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Electrical conductivity and dielectric behaviour of manganese and vanadium mixed oxide prepared by conventional solid state method

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ABSTRACT

Investigation on electrical conductivity and dielectric properties of manganese (Mn) and vanadium (V) mixed oxides were carried out to study the extrinsic semiconductor behaviour. The XRD pattern shows that Mn–V oxide is multiphase and quantitative phase analysis was performed to determine the relative phases. Overall results indicate that with increasing temperature, the DC conductivity, AC conductivity, dielectric constant, dielectric loss factor and loss tangent of Mn–V mixed oxide increases. Activation energy of AC conduction decreases with increase in frequency, confirms that the hopping conduction is the dominant mechanism. The activation energy of DC conduction ΔE_{dc} is 0.54 eV which is greater than ΔE_{dc}. There are three types of dielectric constant spectrum found in the measuring temperature range 30–250 °C. This is possibly due to the extrinsic behaviour of the Mn–V oxide. Dielectric relaxation characteristic was obtained from the spectrum of the imaginary part of electric modulus. The activation energy of the relaxation process and the relaxation time at infinite temperature are 0.42 eV and 5.40 ps respectively. The Nyquist plot of complex impedance fitted the equivalent circuit model of two RC circuits in series with R and C in parallel. The relaxation time was estimated from the circuit model.

1. Introduction

Transition element has mixed valence ions, hence these compounds have unique properties and very useful in various fields. Manganese is one of the transition element which has a formal oxidation state from −3 to +7. Manganese oxides and vanadium oxides which include MnO, Mn_2O_3, Mn_2O_7, etc [1] and V_2O_3, V_2O_5, V_6O_{13}, VO_2, etc. respectively show a phase transition from semiconductor phase to metal phase when measuring temperature increases [2].

In the past two decades, there were reports on characterization of mixed oxides of Mn and V due to its interesting application in various areas such as, energy conversion, thermistor, temperature sensors and thermal imaging detectors [3,4]. Gouda et al. [4] prepared mixed oxides of manganese and vanadium at different mass ratio of Mn_2O_3 and VO_2. They found that the resistivity and the thermistor constant of β-$Mn_2V_2O_7$ and γ-$Mn_2V_2O_7$ were higher compared to the well known oxides of vanadium and binary/ternary oxides of manganese, nickel and cobalt. It meant that the d-block electronic configuration of V^{5+} in $Mn_2V_2O_7$ contributed to higher resistivity [5].

From previous works, there were several investigations and reports on the structural and electrical properties of MnV_2O_6 and $Mn_2V_2O_7$ [3,4,6,7] related to Mn and V oxides prepared by different methods which were pulsed laser deposition [6], solid state reaction [4,7] and high pressure synthesis [8], but it lacks a comprehensive electrical studies on Mn–V oxide system. In this paper, the electrical conductivity and dielectric properties of Mn–V oxide were investigated at different measuring temperatures from 30 °C to 250 °C.

2. Experimental details

The mixed oxides were prepared by conventional solid state method. The starting materials, Vanadium (V) oxide, V_2O_5 (99.5%), Manganese (IV) oxide and MnO_2 (99.95%) were weighed according to the stoichiometric ratio of 40 mol% V_2O_5 and 60 mol % $2MnO_2$. These powders were wet milled and precalcined in air at 450 °C for 4 h. The precalcined powder were added with the binder Polyvinyl Alcohol (PVA) at 1 wt% and pressed at 4.5 tonnes for 4 min to produce Mn–V oxide pellets. These pellets were finally sintered at 600 °C for 4 h and ready for characterization.

The samples were characterized by XRD to determine the microstructure and phase identification of the samples and the surfaces of the sample were visualized by using Field Emission Scanning Electron Microscopy (FESEM). For DC conductivity, a

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simple circuit was set up where Picoammeter Model 6485 and Escort 95T multi-display multimeter were used to measure the current, I and the resistance, R respectively. The DC conductivity was measured from 30 °C to 250 °C by using the $R = V/I$, $\rho = RA/l$ and $\sigma = 1/\rho$ where V is potential difference, I is current, ρ is the resistivity, l is the length A is the cross-sectional area and σ is conductivity. The dielectric properties were determined by using the Agilent 4294A Precision Impedance Analyzer from 30 °C to 250 °C. The dielectric constant and loss factor were calculated using $\varepsilon_r' = Cd/\varepsilon_o A$ and $\varepsilon_r'' = Gd/\varepsilon_o \omega A$ respectively, where C is the capacitance, d is the thickness, ε_o is permittivity of free space, G is the conductance, ω is the angular velocity and A is the cross-section area of the sample. The AC conductivity is determined from the dielectric parameter using the formula, $\sigma_{ac} = \omega \varepsilon_o \varepsilon_r''$.

3. Results and discussion

XRD were done to determine the phase identification and phase composition of the samples. The composition of the phase in each sample was determined using Rietveld Refinement analysis. The surface of the samples was viewed using FESEM and the average grain size was calculated. For conductivity measurements, AC and DC conductivities were measured over the temperature range from 30 °C to 250 °C and their activation energies were determined and discussed. The dielectric behaviour of the samples was discussed at different measuring temperatures, 30–250 °C in the frequency range of 40 Hz to 1 MHz.

3.1. X-ray diffraction and microscopy analysis

The phase contained in the sample was identified by comparing the observed XRD patterns with Inorganic Crystal Structure Database (ICSD) pattern. Fig. 1 shows the X-ray diffraction pattern of Mn–V oxide and the compounds present which are Manganese Divanadate, MnV_2O_6 (ICSD: 98-004-7436), Dimanganese Divanadate (V)-alpha, $Mn_2V_2O_7$ (ICSD: 98-004-0958) and Manganese(IV) Oxide-beta, MnO_2 (ICSD: 98-001-2180). There are two phases of Mn–V oxides, which are MnV_2O_6 and $Mn_2V_2O_7$, while MnO_2 in excess remained. Practically, the single phase material is hard to obtain because manganese and vanadium have many oxidation states [1,2] and quantitative phase analysis should be performed in order to determine the percentage of the relative phases. As a result, the Rietveld Refinement analysis is needed and the X'pert HighScore Plus software was used [9]. MnV_2O_6 and $Mn_2V_2O_7$ are the Mn–V oxide which is 61.7% and 19.3% respectively and a small amount of the starting material MnO_2, about 19% remained. According to Table 1, the profile parameter (R_{exp}, R_p and Goodness of fit) for the Mn–V oxide is less than 10, hence the result obtained from refinement is reliable [10]. Finally, we can conclude that a multiphase compound or an extrinsic semiconductor was prepared.

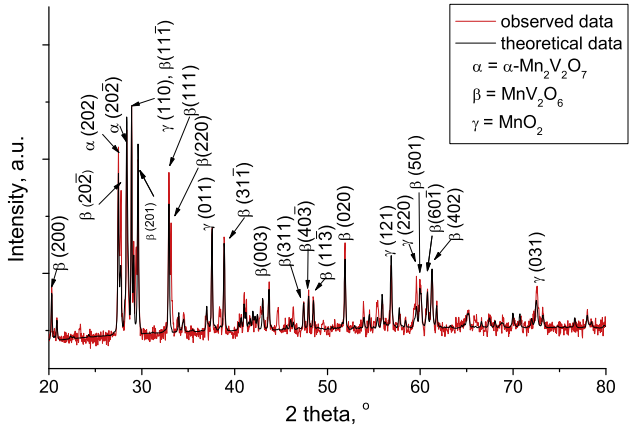

Fig. 1. The Rietveld refinement analysis of Mn–V oxide.

Table 1
Profile parameters (R_{exp}, R_p and Goodness of fit) of Mn–V oxide.

Profile parameters	Mn–V oxide
R_{exp}	7.52
R_p	7.62
Goodness of fit	2.11

The morphology and grain size of the sample were determined by FESEM. Fig. 2(a) shows that even though the particles are irregular, but they had begun to attach to the neighbouring particles to grow and form a larger grain at 600 °C [11]. Hence, better densification is possible at higher sintering temperatures. 150 grains were taken randomly from the micrographs with grain size distribution in the range 0.4–2.8 μm as shown in Fig. 2(b). The average grain size based on the histogram is around 1.2 μm.

3.2. DC conductivity and activation energy of DC conduction

Conductivity is a material's ability to conduct an electric current. The DC conductivity, σ_{dc} of Mn–V oxide varies at different temperatures as shown in Fig. 4. It decreases to 59.05 $n\Omega\,m^{-1}$ at 50 °C and constantly increases at higher temperature region with the highest value of 70.94 $\mu\Omega^{-1}\,m^{-1}$ at 250 °C.

The Mn–V oxide successfully reduces the σ_{dc} as compared to MnO_2 and V_2O_5 which is $2.0 \times 10^{-7}\ \Omega^{-1}\,m^{-1}$ at room temperature. From the previous findings, the σ_{dc} of MnO_2 and V_2O_5 at room temperature were 6.8×10^{-7} and $2.1 \times 10^{-5}\ \Omega^{-1}\,m^{-1}$ respectively [12,13]. Usually, conductivity for a standard semiconductor increases with temperature where more electrons are excited and enter the conduction band [14]. However, the Mn–V oxide is a multi phase material and it behaves like an extrinsic semiconductor because each phase participated in changing the properties of the samples [14]. Extrinsic semiconductor has extra electrons in the conduction band and/or holes in valence band and we would expect to have two activation energies [14]. Fig. 4 indicates that there is an intrinsic region 50–250 °C, while the extrinsic region is predicted to happen at temperatures below 30 °C. The region of conductivity decreasing from 30 °C to 250 °C is the region between these two slopes as shown in Fig. 3 [14]. The heat applied is able to ionize the donors but not enough to ionize the electrons from the host lattice. The decrease in conductivity shows that the carrier density is not greatly influenced by temperature and the variations in mobility will determine the shape of the curve [14,15]. Also, extrinsic semiconductor has more free mobile charge carriers compare to intrinsic semiconductor. The vibration of lattice structure of semiconductor when heated may contribute to the resistance and consequently decreases the conductivity [14,16]. Beyond 50 °C, the intrinsic contribution to the electrons to enter the conduction band become significant and rapidly dominates [16].

Activation energy ΔE is the minimum energy needed for conduction from one site to another. The DC activation energy, ΔE_{dc} is calculated by using the well-known Arrhenius equation [17],

$$\sigma = \sigma_o \exp\left(\frac{-\Delta E}{k_B T}\right) \quad (1)$$

where σ_o is the pre-exponential factor and k_B is Boltzmann constant. The inset figure in Fig. 4 shows the plot of Lnσ against 1000/T. It is clear that the Ln σ_{dc} linearly decreases with reciprocal of absolute temperature and the ΔE_{dc} of Mn–V oxide is 0.54 eV.

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