Effects of different amount of As$_2$O$_3$ and TiO$_2$ on the chemical, physical and electrical properties of the base material MnO$_2$

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Received 7 September 2004; received in revised form 18 November 2004; accepted 27 November 2004
Available online 4 January 2005

Abstract

MnO$_2$ oxide systems containing different weight percent of TiO$_2$ and As$_2$O$_3$ were prepared. A number of studies, i.e., Fourier Transform Infrared, X-ray powder diffraction, electrical conductivity and dielectric properties on these mixed oxide systems, were carried out. These investigations show that the doping amount of As$_2$O$_3$ and TiO$_2$ influences structure, conductance, electrical and dielectric behavior of MnO$_2$ system. The optical investigations show that MnO$_2$ reacts with As$_2$O$_3$ to form Mn$_2$As$_2$O$_7$ and Mn$_2$O$_3$. TiO$_2$ appears in the form of rutile phase. Dielectric constants $\varepsilon'$ and $\varepsilon''$ of 5 wt.% As$_2$O$_3$-doped composite were calculated to be ~30 and ~38 at 13.5 kHz, respectively. The formation of Mn$_2$As$_2$O$_7$, Mn$_2$O$_3$ and the presence of TiO$_2$ rutile phase and the degree of polarization or charge displacement depending on frequency played an effective role in the magnitude of $\varepsilon'$, $\varepsilon''$ and $\sigma$.

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Keywords: Manganese (IV) oxide; Rutile phase; Mixed oxide systems; Physical and chemical properties

1. Introduction

There is currently great interest in the technological properties of composites because of the demands for various application fields such as catalysts, capacitors, thermistors, transducers, fuses, sonar generators, electrical insulators [1–5]. The mixed oxide systems such as ZrO$_2$–CeO$_2$–Y$_2$O$_3$ [6–8], ZrO$_2$–TiO$_2$–Y$_2$O$_3$ [9], Al$_2$O$_3$–TiO$_2$ [10], (Pb, Nb)–TiO$_2$ [11], (Ba, Bi, Nb)–TiO$_2$ [12], (Cr, Nb)–TiO$_2$ [13], (Ca, Ta)–TiO$_2$ [14], Sb$_2$O$_3$–As$_2$O$_3$–alkali halides [15], etc., have been studied in detail. Interesting studies on As$_2$O$_3$ mixed with different semiconducting oxides such as SiO$_2$, GeO$_2$ and V$_2$O$_3$ are also available in the literature [16–18]. In particular, MnO$_2$ as doped material is an interesting one since it exists in different valence oxidation state in different mixed oxide system [19]. The MnO$_2$ was considered as base material in this study. Any study on Mn–Ti–As mixed oxide systems has not been reported yet. The effects of arsenic (III) oxide and titanium (IV) oxide on the MnO$_2$-based composite were not investigated either. The purpose of this study is to characterize the structure of composites and also to understand the electrical and dielectric properties of the Mn–Ti–As mixed oxide mixture over a wide range of frequencies at room temperature.

2. Experimental procedure

In this study, the solid–solid reaction was chosen though there are a number of preparative methods such as crystallization of solutions, vapor phase transport and electrochemical reduction methods. This route was mainly chosen due to its simplicity and suitability to starting materials in order to obtain thin films and single crystals. Manganese (IV) oxide (MnO$_2$, 90%, Aldrich), titanium (IV) oxide (TiO$_2$, 99.9%, Aldrich) and arsenic (III) oxide (As$_2$O$_3$, 99%, Fluka) were used as received. Composites were
pure crystalline MnO2 shows double degenerate vibrations of 800–600 cm\(^{-1}\) in the FTIR spectrum of composite. An improvement in the thickness of 9.1\% and 80 wt.% MnO2, 15 wt.% TiO2 and 5 wt.% As2O3, prepared as 80 wt.% MnO2, 10 wt.% TiO2, 10 wt.% As2O3 and 80 wt.% MnO2, 15 wt.% TiO2 and 5 wt.% As2O3, respectively. The oxide mixtures were firstly stirred by a magnetic stirrer for 3 h. The Mn–Ti–As oxide mixtures were kept in an oven at 700 °C for 24 h in air and then cooled slowly to room temperature (25 °C). The melting points of MnO2 (535 °C) and As2O3 (315 °C) were below the chosen temperature. Thus these compounds will be well melted and also any impurities would be removed within those compounds. Although the melting point of TiO2 (1855 °C) is higher than the chosen temperature, it was intended to investigate the diffusion of TiO2 within the composite.

The infrared spectra were taken between 400 and 2000 cm\(^{-1}\) using a Shimadzu 8201/86601 PC spectrometer. The Mn–Ti–As oxide powders were mixed with KBr and pressed at 7 tons to form pellets which have diameter of 13 mm. The vibrational measurements were performed using these pellets.

For dc conductivity and capacitive measurements, a new set of pellets was prepared by pressing the Mn–Ti–As oxide systems at 7 tons having an area of \(4.96 \times 10^{-2} \text{ cm}^2\) and thickness of 9.1\% \(\times 10^{-2} \text{ cm}\). The both faces of resulting pellets were coated with aluminum under high vacuum atmosphere (~10\(^{-6}\) torr). The coating was done using a Univex 300 Leybold vacuum apparatus. The dc conductivity was measured using a Keithley 2400 Source-meter. The capacitive measurements were performed in the frequency range 1 kHz to 5 MHz and in the voltage range 0–5 V with an Impedance/Gain-Phase Analyzer HP 4194A.

X-ray spectra were taken using an XRD Rigaku DMAX 2200. The X-ray wavelength was CuK\(\alpha\) radiation, \(\lambda = 1.5405 \text{ A}\). All measurements were taken at room temperature.

3. Results and discussion

3.1. FTIR and XRD measurements

The FTIR spectra of the pure MnO2 (base material) and the composite having 80 wt.% MnO2, 10 wt.% TiO2 and 10 wt.% As2O3 are shown in Fig. 1. The FTIR spectrum of pure crystalline MnO2 shows double degenerate vibrations at 660–670 cm\(^{-1}\) and strong peaks at 530 and 608 cm\(^{-1}\). FTIR spectrum of pure As2O3 exhibits four fundamental absorption bands at 1050 cm\(^{-1}\) (symmetric stretching vibrations), 618 cm\(^{-1}\) (symmetric bending vibrations), 795 cm\(^{-1}\) (doubly degenerate stretching vibrations) and 505 cm\(^{-1}\) (doubly degenerate bending vibrations) [19]. Rutile phase of TiO2 exhibits strong absorption bands in the region of 800–600 cm\(^{-1}\) [20].

Because of the structural change in MnO2, after reacting with As2O3 and TiO2, an intense peak appears at 655 cm\(^{-1}\) in the FTIR spectrum of composite. An improvement in the region between 650 and 600 cm\(^{-1}\) was noted suggesting that the peak at 608 cm\(^{-1}\) of MnO2 and the peak at 618 cm\(^{-1}\) of As2O3 overlapped with the peaks of TiO2. In the FTIR spectrum (Fig. 1) of composite, bands due to vibrations at 1050 and 795 cm\(^{-1}\) of As2O3 are observed to be shifted to 990 and 850 cm\(^{-1}\), respectively. This can be interpreted as result of the solid–solid interactions at 700 °C. As2O3 gets incorporated into the structure of MnO2 via oxygen bridges to form Mn2As2O7 which was confirmed with XRD observations.

The composite consisting of 80 wt.% MnO2, 15 wt.% TiO2 and 5 wt.% As2O3 gave almost the same FTIR spectrum. However, the intensities of peaks were different because the composite had different amount of components. These results are consistent with the XRD results. XRD patterns (Figs. 2 and 3) of both composites confirm the formation of Mn2As2O7 (JCPDS Files No. 44-0076) and Mn2O3 (bixbyite-C, JCPDS Files No. 41-1442) and also show the presence of TiO2 rutile phase (JCPDS Files No. 21-1276). The results were summarized in Tables 1 and 2. The XRD observations reveal an information about the reactivity of As2O3 towards MnO2.

As can be seen in Figs. 2 and 3, no diffraction lines due to As2O3 and compounds between TiO2 and MnO2 are observed. With increase in the amount of As2O3 from 5 wt.% to 10 wt.%, an increase in the intensity of the lines at \(d = 4.3667, 3.1974\) and \(3.0214 \text{ Å}\) due to Mn2As2O7 can be seen (Tables 1 and 2). Weak lines due to Mn2As2O7 and intense lines due to TiO2 rutile phase overlap at \(d = 3.2384\) and 1.6852 Å (Table 1). From Tables 1 and 2, it can be noted that some values of \(d, 2\theta\) and intensity are the same because of overlapping the lines of Mn2As2O7, TiO2 and also Mn2O3. Although some of the TiO2 had been expected to diffuse into the structure of MnO2, XRD results did not support this assumption.
3.2. Electrical conductivity measurements

Conductivities ($\sigma$) were calculated using resistivity ($\rho$) values with the following equations:

$$\rho = \frac{V}{\left(\frac{d}{i} \cdot \frac{A}{1}\right)} \quad (\Omega \text{cm})$$

and

$$\sigma = \frac{1}{\rho} \quad (\Omega^{-1} \text{ cm}^{-1})$$

where $V$ is the applied voltage, $d$ is the distance between electrodes, $i$ is the current and $A$ is the area of pellet as a unit-section.

Dc current–voltage plots of composites prepared in various amount of TiO$_2$ and As$_2$O$_3$ are shown in Fig. 4. It shows that As$_2$O$_3$ has significant impact on the conductivity of MnO$_2$. The conductivity was higher for 5 wt.% As$_2$O$_3$-doped composite than that of 10 wt.% As$_2$O$_3$-doped composite. In other words, the conductivity increases as the doping amount of TiO$_2$ is increased from 10 wt.% to 20 30 40 50 60 70

<table>
<thead>
<tr>
<th>Compound</th>
<th>$2\theta$</th>
<th>$d$-Value ($\text{Å}$)</th>
<th>Intensity</th>
<th>$I/I_0$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_2$As$_2$O$_7$ (a)</td>
<td>27.520</td>
<td>3.2384</td>
<td>356</td>
<td>86</td>
</tr>
<tr>
<td>Mn$_2$O$_3$ (b)</td>
<td>23.180</td>
<td>3.8340</td>
<td>94</td>
<td>24</td>
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<tr>
<td>TiO$_2$ (c)</td>
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Table 1

XRD data for the composite containing 80 wt.% MnO$_2$ +15 wt.% TiO$_2$ +5 wt.% As$_2$O$_3$

Table 2

XRD data for the composite containing 80 wt.% MnO$_2$ +10 wt.% TiO$_2$ +5 wt.% As$_2$O$_3$
15 wt.% TiO2. These changes can also be explained the cross linking of a part of AsO3 units with Mn4+ ions to form As–O–Mn bonds [19]. When the amount of As2O3 is increased from 5 wt.% to 10 wt.%, the amount of the formation of cross links increased. This is confirmed by the XRD patterns which include no diffraction lines due to the As2O3. In addition, an increase in the intensity of lines due to Mn2As2O7 supports the formation of crosslinks. Thus, these crosslinks decrease the polarizability leading to an increase in the values of conductivity. The reduction of MnO2 (Mn4+, d3 configuration) to Mn2O3 (Mn3+, d4) by heating at 700 °C also effects the conductivity. Conductivity (\(\sigma\)) corresponds to 1.4 V was calculated as 4.7 × 10^{-7} \(\Omega\) cm^{-1}, 1.5 × 10^{-8} \(\Omega\) cm^{-1} and 9.2 × 10^{-9} \(\Omega\) cm^{-1} for pure MnO2, composite of 80 wt.% MnO2+15 wt.% TiO2+5 wt.% As2O3 and composite of 80 wt.% MnO2+10 wt.% TiO2+10 wt.% As2O3, respectively. As seen from calculated values, the conductivity becomes lower than that of pure MnO2 which has IV oxidation state (or d3 configuration). In the study of the previous paper, the conductivity values of SnO-doped material were found higher compared to the conductivity of TiO2-doped material [21].

3.3. Dielectrical properties

The real part of dielectric constant (relative permittivity), \(\varepsilon'\), is a measure of the capacitance whereas the imaginary part of dielectric constant, \(\varepsilon''\), is a measure of conductance. Dielectric constant (\(\varepsilon'\) and \(\varepsilon''\)) and loss factor (\(\tan\delta\)) were calculated with the contribution of the following equations:

\[
C = \varepsilon' \varepsilon_0 A/d
\]  \hspace{1cm} (3)
\[
\tan\delta = \varepsilon'' / \varepsilon'
\]  \hspace{1cm} (4)

and

\[
\varepsilon'' = \sigma / \omega \varepsilon_0 A/d
\]  \hspace{1cm} (5)

\(C\): measured capacitance, \(\varepsilon_0\): space constant: 8.85 × 10^{-12} F/m and \(\omega\): angular frequency, \(\sigma\): conductance.

The plots of \(\varepsilon'\) versus frequency, \(\varepsilon''\) versus \(\varepsilon'\), \(\varepsilon''\) versus frequency and \(\tan\delta\) versus frequency are shown in Figs. 5–8. The variations corresponding to 1 kHz to 5 MHz frequencies are interpreted as the following: The real part of dielectric constant, \(\varepsilon'\), of these composites gradually
decreased with an increase in the frequency values (Fig. 5). Fig. 5 clearly reveals that the values of composite 80 wt.% MnO$_2$+15 wt.% TiO$_2$+5 wt.% As$_2$O$_3$ measured in 1 kHz to 5 MHz regions is larger than those of base material MnO$_2$. Different weight percentage was also effective in the properties mentioned above. For instance, the first composite 80 wt.% MnO$_2$+15 wt.% TiO$_2$+5 wt.% As$_2$O$_3$ had higher conductivity than the second one 80 wt.% MnO$_2$+10 wt.% TiO$_2$+10 wt.% As$_2$O$_3$. The magnitude of $\varepsilon'$, $\varepsilon''$ and tan $\delta$ changed depending on frequency.

4. Conclusion

In summary, composites having 80 wt.% MnO$_2$+15 wt.% TiO$_2$+5 wt.% As$_2$O$_3$ and 80 wt.% MnO$_2$+10 wt.% TiO$_2$+10 wt.% As$_2$O$_3$ were prepared by solid–solid reaction at 700 °C and characterized by FTIR and XRD measurements. The optical measurements showed that the formation of Mn$_2$As$_2$O$_7$ and Mn$_3$O$_2$ (bixbyite-C) and the presence of TiO$_2$ rutile phase. The formation of these compounds and the presence of TiO$_2$ affected the conductivity, electrical and dielectrical properties compared to those of base material MnO$_2$. Different weight percentage was also effective in the properties mentioned above. For instance, the first composite 80 wt.% MnO$_2$+15 wt.% TiO$_2$+5 wt.% As$_2$O$_3$ had higher conductivity than the second one 80 wt.% MnO$_2$+10 wt.% TiO$_2$+10 wt.% As$_2$O$_3$. The magnitude of $\varepsilon'$, $\varepsilon''$ and tan $\delta$ changed depending on frequency.

Acknowledgements

This work was supported by the Research Foundation of Kocaeli University, Project No.: 2002/57.

References