Original Article

Modification of optical and electrical properties of nanocrystalline VO₂·0.5 H₂O/ZrV₂O₇: influence of Cs, Cr and Ga doping

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A facile and economical route has been demonstrated for large-scale synthesis of nano VO₂·0.5 H₂O/ZrV₂O₇ and it is doping with Cs, Cr and Ga using combined precipitation-hydrothermal that followed by a gentle heating at low temperature. The growth mechanism of doping is discussed and investigated by XRD, SEM, TEM, Raman, TGA, DSC, and UV-vis spectroscopy. The band gap is enhanced with doping. The results show that the all composites have a negative thermal coefficient in the range 25–100 °C while it has a positive thermal coefficient in the range 100–300 °C. Also, Cs doped has increase in conductivity as compared to Cr doped which may be due to the enhancement of oxygen vacancies as resulted from addition of low valence cations. Doping with Cr or Cs show the contribution of grain and grain boundary properties, respectively, while the doping with Ga shows the insulating behavior.

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1. Introduction

Zirconium pyrovanadate (ZrV₂O₇) belongs to the cubic AM₂O₇ family with an A⁴⁺ cation (Zr, Ti, Pb, Sn, Si, Th, Hf, etc.) and (M₂O₇)⁻ anion. It also has a framework structure with space group symmetry Pm3m, Z = 4. It is built on corner linked AO₆ octahedra and linear M₂O₇ units [1,2]. It displays two first order structural phase transitions at 77 and 102 °C [3]. ZrV₂O₇ is attributed to a 3 × 3 × 3 superstructure at room temperature (RT) which vanishes above 102 °C.

The superstructure of ZrV₂O₇ is established from single crystal synchrotron data, high-resolution neutron powder diffraction data, and electron diffraction studies [4,5]. ZrV₂O₇ has attracted great attention because it exhibits a strong isotropic negative thermal expansion (NTE) behavior for the

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temperature up to 800 °C which can be added to a positive thermal expansion material in order to create composite materials which exhibit a low or zero thermal expansion [5]. Also, it has exhibited good electrical conductivity which, related to semiconductor n-type, behavior ranged from $10^{-3}$ to $10^{-6}$ Ω⁻¹ cm⁻¹ with an activation energy of 0.2 eV devoted to be due to V⁴⁺ defects [6]. Moreover, it has been successfully utilized as an inorganic ion exchange for removing heavy metal ions from an aqueous solution as well as it has good photocatalytic activities for degradation of different dyes [2,7–10]. From the aforementioned characteristics of ZrV₂O₇, it is evident that it has many important functions with great research value.

It is well-known that various applications especially in catalysis or composites having a high purity, and homogeneous morphology is essential [11]. The difficulties of the fabrication of ZrV₂O₇ are significant as well as the reaction between ZrO₂ and V₂O₅ has been described as “extraordinarily slow”. Several preparation methods have been reported for the synthesis of ZrV₂O₇ nanopowder such as the solid-state reaction between ZrO₂ and V₂O₅ at high temperatures [12], sol–gel [6], co-precipitation route [13], and the solution combustion method [2]. But these methods are complex, which may reduce the large scale application of ZrV₂O₇. Therefore, it is crucial to develop simple and environmentally friendly synthesis methods for practical application of ZrV₂O₇ and hence becomes a significant topic for investigation.

Another severe challenge for the alteration of the structure, morphology, thermal and electrical properties of ZrV₂O₇ is through doping, which is the practice of adding impurities to ZrV₂O₇. Many efforts have been devoted to modifying the properties of ZrV₂O₇. It is doped with zirconia and vanadium (V) oxide by solid state reaction and sol–gel methods. It has been found that the doping does not affect the crystal structure neither nor its thermal properties [14]. While other researchers found out that the photo-catalytic activity of synthesized molybdenum doped zirconium vanadate produced from the solution combustion method is enhanced toward the degradation of non-azoic dyes compared with its parent zirconium vanadate [2]. Yanase et al. [13] reported that the substitution (Nb,Y) for Zr of ZrV₂O₇ is effective for the suppression of superstructure formation, and that such suppression is more effective than that in the case of P substitution for V of zirconium vanadate. According to the literature, the substitution of Fe for Zr⁴⁺ in ZrV₁.₅P₀·₅O₇ could further reduce the phase transition temperature and thermal expansion [15].

The purpose of this study is to allow us to establish the fundamental relationship between the physicochemical characteristics of the doping Cs, Cr, and Ga onto VO₂-0.5 H₂O/ZrV₂O₇ and the reactive properties and provide an important understanding about how to alter the properties by doping of ZrV₂O₇. The goal of this research will be highlighted through (i) developing a versatile, effective, low-cost and simple synthesis of (Cs, Cr or Ga)-doped VO₂-0.5 H₂O/ZrV₂O₇ using hydrothermal technique, (ii) discussing the effect of doping on the morphological, structural, thermal and optical properties by employing the physicochemical methods, (iii) investigating the electrical and ionic conductivity of prepared samples, in which the ionic conductivity in VO₂-0.5 H₂O/ZrV₂O₇ is closely related to oxygen-vacancy formation and migration properties.

2. Materials and methods

2.1. Synthesis of VO₂-0.5 H₂O/ZrV₂O₇ nanopowder and its doping by hydrothermal method

A sodium vanadate (NaVO₃, 99%, Acros, USA) solution was prepared by dissolving 2.5 g with 100 ml ultra pure water in the presence of 0.1 M hydrochloric acid (HCl, 37%, Aldrich, USA) with gentle heating at 40 °C and then after cooling, a sodium vanadate solution was added into a solution of 0.1 M zirconium oxychloride (ZrOCl₂·8H₂O, 98%, Acros, USA) containing 0.01 M of doped element cesium chloride (CsCl, 99%, Applichem, Germany) or chromium chloride (CrCl₃·6H₂O, 95%, Shree Ganesh Chemicals Pvt. Ltd., India) or 0.02 M of gallium III sulfate (Ga₂(SO₄)₃, 99.99%, Aldrich, USA). A fine yellow precipitate of VO₂-0.5 H₂O/ZrV₂O₇ with doped element was obtained and the mixture was heated under pressure 500 KPa (5 bar) at 120 °C for 1 hour using stainless steel lined autoclave. The reaction mixture was diluted in 11 of ultra pure water and allowed to settle for 24 h for complete digestion. The formation of the precipitate was free from the chloride ions and then washed, filtered thoroughly and dried by gentle heating at 40 °C.

2.2. Characterization of the synthesized doped VO₂-0.5 H₂O/ZrV₂O₇

X-ray diffraction analysis (XRD) was carried out with a Shimadzu-XRD-7000 Diffractometer (Japan), at room temperature with Cu Ka radiations of wavelength ($\lambda$ = 1.5406 Å), generated at 30 kV–30 mA. Morphology of the synthesized powders was studied with a scanning electron microscope (SEM) (JEOL JSM-6360 LA, Japan) with a power supply of 30 kV. The composition and elemental studies of VO₂-0.5 H₂O/ZrV₂O₇ and its doped samples were carried out by energy dispersive X-ray (EDX) combined with transmission electron microscope (TEM) (JEOL JEM 1230, Japan) with Max. Mag. 600x and resolution 0.2 nm. Thermal characteristics were measured by thermogravimetric analysis (TGA-50H, Shimadzu [Japan]) with heating rate 10 °C/min up to 800 °C under flow of N₂. Differential scanning calorimetry (DSC) was performed with a heat flux Shimadzu DSC-60A (Japan) in N₂ atmosphere, flow rate 30 ml/min, temperature range 30–800 °C and heating rate 10 °C/min. The optical properties of VO₂-0.5 H₂O/ZrV₂O₇ with different dopant elements were studied at room temperature using UV–vis. Spectroscopy (Labomed, Inc., model: UVD-2950, USA) can be used to determine the nature and value of the optical band gap. The relation between the absorption coefficients ($\alpha$) and the incident photon energy ($hv$) is shown in the following equation

$$\alpha hv = A(hv - E_g)^n$$  

where A is a constant and $E_g$ is the band gap of the material and exponent n depends on the type of transition. For direct allowed $n = 1/2$, indirect allowed transition, $n = 2$, and for direct forbidden, $n = 3/2$. To measure the energy band gap from the absorption spectra a graph of ($\alpha hv$)² versus hv was plotted and
the extrapolation of the straight line to \((ahv)^2 = 0\) axis gives the value of the energy band gap.

The different synthesized samples were pressed in cold in discs of about 13 mm diameter at a pressure of 80 MPa using a hydraulic press to facilitate the measurement of electrical properties. Pellets of two opposite sides were coated with silver paste. The impedance analysis of these materials was carried out using a computer controlled Gamry instrument a potentionstat/galvanostate, Gamry Instruments (model: Zr,G750) at frequency range 0.01–300 kHz. The data collected was analyzed in the form of impedance plots. The bulk resistance of the samples was determined for the complex impedance plots.

The relation between bulk electrical conductivity \(\sigma\) and the temperature from 25 to 300 °C can be expressed as an exponential function of the activation energy \(E_a\) [16].

\[
\sigma = \sigma_0 / T \cdot \exp(-E_a / k_B T)
\]

where \(T\) stands for temperature, \(k_B\) for the Boltzman constant, and \(\sigma_0\) for a temperature independent prefactor. The resistance of the discs was measured using the Digital multimeter Keithley (model: 6514, USA). The discs were heated at the rate of 5 °C/min using furnace (Carbolite, Aston Lane, England).

The bulk conductivity of various samples was studied using AC impedance and DC resistance measurements. The DC resistance remains constant provided that the external conditions like temperature, moisture, pressure, etc. are fixed. The current flows uniformly through the cable and for most cases; the current density at all points is the same.

\[
R = \rho l / A
\]

where \(R\) is AC resistance (measured in ohms, \(\Omega\), \(\rho\) is electrical resistivity (measured in ohmometers, \(\Omega\) m), \(l\) is the length of the piece of material (measured in meters, m) and \(A\) is the cross-sectional area of the specimen (measured in square meters, m²).

The AC resistance is frequency dependent and it does not remain constant with a variation in frequency. The following equation represents the different components of the impedance:

\[
Z = R + jX
\]

where \(Z\) is the impedance, \(R\) is the real part of the impedance which is the resistance and \(X\) is the imaginary part composed of the inductive and capacitive reactance. At zero frequency \(Z = R\). The AC conductivity is calculated by using the relation:

\[
\sigma_{\text{total}} = \tau / \text{R}_{\text{total}} \times A
\]

where \(\tau\) is the thickness, \(A\) is the area of cross-section area and \(R\) is the resistance of the sample [17]. The total AC electrical conductivity of a substance is the sum of the partial conductivities \(\sigma_i\):

\[
\sigma_{\text{total}} = \sum \sigma_i = \sigma_g + \sigma_{gb} + \sigma_e
\]

where \(\sigma_g\) is the electrical conductivity of grains, \(\sigma_{gb}\) is the electrical conductivity of grain boundary and \(\sigma_e\) is the electrical conductivity of the electrodes.

### 3. Results and discussions

#### 3.1. Mechanism formation of VO$_2$.9 H$_2$O/ZrV$_2$O$_7$ and its doping

The ideal cubic structure of ZrV$_2$O$_7$ can consist of corner-sharing VO$_4$ (green) tetrahedral and ZrO$_6$ (rose) octahedral which has been shown in Fig. 1. It is considered as related to the NaCl structure type (space group Fm3m), with the ZrO$_6$ octahedron centered at the ideal Na site and the bridging oxygen of the VO$_2$O$\gamma$ group (O$_2$V-O-VO$_3$) at the Cl site [18]. The Zr cations lie in the interlayer space, coordinating with the nearest six oxygen atoms to build ZrO$_6$ octahedral chains, which are separated from each other by VO$_4$ tetrahedral double chains. Each VO$_4$ tetrahedra share three of its four O atoms with a ZrO$_6$ octahedron, whilst the fourth is shared with another VO$_4$ tetrahedron leading to a V$_2$O$_7$ pyrovanadate group (Fig. 1) [18,19].

The weaker reflection of the superstructure of cubic ZrV$_2$O$_7$ indicates the two linear V-O-V linkages [17]. The six linear V-O-V linkages endow much higher structure symmetry than superstructure ZrV$_2$O$_7$. The cell edge at room temperature is \(3 \times 8.77\) Å = 26.3 Å [20]. Zr is located at the 4a (3 fold axis) Wycoff site. V atom occupies 8c (3-fold axis) Wycoff site [2]. The Cs position is assigned to this site. It is noticeable that in the crystal structure of VO$_2$.05 H$_2$O/ZrV$_2$O$_7$ and other substituted compounds such as Cr and Ga, there has been only one position identified for V and the substituted surrogate atom [2]. In ZrV$_2$O$_7$, because of the presence of the “bridging” O atom, the tetrahedra form a pyrovanadate group, and a center of inversion is introduced in the system unlike that in cubic ZrW$_2$O$_8$ [21].

The ionic radius is the most important condition, which can strongly influence the ability of the dopant to enter into VO$_2$.05 H$_2$O/ZrV$_2$O$_7$ crystal lattice. If the ionic radius of the
doping metal ions matches those of the lattice metal ion in oxides, the doping metal will substitute the metal ion for the lattice in the doping reaction process (substitution mode) that may happen to (Cr\(^{3+}\) = 0.0755 nm or Ga\(^{3+}\) = 0.076 nm) to substitute V\(^{3+}\) = 0.078 nm in VO\(_2\)·0.5 H\(_2\)O/ZrV\(_2\)O\(_7\) crystal lattice. While if the ionic radius of the dopant is much bigger (Cs\(^{+}\) = 0.181 nm) or smaller (Cr\(^{3+}\) = 0.0755 nm, Ga\(^{3+}\) = 0.076 nm) than that of Zr\(^{4+}\) = 0.087 nm, the dopant substituting for VO\(_2\)·0.5 H\(_2\)O/ZrV\(_2\)O\(_7\) crystal lattice ions must result into crystal lattice distortion (CLD). So, the different dopant can be isomorphously substituted or interstitially introduced into the matrix of VO\(_2\)·0.5 H\(_2\)O/ZrV\(_2\)O\(_7\) to produce oxygen vacancies. The introduced Cr\(^{3+}\), Ga\(^{3+}\) has a larger possibility to substitution V\(^{3+}\) rather than Zr\(^{4+}\) due to the larger valence difference between Cr\(^{3+}\), Ga\(^{3+}\) and Zr\(^{4+}\) [22]. The bond angle of V–O–V extends from an obtuse to a flat angle after doping. The extension of bond angles could cause the phase transition from a 3 × 3 × 3 cubic superstructure to a normal parent cubic structure in the material at room temperature [22].

3.2. Effect of the doping on the crystalline properties

Room temperature X-ray diffraction (XRD) patterns of VO\(_2\)·0.5 H\(_2\)O/ZrV\(_2\)O\(_7\) and its doped samples are shown in Fig. 2. It shows that the XRD pattern of VO\(_2\)·ZrV\(_2\)O\(_7\) indicates some degree of crystallinity of ZrV\(_2\)O\(_7\) and the compound can be considered as a polycrystalline. Where the (002) reflection (plane) of VO\(_2\)·0.5 H\(_2\)O tetragonal phase (JCPDS 01-089-6930) that appear at 2\(\theta\) = 11.320\(^\circ\) [2], while the (421), (630) and (127) reflection planes which are presented at 2\(\theta\) = 15.438\(^\circ\), 22.754\(^\circ\) and 24.861\(^\circ\) respectively for cubic phase ZrV\(_2\)O\(_7\) (JCPDS 16-0422) is due to the interaction between ZrO\(_2\) and V\(_2\)O\(_5\) which is extraordinarily slow. Also, it is indicated that the vanadium ions occupied the zirconium ions at their lattice position and low dispersion of vanadia ions on the zirconium surface [23].

In contrast to the pure VO\(_2\)·0.5 H\(_2\)O/ZrV\(_2\)O\(_7\) nano powder, the characteristic peaks of VO\(_2\)·0.5 H\(_2\)O are broadened when the ions doped into VO\(_2\)·0.5 H\(_2\)O/ZrV\(_2\)O\(_7\). This leads to the formation of a very fine size particles. In addition, no obvious diffraction peaks arising from the possible impurity phases such as Cs\(_2\)ZrO\(_3\), Cr\(_2\)O\(_3\), Cs\(_2\)O or Ga\(_2\)O\(_3\), etc. are observed in X-ray (Fig. 2b, c or d). It is indicated that the Cs\(^{+}\), Cr\(^{3+}\), and Ga\(^{3+}\) are dispersed uniformly onto VO\(_2\)·0.5 H\(_2\)O/ZrV\(_2\)O\(_7\) nanoparticles in the form of small clusters Cr\(_2\)O\(_3\), Cs\(_2\)O or Ga\(_2\)O\(_3\). Also, it demonstrates that the quantity of the dopant elements is very small that cannot be detected by XRD [24]. However, a reduction in intensity is observed with the addition of dopant elements which may be referred to the crystallization of the VO\(_2\)·0.5 H\(_2\)O is reduced [25]. In addition, by comparing the XRD patterns of the pure VO\(_2\)·0.5 H\(_2\)O nanoparticles with Cs dopant (Fig. 2c), there is less shifting of all peaks toward a lower diffraction angle, which corresponds to the increase of the interlayer distance due to the partial replacement of V atoms in VO\(_2\)·0.5 H\(_2\)O by Cs atoms with a larger ionic radius, while by comparing the XRD patterns of the pure ZrV\(_2\)O\(_7\) nanoparticles with Ga dopant (Fig. 2d), there is less shifting of all peaks toward a higher diffraction angle, which corresponds to the decrease of the interlayer distance due to the partial replacement of V atoms in ZrV\(_2\)O\(_7\) by Ga atoms with a smaller ionic radius. According to the XRD results discussed above, it can be concluded that the order–disorder transformation is also affected by doping but it is not observed from XRD due to the low amount of doping.

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Fig. 2 – XRD of: (a) VO\(_2\)·0.5 H\(_2\)O/ZrV\(_2\)O\(_7\) without dopant, (b) Cr doped VO\(_2\)·0.5 H\(_2\)O/ZrV\(_2\)O\(_7\), (c) Cs doped VO\(_2\)·0.5 H\(_2\)O/ZrV\(_2\)O\(_7\) and (d) Ga doped VO\(_2\)·0.5 H\(_2\)O/ZrV\(_2\)O\(_7\).
Fig. 3 – SEM image of: (a) VO$_2$·0.5 H$_2$O/ZrV$_2$O$_7$, (b) Cr doped VO$_2$·0.5 H$_2$O/ZrV$_2$O$_7$, (c) Cs doped VO$_2$·0.5 H$_2$O/ZrV$_2$O$_7$ and (d) Ga doped VO$_2$·0.5 H$_2$O/ZrV$_2$O$_7$.

Fig. 4 – TEM of: (a) VO$_2$·0.5 H$_2$O/ZrV$_2$O$_7$, (b) Cr doped VO$_2$·0.5 H$_2$O/ZrV$_2$O$_7$, (c) Cs doped VO$_2$·0.5 H$_2$O/ZrV$_2$O$_7$ and (d) Ga doped VO$_2$·0.5 H$_2$O/ZrV$_2$O$_7$. 

3.3. Effect of doping on the morphological properties

The morphological characteristics of VO$_2$·0.5 H$_2$O/ZrV$_2$O$_7$ and its dopant samples have been observed by SEM and TEM images (Figs. 3–5). It can be seen that the morphological features are the nonuniform distribution of nanoparticles for all prepared samples. This is due to the multiple nucleation processes during the reactions. A VO$_2$·0.5 H$_2$O/ZrV$_2$O$_7$ and its dopant samples consist of the agglomerated particles, and particle morphology exhibits an irregular shape. While for doped samples, it is observed that all samples have a pseudo-spherical structural morphology and a higher homogeneity than the parent VO$_2$·0.5 H$_2$O/ZrV$_2$O$_7$ (Fig. 3b–d).
The same results agree with the TEM images of the samples (Fig. 4). It is indicated that the all samples are very fine and agglomerated with sizes in the few tens of nanometers. The average particles size of the Cr and Ga dopant samples is smaller than that of the parent VO$_2$/ZrV$_2$O$_7$ while for Cs dopant, the particles obviously are not affected significantly. These results may be attributed to the presence of dopant components in the VO$_2$/ZrV$_2$O$_7$ as well as the ionic radius of the dopant.

The EDX analysis of the doped samples shows homogeneous Cr, Cs, Ga-distribution at Fig. 5. The high amount of Cs in the distribution TEM is due to the larger ionic radii of Cs$^{3+}$ rather than Zr$^{4+}$ and V$^{4+}$ which is difficult to make a substitution. On the contrary, the substitution of Cs$^{3+}$ or Ga$^{3+}$ is easier thanks to the smaller ionic radii than those of V$^{4+}$.

3.4. **Effect of doping on the structural properties**

Raman spectroscopy is also useful to identify the dependence on the crystalline structure of VO$_2$-0.5 H$_2$O/ZrV$_2$O$_7$ and its effect of the doping on the substitution of Cs, Ga, and Cr of the lattice structure. The assignments of observed Raman bands are made on the basis of the reported literature [24,25]. No significant spectral changes can be seen upon the doping of Cs, Cr and Ga into the VO$_2$-0.5 H$_2$O/ZrV$_2$O$_7$. In Fig. 6, it is shown that the Raman shifts at 138, 241, 281, 372, 673, 963 and 992 cm$^{-1}$ are characteristic for ZrV$_2$O$_7$ [26]. The strong band at 673, 963 and 992 cm$^{-1}$ is basically assigned to the V=O symmetric stretching mode of the bulk V$_2$O$_5$ (VO$_x$ tetrahedra) [27,28]. Also, the Raman bands located between 300 and 550 cm$^{-1}$ are assigned to symmetric and asymmetric bending of the VO$_4$ tetrahedra [29]. The weak intensity of this band at Cs and Cr doped VO$_2$-0.5 H$_2$O/ZrV$_2$O$_7$ indicated that the low concentration of bulk V$_2$O$_5$ and doping is occurring successfully [22]. The mode located at 372, 281, and 241 cm$^{-1}$ is attributed to symmetric bending of the VO$_4$ tetrahedron while that at 508 cm$^{-1}$ is caused by asymmetric bending of VO$_4$ tetrahedron [5]. The mode centered at 992 and 673 cm$^{-1}$ represents the symmetric stretching and asymmetric stretching of the VO$_4$ tetrahedra in the VO$_2$-0.5 H$_2$O/ZrV$_2$O$_7$, respectively [5]. The band at 330, 482 cm$^{-1}$ indicate that the presence of VO$_2$ is not obtained and it is included in VO$_2$-0.5 H$_2$O/ZrV$_2$O$_7$ [30]. The lower Raman bands below 300 cm$^{-1}$ may arise from the lattice modes especially the band at 138 cm$^{-1}$ [31]. The band at 281 cm$^{-1}$ is assigned to the symmetric ZrO$_6$ octahedral stretching. The first obvious change of the Raman spectra is that the symmetric stretching band becomes a weaker and broader in the samples Cr and Cs. Simultaneously distinct change and shifts take place to the new higher and broader Raman band around at 955 cm$^{-1}$ with an increase of the relative intensity as well as the disappearance of the band 963 cm$^{-1}$ for the sample of Ga (Fig. 6d). These results are consistent with previous studies V$_2$O$_5$/ZrO$_2$ which have also confirmed the formation of ZrV$_2$O$_7$ [18].

3.5. **Effect of doping on the thermal properties**

It is clear from Figure S1 that the TGA is similar for all samples, but the percentage of mass losses varied slightly at all samples. The percentage of the weight loss of VO$_2$-0.5 H$_2$O/ZrV$_2$O$_7$ and its doped samples is presented in Table 1. It decreases with increasing temperature up to 400°C. Above 400°C, the weight losses of material tend to be negligible. This means that, no structural change occurs in the materials, and the external and structural water is lost [27,32,33]. The weight loss at temperatures from room temperature to 128°C corresponds to the removal of physically adsorbed water while the weight lost is observed over 128°C to 400°C which indicates structural water. It has also been noted that the total weight loss for a sample prepared by hydrothermal technique is 18.13% [27,34]. These weight losses are approximately equivalent to the removal of both physically adsorbed and structural water.

\[
\text{VO}_2 \cdot 0.5 \text{H}_2\text{O}/\text{ZrV}_2\text{O}_7 \xrightarrow{\Delta} \text{ZrV}_2\text{O}_7 + \text{VO}_2 + 0.5 \text{H}_2\text{O} \uparrow \tag{7}
\]

The DSC profiles for samples are studied in Figure S2 which showed a broad endothermic peak in the temperature region from room temperature to about 160°C which is attributed to the gradual loss of external water molecules. The broad peak at 70°C is assigned to the VO$_2$ nanoparticles for undoped samples while it shifts to around 83°C for the doped samples. This peak followed by a broad shoulder, which is terminated in another small inflexion peak at

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Residues (%)</th>
<th>Band gap (eV)</th>
<th>$\sigma_{AC} \times 10^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO$_2$-0.5 H$_2$O/ZrV$_2$O$_7$</td>
<td>81.63</td>
<td>2.14</td>
<td>3.5 Ω$^{-1}$ cm$^{-1}$</td>
</tr>
<tr>
<td>Cr doped VO$_2$-0.5 H$_2$O/ZrV$_2$O$_7$</td>
<td>83.23</td>
<td>2.34</td>
<td>0.8 Ω$^{-1}$ cm$^{-1}$</td>
</tr>
<tr>
<td>Cs doped VO$_2$-0.5 H$_2$O/ZrV$_2$O$_7$</td>
<td>84.89</td>
<td>2.42</td>
<td>1.83 Ω$^{-1}$ cm$^{-1}$</td>
</tr>
<tr>
<td>Ga doped VO$_2$-0.5 H$_2$O/ZrV$_2$O$_7$</td>
<td>82.57</td>
<td>2.17</td>
<td>Insulator</td>
</tr>
</tbody>
</table>

![Raman spectra of (a) VO$_2$-0.5 H$_2$O/ZrV$_2$O$_7$, (b) Cr doped VO$_2$-0.5 H$_2$O/ZrV$_2$O$_7$, (c) Cs doped VO$_2$-0.5 H$_2$O/ZrV$_2$O$_7$, and (d) Ga doped VO$_2$-0.5 H$_2$O/ZrV$_2$O$_7$.](image)
\[ \text{ZrV}_2\text{O}_7 \rightleftharpoons \text{ZrO}_2 + \text{V}_2\text{O}_5 \] (8)

3.6. Effect of doping on the optical properties

The optical properties of VO\(_2\cdot0.5\) H\(_2\)O/ZrV\(_2\)O\(_7\) and its doped samples are investigated at room temperature as shown in Fig. 7. Extrapolating of the straight-line portion of the plots to the X-axis gives the corresponding \(E_g\) (optical band gap) value of VO\(_2\cdot0.5\) H\(_2\)O/ZrV\(_2\)O\(_7\) which is approximately 2.14 eV. From Fig. 7, it is clearly demonstrated that the electronic structure of VO\(_2\cdot0.5\) H\(_2\)O/ZrV\(_2\)O\(_7\) is changed by Cr, Cs, and Ga doping. When Cr\(^{3+}\), Cs\(^{1+}\) and Ga\(^{3+}\) are doped, the spectra moved toward a shorter wavelength region compared to that of pure VO\(_2\cdot0.5\) H\(_2\)O/ZrV\(_2\)O\(_7\). Hence, there is an increase in the band gap value of 2.34 and 2.42 for doping of Cr\(^{3+}\) and Cs\(^{1+}\), respectively, while the band gap of Ga\(^{3+}\) changed to longer wavelength to 2.17 (Table 1). These results may be attributed to the quantum confinement effect and changes in the density of dislocations [36–38].

3.7. The electrical behavior of doped nano VO\(_2\cdot0.5\) H\(_2\)O/ZrV\(_2\)O\(_7\)

In this study, the electrical properties of VO\(_2\cdot0.5\) H\(_2\)O/ZrV\(_2\)O\(_7\) and that with different dopants are checked by using two-point DC conductivity and impedance measurements.

3.8. Effect of temperature on the electrical conductivity

The relationship between bulk electrical conductivity and temperature from 25 to 300 °C for nano VO\(_2\cdot0.5\) H\(_2\)O/ZrV\(_2\)O\(_7\) and its dopant are investigated. Fig. 8a presents the variations of conductivity (\(\sigma\)) with reciprocal temperature from 25 to 100 °C for VO\(_2\cdot0.5\) H\(_2\)O/ZrV\(_2\)O\(_7\) and its dopant as Arrhenius plots. It is notable that VO\(_2\cdot0.5\) H\(_2\)O/ZrV\(_2\)O\(_7\) and its dopants have a negative thermal coefficient, and the conductivity of VO\(_2\cdot0.5\) H\(_2\)O/ZrV\(_2\)O\(_7\) is approximately affected by the dopant addition with order undoped > Cr doped > Ga doped > Cs doped. While, as shown in Fig. 8b, VO\(_2\cdot0.5\) H\(_2\)O/ZrV\(_2\)O\(_7\) and its dopants have an increase in the conductivity with rise in temperature. In other words, they have a positive thermal coefficient in the temperature range 100–300 °C, which indicates the behavior of the samples like that of a semiconductor. The addition of a dopant is not affected significantly at this range. Generally, it is clear noted that when the material has been heated up to 300 °C, the conductivity values have obviously increased with the amount...
of oxygen vacancy which is caused by the addition of low valance cations as Cs\textsuperscript{+} content \cite{39,40}. These results have led to the discovery of a novel type of oxygen-ion conductor which can be developed by improving the ionic conductivity of VO\textsubscript{2}·0.5 H\textsubscript{2}O/Zr\textsubscript{2}O\textsubscript{7} as mentioned regarding the ceramic material ZrW\textsubscript{2}O\textsubscript{8} \cite{40}.

### 3.9. Effect of doping of VO\textsubscript{2}·0.5 H\textsubscript{2}O/Zr\textsubscript{2}O\textsubscript{7} on ionic conductivity

Cubic Zr\textsubscript{2}O\textsubscript{7} structure has the unshared terminal oxygen ion of the VO\textsubscript{4} tetrahedron may be hopped between two equivalent sites accompanied by breaking and rebuilding of the bond between vanadium and the terminal oxygen \cite{2}. This process seems to be similar to the oxygen migration responsible for the ionic conductance observed in Ln\textsubscript{2}O\textsubscript{3} stabilized ZrO\textsubscript{2} and CeO\textsubscript{2} solid electrolytes \cite{2,40}. It is well known that more oxygen vacancies can be produced in selected solid solutions containing substituted low-valent ions \cite{40–42}. Thus, it may be expected that low-valent ions introduced in the crystal lattice of Zr\textsubscript{2}O\textsubscript{7} or VO\textsubscript{2} may modify its conductivity. With this consideration in mind, a study has been made referring to the mono-valent cations of cesium and tri-valent cations as chromium and gallium.

Impedance spectroscopy (IS) is used to evaluate the grain and grain boundary resistances (R\textsubscript{g} and R\textsubscript{gb}) of undoped and doped VO\textsubscript{2}·0.5 H\textsubscript{2}O/Zr\textsubscript{2}O\textsubscript{7}. Fig. 9 shows the complex impedance spectrum (Nyquist plots, i.e., Z’ versus Z”) at room temperature for undoped and doped VO\textsubscript{2}·0.5 H\textsubscript{2}O/Zr\textsubscript{2}O\textsubscript{7}. The impedance spectra are composed of one arc or two and the intercepts of the semicircular arc at high frequency with the real axis [Z] give us the bulk resistance of the material. The bulk conductivity values are tabulated in Table 1. Characteristically, as shown before from XRD and SEM and TEM data, the VO\textsubscript{2}·0.5 H\textsubscript{2}O/Zr\textsubscript{2}O\textsubscript{7} acts as a polycrystalline material that exhibited the intergranular films. Thus, their oxygen ion conductivity comprises grain and grain boundary contributions \cite{40,43}.

The electrical properties and crystal structure of the prepared materials are well known to be closely related. As shown in Fig. 9a, a single semicircle obtained at high frequency is attributed to the superposition of grain and grain boundary effects. The bulk conductivities (grains and grain boundaries conductivities), as terminated from the high frequency intercepts on the real axis for polycrystalline VO\textsubscript{2}·0.5 H\textsubscript{2}O/Zr\textsubscript{2}O\textsubscript{7}, show no dependence on the grain size. This effect which is due to the distinction between grain and grain boundary regions tends to be vanished as the grain size is reduced to the nanometer regime \cite{44}. In other words,
the grains conductivities are the dominant element in this phenomenon.

On the other hand, Cr doped VO₂·0.5 H₂O/ZrV₂O₇ Nyquist plots also obtained as a single semicircle at high frequency which attributed to the contribution of grain properties (Fig. 9b). While Nyquist plots for Cs doped VO₂·0.5 H₂O/ZrV₂O₇ have been observed as two overlapping semicircular arcs at low frequencies which attributed to the contribution of grain boundary properties as in Fig. 9c [38–40,45]. This indicates that the electrolyte/electrode interfaces are not blocking the charge-carrying species. This may be due to the presence of some electronic conductivity. Moreover, if the charge transport is entirely due to the electronic species may be present at low frequencies which indicate that the conductivity has two components namely electronic and ionic conductivity but the ionic conductivity is the dominant [20]. But Nyquist plots for Ga doped VO₂·0.5 H₂O/ZrV₂O₇ have been observed as the straight lines with large slopes (Fig. 9d), which indicates the insulating behavior of the material [45] which may be due to the fact the gallium doped ZrV₂O₇ has higher molar dopants concentration (0.02 M) than that for Cr and Cs doped ZrV₂O₇ molar concentration (0.01 M). Therefore, by increasing the concentration of the dopants, which may decrease the number of mobile oxygen ions due to trapping of the oxygen ion vacancies [20,38]. In conclusion, the oxygen vacancies is produced from point defect chemistry and stoichiometry which can be controlled by doping in different oxygen partial pressure conditions [46].

It is clear from the SEM and TEM results and Table 1, that the addition of Cr and Cs dopants led to decreased particle size (due to boundary pinning), increased particle boundary volume, and reduced total ionic conductivity [45]. The increase in conductivity of the undoped VO₂·0.5 H₂O/ZrV₂O₇ is probably due to its high densification structure (less porosity). Also, the correlation of the intragranular conductivity and intergranular conductivity with the microstructures of the material explains the transportation of oxygen ions through the material. The schematic diagram for the oxygen ions transported through the intragranular is proposed and shown in Fig. 10. The intragranular conductivity dominates almost exclusively the relative density and insensitivity of the electrolyte grain size, while conversely, the apparent intergranular conductivity is strongly related to both the relative density and the grain size of the electrolyte grain [47]. As to the Cs doped VO₂·0.5 H₂O/ZrV₂O₇, the conductivity value obviously increases compared to Cr doped VO₂·0.5 H₂O/ZrV₂O₇. This may be attributed to the increase in the amount of oxygen vacancy which is caused by the addition of low valance cations as Cs⁺⁺ content [39,40].

4. Conclusions

Based on the results of this study, the following points can be concluded:

1. The XRD patterns show there is no obviously effect when different dopants are added to the crystal structure of nano composite VO₂·0.5 H₂O/ZrV₂O₇.
2. The doping greatly affects the morphology of nano composite VO₂·0.5 H₂O/ZrV₂O₇.
3. The optical band gap is increased by doping addition which may be the effect of quantum size and reduction in the particle size.
4. The relationship between conductivity and temperature obey the order: undoped > Cr > Ga > Cs in terms of negative thermal coefficient at the range 25–100 °C while at the range 100–300 °C it has a positive thermal coefficient without any effect of doping.
5. Cs doped has increase in conductivity as compared to Cr doped which shows the contribution of grain and grain boundary properties, respectively, while the doping with Ga shows the insulating behavior.

Conflicts of interest

The authors declare no conflicts of interest.

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Appendix A. Supplementary data


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