray data by Post and Bish [35]. However, (Rdx-TOD) showed the lowest (001) peak intensity (Table 1) and reversed relative intensities of the peaks at (001) and (002). This is probably because (Rdx-BIR) may be more difficult to transform to todorokite than other samples. The two peaks of (Rdx-TOD) (7.23 $\text{\AA}$) and (Rdx_{Mg}-TOD) (7.14 $\text{\AA}$) were slightly different from the (10 $\bar{1}$) peak (7.05 $\text{\AA}$) of the natural sample data and appeared to be closer to the (001) peak of birnessite (7.14 $\text{\AA}$), suggesting that birnessite may not be completely converted to todorokite. The XRD peaks of (Red-TOD) were considerably similar to those of the natural todorokite sample. (Oxi-TOD) exhibited a wide and weak peak at $\sim 11^\circ$, which was also observed by Atkins et al. [104] in case of the todorokite samples having long hydrothermal process time (more than 72 h). Our results also showed that different forms of todorokite were synthesized based on different precursor synthesis mechanisms or conditions.

3.2. Chemical Analysis

Table 2 presents the mineral formulas of the synthesized samples based on the chemical data obtained in this study. (Red-BIR) had the highest Na content, which can be related to its high crystallinity as reported by Liu et al. [70]. The Mg content of todorokite was almost similar to those of the (Oxi-TOD) and (Red-TOD) samples. (Rdx-TOD) had the lowest Mg content, probably hindering the phase

change. This may be attributed to the insufficient exchange of the Mg^{2+} ion in the birnessite interlayer. In addition, the water content of todorokite tended to increase after birnessite phase change.

Table 2. Chemical composition, specific surface area, and X-ray photoelectron spectroscopy (XPS) results of the synthesized manganese oxides.

Sample	Chemical Composition	BET (m^2/g)	Bes ($\text{Mn}2p_{3/2}$, eV)	Bes ($\text{Mn}3s$, eV)
Oxi-BIR	$\text{Na}_{0.91}\text{Mn}_6\text{O}_{12}\cdot 4.54\text{H}_2\text{O}$	80	642.1	4.5
Oxi-TOD	$\text{Na}_{0.27}\text{Mg}_{0.62}\text{Mn}_6\text{O}_{12}\cdot 5.07\text{H}_2\text{O}$	185	641.9	4.5
Rdx-BIR	$\text{Na}_{0.4}\text{K}_{0.02}\text{Mn}_6\text{O}_{12}\cdot 2.67\text{H}_2\text{O}$	52	641.8	5.1
Rdx-TOD	$\text{Na}_{0.08}\text{K}_{0.03}\text{Mg}_{0.23}\text{Mn}_6\text{O}_{12}\cdot 4.31\text{H}_2\text{O}$	146	641.8	4.9
Rdx_{Mg} -BIR	$\text{Na}_{0.36}\text{K}_{0.06}\text{Mg}_{1.04}\text{Mn}_6\text{O}_{12}\cdot 4.44\text{H}_2\text{O}$	67	642.1	4.5
Rdx_{Mg} -TOD	$\text{Na}_{0.11}\text{K}_{0.04}\text{Mg}_{0.73}\text{Mn}_6\text{O}_{12}\cdot 5.24\text{H}_2\text{O}$	95	642.0	4.2
Red-BIR	$\text{Na}_{1.5}\text{Mg}_{0.62}\text{Mn}_6\text{O}_{12}\cdot 3.99\text{H}_2\text{O}$	76	642.4	4.4
Red-TOD	$\text{Na}_{0.39}\text{Mg}_{0.62}\text{Mn}_6\text{O}_{12}\cdot 4.77\text{H}_2\text{O}$	153	642.0	4.8

3.3. Specific Surface Area

The BET results showed that the specific surface area of birnessite was 52–80 m^2/g and that of todorokite was 95–185 m^2/g (Table 2), indicating that the surface area of birnessite and todorokite may vary based on the synthesis method. The specific surface area of todorokite was more diverse than that of birnessite based on the synthesis methods. The surface areas of all tunnel structures increased when compared with those of the layered precursors. The ratios of the increase in specific surface area increases were approximately (Oxi) = 2.3, (Rdx) = 2.7, (Rdx_{Mg}) = 1.4, and (Red) = 2.

3.4. XPS

The binding energies (BEs) calculated from XPS data were compared with those obtained in previous studies in which pure chemical reagents were used for determining the oxidation states of manganese in our samples. The BEs of MnO (+2), Mn_3O_4 (+2.7), Mn_2O_3 (+3), and MnO_2 (+4) for $\text{Mn}2p_{3/2}$ were 641.0, 641.4, 641.8, and 642.2 eV, respectively [96–99,105]. Based on our results, the BE was 641.8–642.4 eV (Table 2), indicating that the oxidation states were approximately between +3 and +4. However, there can be an error when determining the oxidation state of manganese based only on the BE of $\text{Mn}2p_{3/2}$ [106–108]. Therefore, we used the interval of two peaks and the spectra of $\text{Mn}3s$ binding energy [97,99,100]. The interval of two peaks of several manganese oxides were MnO (+2) = 5.8 eV, Mn_3O_4 (+2.7) = 5.6 eV, Mn_2O_3 (+3) = 5.4 eV, MnO_2 (+4) = 4.6 eV [96,97,99,105,107]. The XPS results showed values of 4.2–5.1 eV (Table 2), which are similar to the results obtained in case of $\text{Mn}2p_{3/2}$, indicating that the oxidation states of our samples were between +3 and +4.

3.5. TGA

Figure 3 presents the results of TGA. The TGA curves provided the characteristic thermal behaviors of birnessite and todorokite with the increasing temperature. The decrease in TGA curve can be interpreted as decomposition, evaporation, reduction, and/or desorption. The four samples exhibited similar temperature ranges at which drastic mass decrease could be observed (from room temperature to 200 °C and between 600 °C and 700 °C). The initial weight loss of birnessite below 100 °C can be attributed to the evaporation of the surface-adsorbed water, whereas that near 150 °C can be attributed to the dehydration of interlayer water [109]. Parant et al. [110] reported the layered structure was partially transformed to an $\text{Na}_{0.4}\text{MnO}_2$ romanechite phase with a (2 × 3) tunnel structure after heating to 500 °C, which causes additional weight loss in birnessite. Except for (Red-BIR) with high crystallinity, the remaining birnessite samples tended to continue losing weight until the end of the temperature range. This result is in agreement with that obtained by the chemical analysis of (Red-BIR) and its Na content.

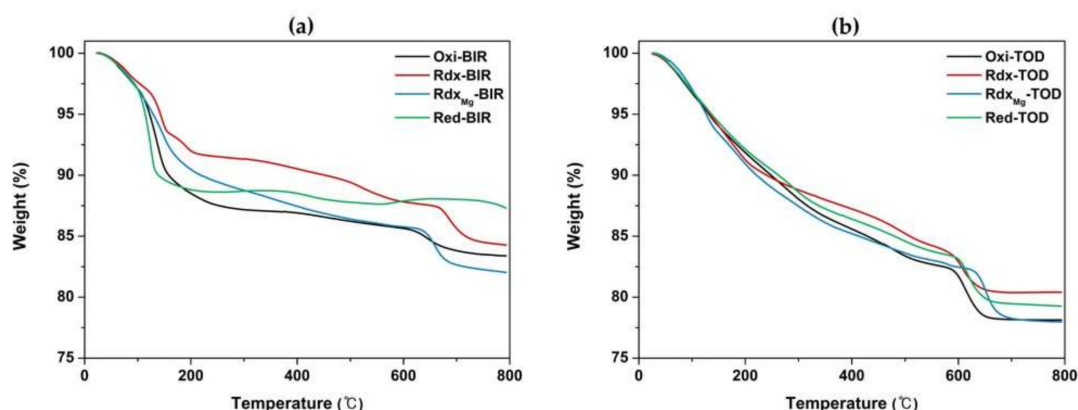


Figure 3. Thermogravimetric analysis (TGA) curve for the synthesized birnessite (a) and todorokite (b).

Further, the TG results for todorokite showed that the mass decreased steadily from the starting temperature to ~ 600 °C and then decreased rapidly. The weight loss observed in case of todorokite at 50–150 °C can be attributed to the loss of water physically adsorbed on the surface and that at 105–240 °C to the one bound in the tunnel [111,112]. Finally, the loss of water at 240–700 °C can be attributed to the decomposition of todorokite and oxygen evolution upon heating with a sudden weight loss at 630 °C, indicating the collapse of the tunnel structure owing to significant structural phase transition [13,111]. In our samples, the mass loss patterns indicated that the thermal behaviors of birnessite and todorokite differed based on their synthesis method and precursors.

3.6. IR Spectroscopy

The IR spectra of the manganese oxides synthesized in this study are shown in Figure 4. Generally, the wide band at $2800\text{--}3600\text{ cm}^{-1}$ and that near 1600 cm^{-1} can be attributed to the reflecting νOH vibration (stretching) and δOH vibration (bending) of water molecules [113]. The bands at $\sim 3435\text{ cm}^{-1}$ that can be attributed to the water molecules of birnessite were stronger than those of todorokite caused by the adsorption of interlayer hydrates. The bands appearing at $400\text{--}800\text{ cm}^{-1}$ in IR spectroscopy for birnessite reflected the properties of the Mn–O stretching vibrations. In particular, the IR absorptions observed at approximately 460 cm^{-1} and 510 cm^{-1} are indicators of the birnessite structure [71]. Owing to the absence of the 510 cm^{-1} band in todorokite samples, the possibility of birnessite remaining in the todorokite samples after the thermal process, as discussed in the XRD results, can be eliminated. As a spectral feature of todorokite, the bands observed at approximately $764\text{--}765$, $630\text{--}601$, and $523\text{--}506\text{ cm}^{-1}$ with their narrow ranges reflect the lattice vibrations of the $\text{Mn}^{\text{IV}}\text{--O}$ and $\text{Mn}^{\text{III}}\text{--O}$ bonds [43,114]. The bands in the range of $748\text{--}764\text{ cm}^{-1}$ are the characteristic bands of tunnel-structured manganese oxide and cannot be observed in layered manganese oxide (Figure 4), indicating that our samples clearly reflect the layer and tunnel structures.

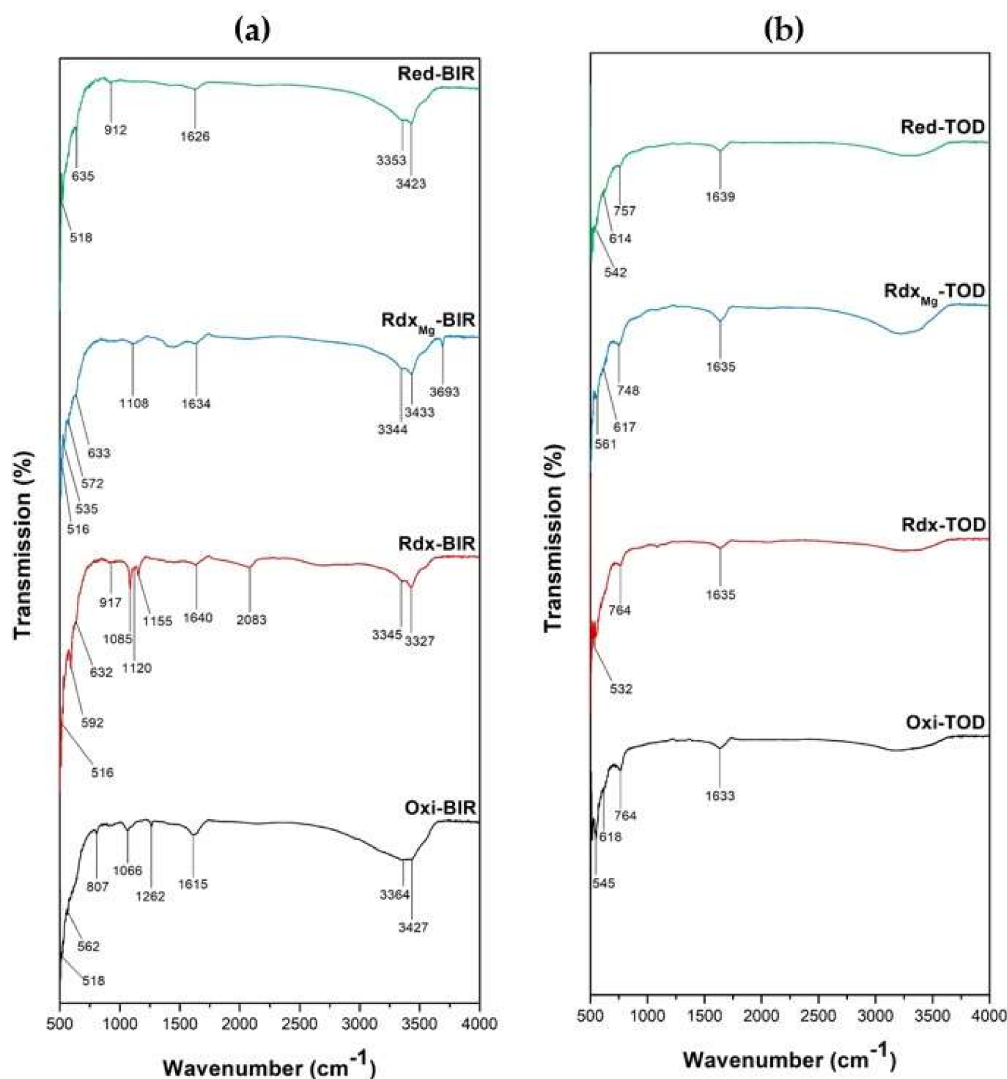


Figure 4. Infrared (IR) spectra of the synthetic manganese oxides: birnessite (a) and todorokite (b).

3.7. SEM Images

The images in Figure 5 indicate that birnessite and todorokite were synthesized with distinct crystal morphologies. Although the crystal size and detailed morphology are slightly different, birnessite generally showed an irregular and plate-like morphology, whereas todorokite exhibited a fibrous or thin acicular morphology (Figure 5). For birnessite, acicular particles with lengths of less than 1 μm were also observed with larger particles for (Rdx-BIR) (Figure 5f). (Rdx_{Mg}-BIR) also showed that thin lines were irregularly entangled to form the particle surface (Figure 5i,j), which was clearly different from those of the remaining birnessite samples. (Red-BIR) showed hexagonal particles with crystal edges (Figure 5n), which were also different from other birnessite samples. In case of (Red-BIR) with the largest crystal size, the TGA and chemical analysis results indicated that it exhibited the highest crystallinity, which may be related to its large particle size.

The morphology of todorokite samples was different from that of precursors, and although they have similar features with acicular or fibrous shapes, their length and aggregate patterns were different from each other. Unlike other samples, the corners of (Red-TOD) exhibited spiky crystal growth in the hexagonal plate-like crystal (Figure 5p).

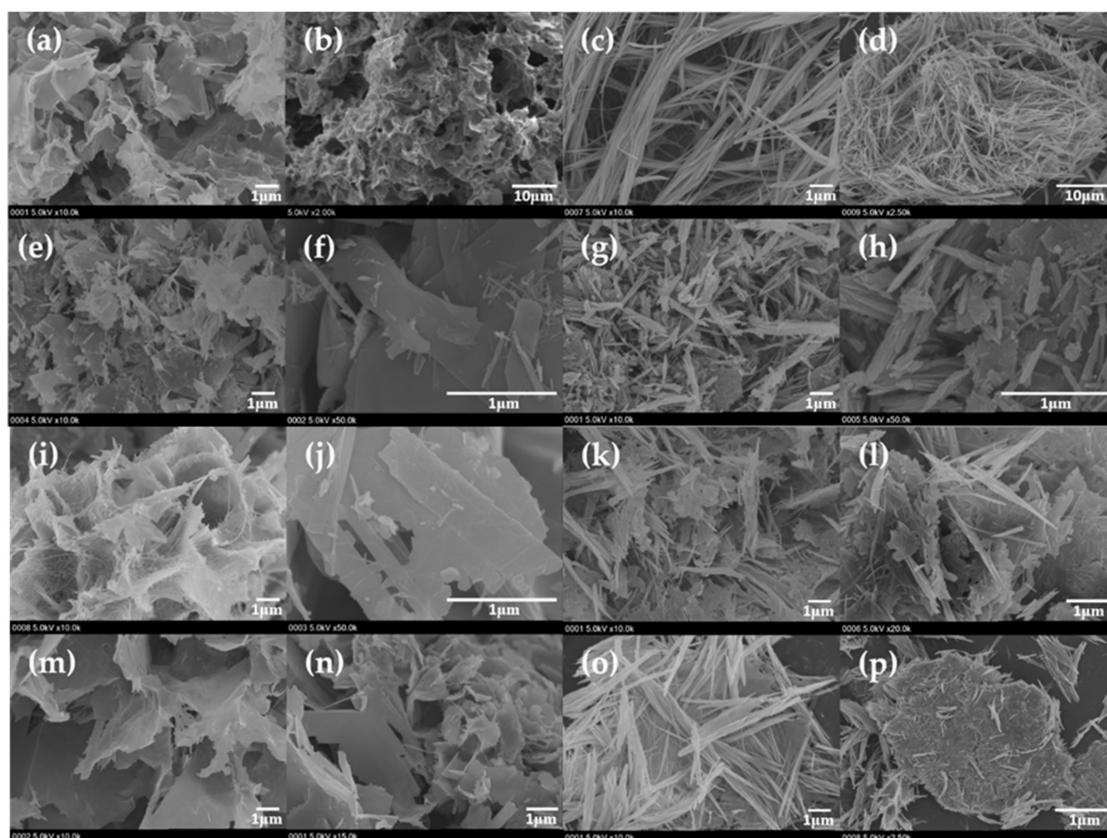


Figure 5. Scanning electron microscopy (SEM) images of the powdered manganese oxide minerals synthesized in the laboratory: (a) Oxi-BIR ($\times 10,000$), (b) Oxi-BIR ($\times 2000$), (c) Oxi-TOD ($\times 10,000$), (d) Oxi-TOD ($\times 2500$), (e) Rdx-BIR ($\times 10,000$), (f) Rdx-BIR ($\times 50,000$), (g) Rdx-TOD ($\times 10,000$), (h) Rdx-TOD ($\times 50,000$), (i) Rdx_{Mg}-BIR ($\times 10,000$), (j) Rdx_{Mg}-BIR ($\times 100,000$), (k) Rdx_{Mg}-TOD ($\times 10,000$), (l) Rdx_{Mg}-TOD ($\times 20,000$), (m) Red-BIR ($\times 10,000$), (n) Red-BIR ($\times 15,000$), (o) Red-TOD ($\times 10,000$), and (p) Red-TOD ($\times 2500$).

Our results showed that the morphologies of birnessite and todorokite varied based on their synthesis mechanism. The morphology of birnessite synthesized through the oxidation (Oxi-BIR) and reduction (Red-BIR) reactions was similar to those of the previously studied products [48]. However, the birnessite synthesized via a redox reaction was slightly different from that reported previously. Our product (Rdx-BIR) contained parallelogram plates, whereas (Rdx_{Mg}-BIR) had plates with thin lines and pseudohexagonal particles. In previous studies, the todorokite that was subjected to heat treatment at low temperatures had an acicular-shaped crystal pattern with an elongated plate-like matrix [43,64,104]. Under the same magnification ($\times 10,000$), the (Oxi-TOD) sample was the longest and contained only acicular particles [115], which is different from other todorokite samples showing similar morphological features observed in previous studies. Our results clearly showed that the morphological features of birnessite differed depending on the used synthesis method and conditions, which further affected todorokite.

3.8. Characteristics of Birnessite and Todorokite

The XRD results showed that the birnessite synthesized by different methods and converted into todorokite exhibited different characteristics. Further, it occasionally contained impurities, such as feitknechtite, depending on their synthesis method. Single-phase birnessite could be obtained via the oxidation and reduction methods. However, the redox reaction method produced a mixed-phase system that included a metastable intermediate phase of feitknechtite, which could be eliminated by

increasing the aging time. In case of todorokite, XRD analysis confirmed that their formation was affected by the characteristics of the starting birnessite; however, some features could not be evaluated based on XRD alone. For example, the relative intensities of the (Rdx-TOD) XRD pattern slightly differed from those of the others. This can be explained by the changes in the birnessite crystal growth conditions or the potential unreacted precursor remaining after the reaction. The chemical analysis showed that in case of (Rdx-TOD), the buserite structure may not have formed because of inactive Mg^{2+} exchange in the interlayers, which did not allow appropriate phase change to todorokite. All the birnessite samples had an IR transmission band at $\sim 510\text{ cm}^{-1}$, indicating the birnessite structure. Similarly, all the todorokite samples had an IR band at 764 cm^{-1} , which is a good indicator of the tunnel structure. However, none of the todorokite samples, including (Rdx-TOD), had a band at 510 cm^{-1} , indicating that (Rdx-TOD) exclusively comprised todorokite even though it exhibited different characteristics than the others. The different features observed via different methods are summarized in Table 3.

Table 3. Summary of the characteristic features of the birnessite and todorokite samples synthesized through different methods.

Features	Oxidation		Redox Reaction				Reduction	
	BIR	TOD	Without Mg^{2+}		Mg^{2+} Doped		BIR	TOD
			BIR	TOD	BIR	TOD		
XRD	Single phase	Single phase	Birnessite + Feitknechtite	Not clear *	Birnessite + Feitknechtite	Single phase	Single phase	Single phase
Crystal Structure	Turbostratic	-	Roughly monoclinic	-	Roughly turbostratic	-	Monoclinic	-
Morphology	Irregular platy	Long acicular (1–10 μm)	Parallelogram plate	Fibrous fragment ($\sim 5\text{ }\mu\text{m}$)	Thin line entangled	Fibrous fragment ($\sim 5\text{ }\mu\text{m}$)	Hexagonal	Fibrous fragment ($\sim 5\text{ }\mu\text{m}$)
Other Features	The highest BET value among birnessite and todorokite		BET increase rate was the largest during the transition from birnessite to todorokite		BET value difference between birnessite and todorokite was the smallest		Highest crystallinity	-

* was verified as single phase by other methods.

The different birnessite synthesis methods can affect the characteristics of the products based on their chemical compositions. Among the birnessite samples, (Red-BIR), which contained the highest amount of Na, had the highest crystallinity, as confirmed by XRD. This is also well correlated with the slower rate of water loss observed in case of (Red-BIR) when compared with others with low crystallinity at a high temperature range.

The highly crystalline layered and tunnel-structured materials can contain significant amounts of cations in their interlayers and can be used for exchanging and scavenging other ions. Our results showed that (Red-BIR) has the high crystallinity and the greatest potential for application as an adsorbent. This is a significant result that should be further investigated. After the transformation process, (Oxi-TOD) contained the longest acicular particles based on SEM analysis and exhibited the highest specific surface area, indicating its potential as an efficient adsorbent. Our results indicate that birnessite and todorokite can exhibit various physicochemical properties depending on the synthesis method. Our results also indicate that suitable methods can be designed for specific applications of these minerals, including adsorbents for geochemically hazardous materials.

4. Conclusions

Our study showed that the physicochemical properties of birnessite and todorokite were greatly affected by the synthesis methods. Birnessite samples synthesized through the oxidation and reduction reactions were identified as single-phase samples, whereas those synthesized through the redox reaction contained an additional phase involving an intermediate product (feitknechtite). Pure birnessite can be obtained by increasing the aging time. XRD results indicated that birnessite exhibited different

crystal characteristics, which can be related to its chemical composition, depending on the synthesis method used. Chemical analysis showed that (Red-BIR) contained the highest amount of interlayer Na, which can be attributed to the highest degree of crystallization. Based on the Na content, the crystallinity of birnessite was of the order (Red) > (Oxi) > (Rdx) = (Rdx_{Mg}). The XPS results obtained based on the BEs of Mn2p_{3/2} and Mn3s showed that the oxidation state of manganese with respect to all the samples was approximately between +3 and +4. Furthermore, the different thermal characteristics of birnessite samples were well correlated with the crystallinity of the samples. (Red-BIR) did not exhibit mass loss above 600 °C, which can be interpreted as a feature of highly crystalline birnessite and was also inferred from the chemical analysis data. Four todorokite samples were produced from the four types of synthesized birnessite. The water content and specific surface area tended to increase with the phase change from the layered birnessite to the tunnel-type todorokite in all the samples. The complete conversion to todorokite for all samples was verified through the IR spectra. Clear morphological differences in birnessite and todorokite, depending on the synthesis conditions, were also observed through SEM. Our results showed that different synthetic methods can be used for specific purposes.

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