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Electrical conductivity and dielectric studies of MnO_2 doped V_2O_5

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ABSTRACT

The investigation on electrical conductivity and dielectric properties of mixed oxide of manganese (Mn) and vanadium (V) was carried out to study the mixed oxides response to different frequencies and different measuring temperatures. The frequency and temperature dependence of AC conductivity, dielectric constant and dielectric loss factor of mixed oxides were studied in the frequency range of 40 Hz–1 MHz and a temperature range of 30–250 °C. Since the mixed oxides are multi phase materials, hence the properties of the pure oxides are also presented in this study to discuss the multi phase behaviour of the mixed oxides. The XRD pattern shows the Mn–V oxide is multiphase and quantitative phase analysis was performed to determine the relative phases. The overall results indicate that with increasing temperature, the AC conductivity, dielectric constant, dielectric loss factor and loss tangent of the Mn–V mixed oxide increases. However, it shows an overlap in the dielectric constant at 225 °C and 250 °C due to the V_2O_5 phase in the mixed oxide. From the AC activation energy, the mixed oxides underwent conduction mechanism transition from band to hopping in the investigated frequency range. The MnV_2O_6 has relatively good resistivity, therefore the mixed oxide sintered at 550 °C with the highest composition of MnV_2O_6 gives the highest dielectric constant of 9845 at 1 kHz, and at 250 °C.

Introduction

Composite materials have a wide variety of applications in electrical devices, mobile communication systems, etc. Therefore, composite tailoring was initiated to suit the specific needs for different usage. In the past decade, there have been several researches carried out with different metal oxides due to their application in various electronic devices such as smart window [1], optical detector [2], cathode coating in high-capacity lithium batteries [3], high performance capacitor [4], thermistor [5] and others.

Transition elements have mixed valence ions, hence those compounds have unique properties and are very useful in various fields. Manganese is one of the transition elements which has a formal oxidation state from −3 to +7 such as MnO, Mn_2O_3, Mn_2O_7, etc [6]. According to pervious works, composites containing MnO_2 such as V_2O_5 [7], SnO, As_2O_3 [8], CaO [4], Fe_2O_3 [9] etc were already investigated. Also, vanadium is a transition element with variation of oxidation state ranging from +5 to +2 and it exists in many phases such as VO, VO_2, V_2O_3 or V_2O_5 [10]. V_2O_5 is widely used in thin-films device application due to its phase transition behaviour which can alter its electrical and optical properties [11].

Gouda et al. prepared mixed oxides of manganese and vanadium at different mass ratio of Mn_2O_3 and VO_2 from 90:10 to 5:95 [7]. They found that the resistivity and the thermistor constant of beta or gamma form of $Mn_2V_2O_7$ are higher compared to the well known oxides of vanadium and binary/ternary oxides of manganese, nickel and cobalt. It meant that d-block electronic configuration of V^{5+} in $Mn_2V_2O_7$ contributed to higher resistivity [12]. Therefore, the mixed oxides with higher resistivity would increase its dielectric properties. Since the dielectric properties of Mn–V oxides system has not been reported, in this paper, the electrical conductivity and dielectric properties of mixed oxides of manganese and vanadium were studied at different measuring temperatures from 30 °C to 250 °C.

Experimental details

The mixed oxides were prepared by the conventional solid state method. The starting materials vanadium (V) oxide, V_2O_5 (99.5%) and manganese (IV) oxide, MnO_2 (99.95%) with high purity were weighed according to 40 mol% of V_2O_5 and 60 mol% of $2MnO_2$.

Acetone was added to the mixture and wet ball milled for 24 h. After the drying process in the oven, the mixture was precalcined in air at 450 °C for 4 h. The precalcined powders were added with the binder Polyvinyl Alcohol (PVA) at 1wt% and pressed at 4.5

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tonnes for 4 min to produce Mn–V oxide pellets. The pellets were finally sintered at 500 °C and 550 °C for 4 h and ready for characterization. To understand the relationship of different phases in the mixed oxide, the pure oxides MnO_2 (MO) and V_2O_5 (VO) were also prepared to compare with the binary oxides. The list of samples and their sintering temperatures are tabulated in Table 1.

The samples were examined by XRD to determine the microstructure and phase identification and the surfaces were visualized by using Field Emission Scanning Electron Microscopy (FESEM). The dielectric properties were determined using the Agilent 4294A Precision Impedance Analyzer from 30 °C to 250 °C and the sample was attached to the analyzer by sandwiching it between two copper electrodes. 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-sectional area of the sample. The AC conductivity σ_{ac} is determined from the dielectric parameter where, $\sigma_{ac} = \omega\varepsilon_o\varepsilon_r''$.

XRD were done to determine the phase identification and phase composition of the samples. Meanwhile, the composition of the phase consisted in each sample was determined by 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 via cooling process and their activation energies were determined and discussed. For dielectric properties, the dielectric behaviour of the samples was discussed at different measuring temperatures 30 °C to 250 °C for the frequency range of 40 Hz to 1 MHz.

Results and discussion

The samples were characterized for their structural, dielectric properties and electrical conductivity.

Structural 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 presented which are Manganese Divanadate, MnV_2O_6 (ICSD: 98-004-7436), Vanadium pentoxide, V_2O_5 (ICSD: 98-001-2286) and Manganese(IV) Oxide-beta, MnO_2 (ICSD: 98-001-2180) [13,14]. Practically, the single phase material is difficult to obtain because manganese and vanadium have many oxidation states [6,15] and quantitative phase analysis were performed in order to determine the percentage of the relative phase. As a result, the Rietveld Refinement analysis and the X'pert HighScore Plus software were used [16].

The XRD pattern of MVO500 and MVO550 are almost similar as shown in Fig. 1. At this stage, the Mn–V oxide is MnV_2O_6. However, the starting materials MnO_2 and V_2O_5 still remained. The increase in sintering temperature gives rise to the reaction between the starting materials to form MnV_2O_6. Therefore, the phase composition of MnO_2 and V_2O_5 decreases while MnV_2O_6 increases from

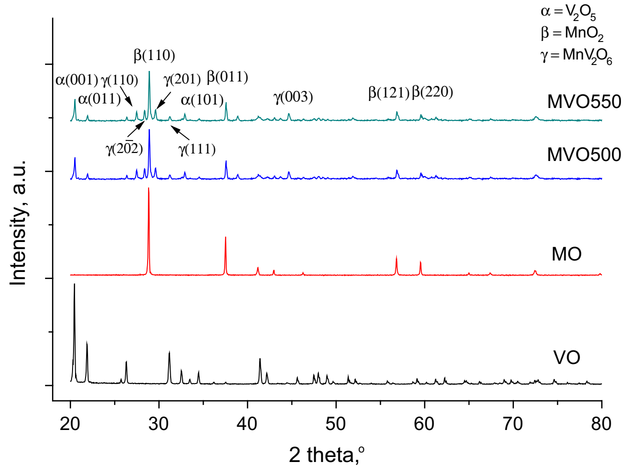

Fig. 1. XRD patterns of MO, VO, MVO500 and MVO550.

500 °C to 550 °C as shown in Table 2. Finally, we can conclude that a multiphase compounds was prepared. On the other hand, the XRD patterns of MO and VO show that the samples were successfully prepared with high purification which are MnO_2 and V_2O_5 respectively.

The morphology and grain size of the sample were determined by FESEM. 150 grains were taken randomly from the FESEM images to calculate their average grain size and this was tabulated in Table 3. Fig. 2(a) and (b) showed that the grain sizes of the starting materials are large. After mixing and wet ball milling for 24 h, the particles sizes were reduced as shown in Fig. 2(c) and (d). The grain size of MVO500 is small because the particles lack energy to react among themselves and only a small amount of diffusion between neighbouring particles occurred [17]. However, MVO550 began to attach to the neighbouring particles to grow and form a larger grain. Hence, better densification is possible at higher sintering temperature.

Electrical conductivity

AC conductivity is an electrical parameter that quantified the electrical conduction due to an applied electrical AC field in a material [18]. The AC conductivity, σ_{ac} of pure oxides and Mn–V oxide varies with different temperatures as shown in Fig. 3. The σ for the samples is found to follow the unique conductive properties of semiconductor that increases with increasing temperature. This may due to that the heat applied is able to excite more electron hops from the valence band to conduction band and increase the σ_{ac} [19]. The σ_{ac} is independent of frequency at low frequency region, but increases with frequency at the high frequency region. As temperature increases, the σ_{ac} becomes independent of frequency within 1 MHz at 250 °C. Therefore, the σ_{ac} can be described via Jonscher's universal power law [20].

$$\sigma_T(\omega) = \sigma_{dc}(0) + A\omega^s \quad (1)$$

where σ_T is the total conductivity, σ_{dc} is the DC conductivity, A is constant, ω is angular frequency and s is frequency exponent where

Table 1
List of samples at different sintering temperatures.

Sample name	Sintering Temperature, °C
MO	450
VO	600
MVO500	500
MVO550	550

Table 2
The phase composition of the compound contained in the sample of MVO500 and MVO550.

Sample	MnO_2 (%)	V_2O_5 (%)	MnV_2O_6 (%)	R-indices
MVO500	49.2	29.8	21.0	2.995
MVO550	40.4	19.5	40.1	1.907