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Effects of different amount of As_2O_3 and TiO_2 on the chemical, physical and electrical properties of the base material MnO_2

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Abstract

MnO_2 oxide systems containing different weight percent of TiO_2 and As_2O_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_2O_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_2O_3 to form $Mn_2As_2O_7$ and Mn_2O_3. TiO_2 appears in the form of rutile phase. Dielectric constants ε' and ε'' of 5 wt.% As_2O_3-doped composite were calculated to be ~30 and ~38 at 13.5 kHz, respectively. The formation of $Mn_2As_2O_7$, Mn_2O_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 ε', ε'' and σ.
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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_2O_3 [6–8], ZrO_2–TiO_2–Y_2O_3 [9], Al_2O_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_2O_3–As_2O_3–alkali halides [15], etc., have been studied in detail. Interesting studies on As_2O_3 mixed with different semiconducting oxides such as SiO_2, GeO_2 and V_2O_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_2O_3, 99%, Fluka) were used as received. Composites were

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prepared as 80 wt.% MnO_2, 10 wt.% TiO_2, 10 wt.% As_2O_3 and 80 wt.% MnO_2, 15 wt.% TiO_2 and 5 wt.% As_2O_3, 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 MnO_2 (535 °C) and As_2O_3 (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 TiO_2 (1855 °C) is higher than the chosen temperature, it was intended to investigate the diffusion of TiO_2 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 4.96×10^{-1} cm^2 and thickness of 9.1×10^{-2} 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 CuKα radiation, λ=1.5405 Å. All measurements were taken at room temperature.

3. Results and discussion

3.1. FTIR and XRD measurements

The FTIR spectra of the pure MnO_2 (base material) and the composite having 80 wt.% MnO_2, 10 wt.% TiO_2 and 10 wt.% As_2O_3 are shown in Fig. 1. The FTIR spectrum of pure crystalline MnO_2 shows double degenerate vibrations at 660–670 cm^{-1} and strong peaks at 530 and 608 cm^{-1}. FTIR spectrum of pure As_2O_3 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 TiO_2 exhibits strong absorption bands in the region of 800–600 cm^{-1} [20].

Because of the structural change in MnO_2, after reacting with As_2O_3 and TiO_2, 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

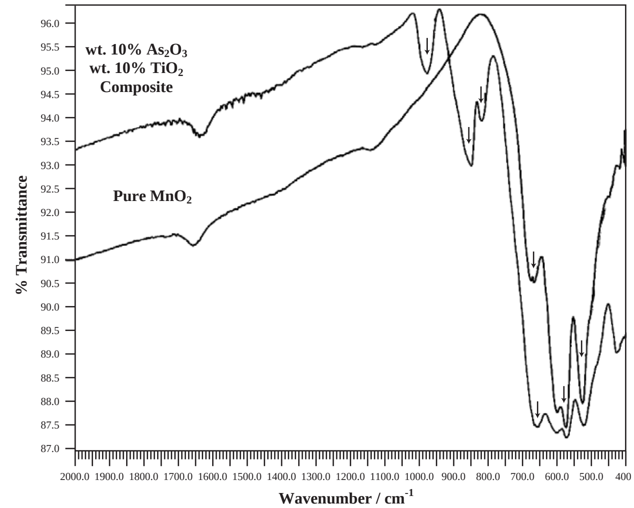

Fig. 1. FTIR spectra of composite (80 wt.% MnO_2+10 wt.% TiO_2+10 wt.% As_2O_3) and pure MnO_2.

that the peak at 608 cm^{-1} of MnO_2 and the peak at 618 $cm^{-1}$of As_2O_3 overlapped with the peaks of TiO_2. In the FTIR spectrum (Fig. 1) of composite, bands due to vibrations at 1050 and 795 cm^{-1} of As_2O_3 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. As_2O_3 gets incorporated into the structure of MnO_2 via oxygen bridges to form $Mn_2As_2O_7$ which was confirmed with XRD observations.

The composite consisting of 80 wt.% MnO_2, 15 wt.% TiO_2 and 5 wt.% As_2O_3 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 $Mn_2As_2O_7$ (JCPDS Files No. 44-0076) and Mn_2O_3 (bixbyite-C, JCPDS Files No. 41-1442) and also show the presence of TiO_2 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 As_2O_3 towards MnO_2.

As can be seen in Figs. 2 and 3, no diffraction lines due to As_2O_3 and compounds between TiO_2 and MnO_2 are observed. With increase in the amount of As_2O_3 from 5 wt.% to 10 wt.%, an increase in the intensity of the lines at d=4.3667, 3.1974 and 3.0214 Å due to $Mn_2As_2O_7$ can be seen (Tables 1 and 2). Weak lines due to $Mn_2As_2O_7$ and intense lines due to TiO_2 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, 2θ and intensity are the same because of overlapping the lines of $Mn_2As_2O_7$, TiO_2 and also Mn_2O_3. Although some of the TiO_2 had been expected to diffuse into the structure of MnO_2, XRD results did not support this assumption.

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