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Synthesis of Cryptomelane-Type Manganese Oxides by Microwave Heating

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Cryptomelane was prepared by the reaction of potassium permanganate and maleic acid. A black gel was initially formed by stirring the mixture of the two reagents for 70 min at room temperature. The gel was split into two parts and calcined in a microwave oven and in a conventional oven. The products were characterized by XRD, TGA, and IR. In microwave syntheses, cryptomelane emerged at 320 °C. Cryptomelane can be obtained only above 370 °C in conventional syntheses. As the temperature continued to rise, another phase with a main XRD peak at 2.72 Å occurred which is due to bixbyite (a CaF_2 type structure material). The formation of bixbyite usually takes place at temperatures above 600 °C in conventional syntheses. By microwave treatment bixbyite was obtained at a temperature as low as 470 °C, and the amount of bixbyite increased as the calcination temperature was increased on the basis of ratios of relative intensities of XRD peaks of bixbyite and cryptomelane. Calcination time had a similar effect on the phase transformation. At 425 °C well-ordered cryptomelane was formed after microwave treatment for 10 min, and bixbyite was detected after 3 h, while at the same temperature cryptomelane was obtained with weak and broad XRD peaks after conventional heating for 20 min. Cryptomelane was the only product with no bixbyite even after heating the sample for 10 h in a conventional oven at 425 °C. These data indicate that microwave heating may have the ability to accelerate the formation of crystalline material and specific phase transformations.

Introduction

Microwave heating has many applications such as removal of moisture or polar organic liquids,[1,2] sintering of ceramics,[3−5] promotion of organic and inorganic reactions,[6−9] and joining of ceramics.[10] Some unique properties of microwaves have been recognized with respect to conventional methods. Microwave irradiation enhanced the reaction speed significantly and reduced the reaction temperatures greatly in some processes.[6,7] In many organic reactions the yield of products was also increased.[11] In the sintering of ceramics it has been reported[3−5] that product uniformity, microstructure, hardness, and fracture toughness were improved.

Recently, microwave techniques have found use in the synthesis of molecular sieves.[12−14,22] Arafat et al.[12] reported that crystallization of zeolite Y under microwaves is faster and more selective than that in conventional ovens. Pure and uniform zeolites were obtained. Zeolites with different cations such as H^+, Na^+, and K^+ showed different abilities for absorption of microwaves.[13] Manganese oxides, however, as a new class of octahedral molecular sieves (referred to as OMS) have not been investigated by microwave methods. It is plausible that OMS materials could interact strongly with microwaves due to the very large dielectric constant of MnO_2.[21] So it is quite possible that microwave heating may show some interesting effects which are

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different from conventional methods in the synthesis of OMS materials.

Cryptomelane is a one-dimensional tunnel structure material with a 2 × 2 MnO_6 unit.[15] Its synthesis by conventional methods has been the subject of numerous studies.[15−19] In this work, we used procedures similar to that of Duan et al.[16] to synthesize cryptomelane. Characterization was done with X-ray powder diffraction (XRD), thermogravimetric analysis (TGA), and infrared (IR) methods. The properties of materials prepared by microwave heating were compared with those prepared by conventional syntheses.

Experimental Section

Syntheses. Cryptomelane was prepared as follows: 4.74 g of $KMnO_4$ in 200 mL of deionized distilled water (DDW) was added to a 0.05 M maleic acid solution with stirring at room temperature for 70 min. The black gel formed was washed with DDW for four times and filtered. First the gel was dried at 85 °C in air for 48 h to remove most of the water. Then it was ground and heated at 110 °C in air for 5 h. The final calcination was carried out in either a microwave oven or a conventional oven, respectively.

The microwave equipment used in this work includes a Model 10-1300 Microwave Furnace (MMT, Knoxville, TN) with a shielded K-type (standard unit) thermocouple with lead wire, a Micristar heat processing controller system, and LabVIEW R2 software. Microwaves were generated at 2.45 GHz with a maximum variable power supply of 1.3 kW.

Characterization. X-ray powder diffraction (XRD) was performed on a Scintag XDS 2000 diffractometer with Cu Kα radiation (tube voltage 45 kV and current 40 mA).

TGA profiles were taken on a Hi-Res TGA 2950 thermogravimetric analyzer (TA Instrument). For TGA experiments, the temperature ramp rate is 10 °C/min, with a carrier gas of oxygen or nitrogen.

IR spectra of the samples are taken on a Nicolet Magna-IR System 750 FT-IR spectrometer, with a MCT-B detector and a KBr beamsplitter, using standard procedures for diffuse reflectance methods. For each sample, 200 scans are employed with a total resolution of 4 cm^{-1}.

Results

XRD. The reaction of permanganate and maleic acid led to the formation of a dark brown gel. No matter how the gel was dried (in microwave or in a conventional oven at 110 °C), XRD patterns showed that no crystalline material existed in the dried gel. Figure 1 shows XRD patterns of samples prepared at different temperatures and different times both in microwave and conventional ovens. The results of Figure 1a show that under microwave irradiation, cryptomelane was formed after calcination at 320 °C for 40 min with broad XRD peaks and low intensity.

Identical conditions were used for all experiments and it was observed that the intensity of XRD peaks for cryptomelane systematically increased with increase of calcination temperature. At 425 °C sharp XRD peaks occurred with *d* spacings and intensities: 6.92 (26), 4.92 (27), 3.48 (11), 3.11 (100), 2.39 (100), 2.20 (7), 2.15 (14), 1.83 Å (12). These data showed a good match with data for cryptomelane-Q of JCPDS card 29-1020.

In microwave syntheses as the temperature rose to 470 °C a new XRD peak with a *d* spacing of 2.72 D emerged (as shown in Figure 1b). According to JCPDS cards and the literature,[16] the new peak is due to bixbyite. As the temperature continued to rise, the intensity of the highest XRD peak of bixbyite increased relative to the peaks of cryptomelane. Above 600 °C the XRD peaks for cryptomelane became broader and lower in comparison to the highest peak of bixbyite at *d* spacing 2.72 Å. At the same time the peaks at *d* spacing 6.92 and 3.48 Å also increased. These two peaks may result from another phase (possibly birnessite).

Table 1. Phases Obtained by Calcining Gel at Different Conditions (Bix/Cry Is the Relative Ratio of Bixbyite to Cryptomelane on the Basis of XRD Peaks)

heating method	temp (°C)				time (min)[a]	
	425	470	510	600	40	180
microwave	Cry	Bix/Cry (0.4)	Bix/Cry (0.8)	Bix/Cry (2.7)	Cry	Bix/Cry (0.4)
conventional	Cry	Cry	Cry	Cry	Cry	Cry

[a] Calcining at 425 °C.

Under conventional heating, cryptomelane began to form at a temperature of 390 °C after 40 min (Figure 1a). At 425 °C the same XRD pattern was obtained as that in microwave synthesis. No bixbyite was observed below the temperature of 650 °C.

Similar results were obtained by changing the calcination times at 425 °C (Figure 1c). Under microwave heating, cryptomelane with sharp XRD peaks was prepared after heating for 10 min. In conventional syntheses, only amorphous material was obtained under identical conditions. After heating for 20 min, cryptomelane was observed with low and broad XRD peaks. Only one phase existed in the product during the 10 h calcination period. For microwave preparation at 425 °C and treatment for 180 min, XRD peaks due to bixbyite were clearly present.

These data indicate that microwave-synthesized products consisted of cryptomelane and considerable amounts of bixbyite. We used the ratio of the intensity of the highest XRD peak (*d* spacing of 2.72 Å) of bixbyite (Bix) to that of the highest XRD peak (*d* spacing of 3.11 Å) of cryptomelane (Cry) as the relative ratio to qualitatively describe the growth of bixbyite as a function of calcination temperature and time. These results are summarized in Table 1.

In microwave heating, when the temperature increased from 470 to 600 °C, the relative ratio (referred to as Bix/Cry) increased from 0.4 to 2.7. When the microwave heating time changed from 40 to 180 min, the ratio went up to 0.4. Obviously, higher temperature and longer time in microwave heating favored the formation of bixbyite. However, cryptomelane is the only crystalline product in conventional heating under the conditions used.

TGA. The TGA curve for the product synthesized at 425 °C for 40 min showed four steps of weight loss. These steps occurred from 100 to about 528 °C, 528 to 694 °C, 694 to 758 °C, and 758 to 900 °C with corresponding weight losses of 1.9%, 2.8%, 3.4%, and 0.6%, respectively. The TGA curves for products obtained in different conditions gave similar steps, but the weight changes were different, especially for microwave-synthesized samples. The temperature range and weight change in each step are summarized in Table 2.

To investigate the weight changes and the phase transformations during calcination, dried gel was used to perform TGA experiments in a mixture of oxygen and nitrogen (Figure 2). TGA data show that the first weight loss took place from room temperature to 450 °C. In this stage the product was amorphous material

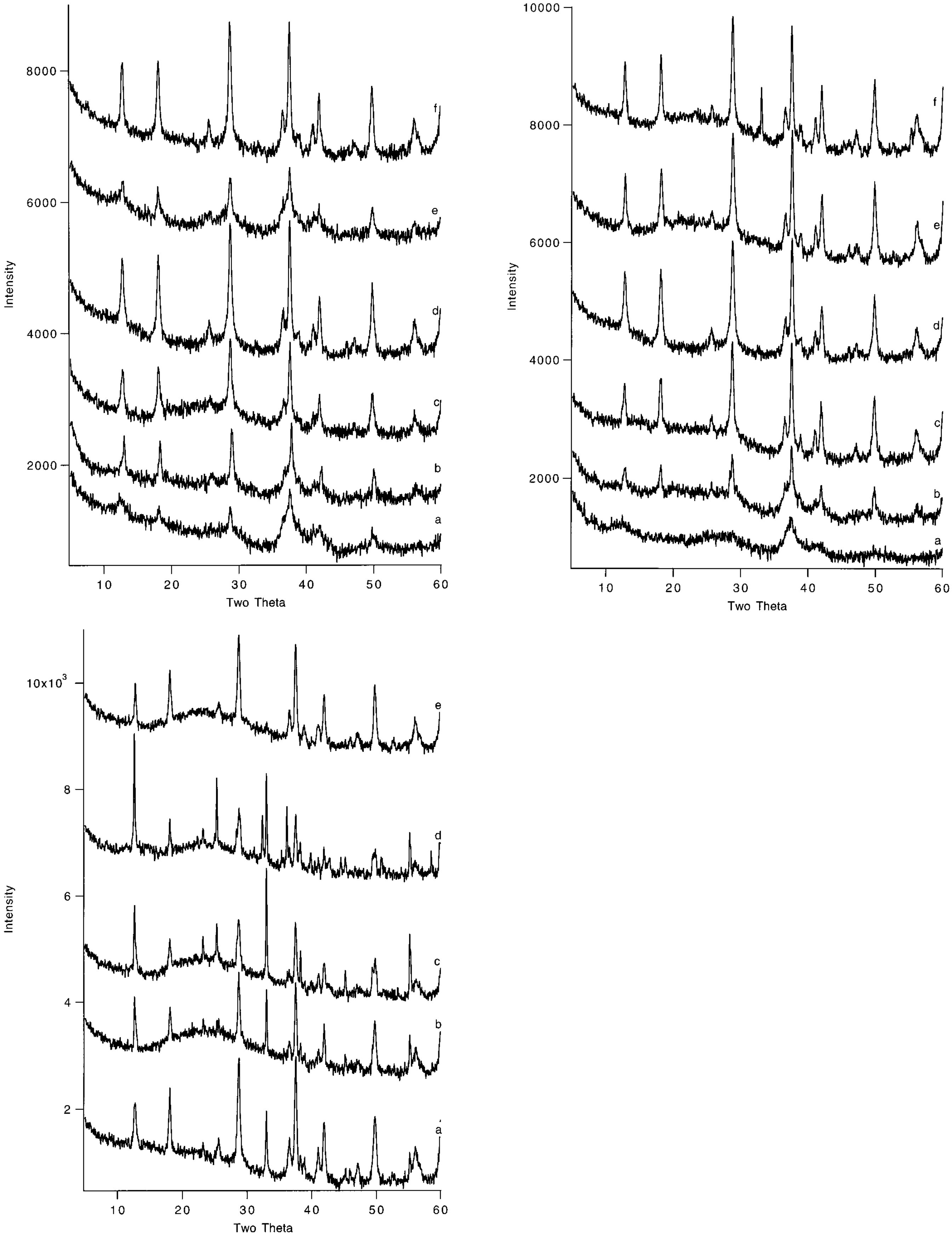

Figure 1. Top left: XRD patterns of cryptomelane synthesized for 40 min at a temperature of (a) 320 °C, microwave, (b) 340 °C, microwave, (c) 360 °C, microwave, (d) 425 °C, microwave, (e) 390 °C, conventional, (f) 425 °C, conventional. Bottom left: XRD patterns of samples synthesized (a) 470 °C for 40 min, microwave, (b) 510 °C for 40 min, microwave, (c) 600 °C for 0 min, microwave, (d) 650 °C for 0 min, microwave, (e) 650 °C for 0 min, conventional. Top right: XRD patterns of samples synthesized at 425 °C for (a) 10 min, conventional, (b) 20 min, conventional, (c) 40 min, conventional, (d) 600 min, conventional, (e) 10 min, microwave, (f) 180 min, microwave.

Table 2. Results of TGA Performed in Nitrogen

	step 1		step 2		step 3		step 4	
sample	temp range (°C)	weight change (%)	temp range (°C)	weight change (%)	temp range (°C)	weight change (%)	temp range (°C)	weight change (%)
CV 425 °C 40 min	100−526	1.7	526−699	3.1	699−758	3.4	758−900	0.6
CV 425 °C 600 min	100−527	1.1	527−691	3.3	691−750	3.3	750−900	0.7
MW 425 °C 40 min	100−528	1.9	528−694	2.8	694−758	3.4	758−900	0.6
MW 425 °C 180 min	100−553	1.1	553−691	2.1	691−787	4.0	787−900	0.5
MW 470 °C 40 min	100−551	1.1	551−699	1.8	699−793	4.3	793−900	0.5
MW 600 °C 0 min	100−544	1.1	544−697	1.6	697−785	4.1	785−900	0.4
MW 650 °C 0 min[a]	100−615	2.2	615−705	0.7	705−795	3.8	795−900	0.5

[a] At step1 there was a rapid loss between 100 and 120 °C with a corresponding weight change of 1.2%.

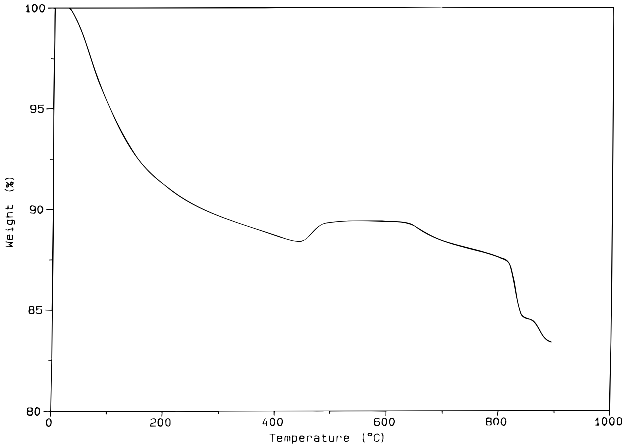

Figure 2. TGA data for the untreated gel (in the mixture of nitrogen and oxygen).

as determined by XRD analysis. The second stage is a gain in weight from 450 to 485 °C. This is an important phase transformation stage in which amorphous material was converted to crystalline cryptomelane. The third stage is a weight-stable period with the product showing an XRD pattern of cryptomelane. Above 650 °C other weight losses began with the formation of bixbyite and hausmanite.

Monitoring of the Production of Cryptomelane by IR. Infrared spectra are presented in Figure 3. For the untreated gel the strongest absorption appeared in the broad region 2500 cm^{-1}−3700 cm^{-1} with a peak position at ca. 3400 cm^{-1} which is due to the OH stretching vibration of hydrogen-bonded water molecules since there was a lot of water in the untreated sample. The bending vibration bands of water molecules were seen at ca. 1640 cm^{-1}. The band in the region of 700−760 cm^{-1} was due to vibrations of Mn−O bonds of the amorphous manganese oxide gel. Two weak bands at 610 and 500 cm^{-1} were also observed.

XRD results show that at 425 °C cryptomelane was formed by both methods. Both microwave and conventionally produced materials showed similar IR spectra (Figure 3a). In comparison to the untreated gel, peaks for water absorption decreased greatly, while those of Mn−O vibrations at 760 cm^{-1} became the main absorption. Bands at 650, 550, and 500 cm^{-1} were present in the spectrum, probably indicating the presence of cryptomelane in the sample.

In Figure 3b the spectrum of the product synthesized at 600 °C in the microwave oven showed that OH stretching vibration bands in the range 3300−3200 cm^{-1} and bending vibrations at 1700−1500 cm^{-1} began to appear. The intensities of these bands increased with calcination temperature. Strong bands at 3293 and 3206 cm^{-1} are present in the spectrum of the microwave-synthesized sample prepared at 650 °C. The shape of these peaks is quite different from that of the untreated gel which shows a broad band in this area. Due to the fact that there is 1.2% of surface adsorbed water in this case, the sharp IR peaks for OH could mainly be assigned to the non-hydrogen-bonded water molecules. In Figure 3b the conventionally synthesized sample prepared at 650 °C gave a similar spectrum as that of the sample prepared at 425 °C. Absorption of cryptomelane can be observed with no bands in the hydroxyl region. This is consistent with the XRD and TGA results.

Discussion

The formation of cryptomelane can take place only above a certain temperature which is high enough to overcome the activation energy in the phase transformation. At the beginning of this transformation, cryptomelane was identified, however, with a high degree of disorder as shown by the broad and weak XRD peaks. As the temperature is increased, the crystallinity was improved gradually, and a well-ordered product was formed. In conventional heating, cryptomelane showed remarkable stability.

Microwave treatment led to not only the quick formation of cryptomelane at 320 °C but also the rapid formation of bixbyite at a temperature as low as 470 °C. Bixbyite has a disordered octahedral edge-shared structure.[20] In ordinary sol−gel synthesis, cryptomelane is often accompanied by bixbyite at high temperatures above 600 °C.[16] In our conventional syntheses, we obtained cryptomelane below 650 °C.

XRD data showed that the temperature and time for the phase transformations in microwave syntheses were reduced in comparison to conventional syntheses. This acceleration of phase transformations may be due to an interaction between the reagents and the microwave irradiation. It has been demonstrated that different materials show different abilities in converting electromagnetic energy into heat energy at a given temperature and frequency. Cryptomelane is a mixed-valent material with Mn^{2+}, Mn^{3+}, and Mn^{4+}. Among these species manganese dioxide is the strongest microwave absorber, especially at high temperatures.[21] The dielectric constant of MnO_2 is 1000 times higher than that of Mn_2O_3.[23] Materials with different structures also show different coupling with microwaves. Maybe the selective heating during microwave preparation favored some phase transformations.

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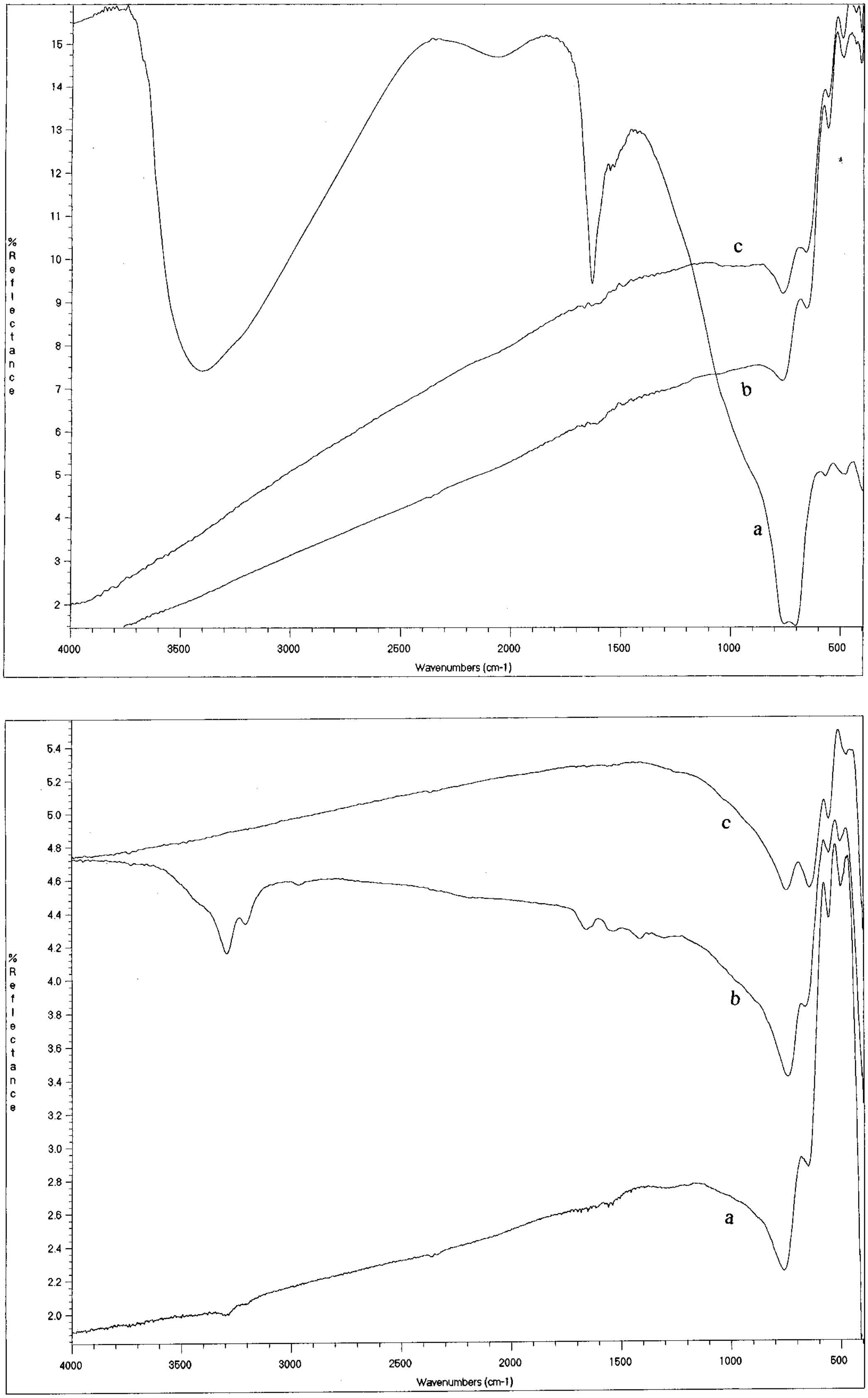

Figure 3. Top: Infrared spectra (a) untreated gel, (b) microwave, 425 °C for 40 min, (c) conventional, 425 °C for 40 min. Bottom: Infrared spectra (a) microwave, 600 °C for 0 min, (b) microwave, 650 °C for 0 min, (c) conventional, 650 °C for 0 min.

In thermogravimetric analyses performed in N_2 the weight loss in step 1 was mainly the loss of water including physically adsorbed, chemically adsorbed water, and tunnel water, as well as perhaps some small amounts of oxygen species. These species cannot be discriminated by TGA experiments. The other three weight loss steps above 520 °C were mainly due to the evolution of different oxygen species. The final product was a hausmanite-type material with a low average oxidation state (8/3).

According to TGA results the microwave synthesized products with bixbyite showed smaller amounts of oxygen loss in step 2. Evolution of oxygen in cryptomelane caused a change of oxidation state from Mn^{4+} to Mn^{3+} and led to the formation of bixbyite. Combining XRD, TGA, and IR results, in relation to the formation of bixbyite, the products showed a high propensity to adsorb water and oxygen. Evolution of oxygen probably caused the appearance of defects (oxygen vacancies) and changed the surface properties. These changes increased with increase of microwave treatment temperature. These data indicate that microwave irradiation accelerated the evolution of oxygen species. The TGA data for the uncalcined gel and the corresponding XRD analysis at these weight change stages yield information about the relationship between weight changes and phase changes during calcination.

There are specific steps during thermal treatment such as: 1) the loss of moisture, 2) the formation of cryptomelane by oxidation which caused a gain in weight, 3) a stable period in which the oxidation reaction and decomposition reaction reached an equilibrium and the weight was unchanged, 4) the decomposition period in which oxygen began to be released.

From the XRD results of the products obtained by microwave heating, similar phase changes were observed. But the differences are: 1) the removal of water was mainly finished before 400 °C, 2) the formation of cryptomelane began at 400 °C, 3) the zone of stability of cryptomelane was considerably reduced and the temperature of oxygen evolution was lower than that in conventional heating.

Conclusions

Cryptomelane can be synthesized either in a microwave oven or in a conventional oven. The temperature and time required were reduced for microwave synthesis. Cryptomelane showed a high stability in oxygen or in air in conventional heating and was the only crystalline material under our experimental conditions. Microwave treatment yields bixbyite that can easily be formed at relatively low temperature and short calcination time. Microwaves accelerated the evolution of oxygen species in cryptomelane, caused the rapid formation of bixbyite, and changed the surface properties of resultant materials.

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