Influence of sodium excess in nanocrystalline xNa-(80-x)V$_2$O$_5$-20MoO$_3$.nH$_2$O thin films on their electrical and structural properties

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Abstract

Nanocrystalline thin film of xNa-(80-x)V$_2$O$_5$-20MoO$_3$.nH$_2$O xerogel obtained by sol gel synthesis. Transimition electron microscopy (TEM), density, electrical properties and thermoelectric power of the as prepared nanocrystalline xNa-(80-x)V$_2$O$_5$-20MoO$_3$.nH$_2$O xerogel thin films ($8 \leq x \leq 26$ mol%) were investigated. These films have been produced by the sol–gel technique (colloidal route). TEM revealed that the samples have nanorods. The particle size was found to be about 10.1 nm. The density of the samples increases with increasing Na-content. The samples are changes in thermoelectric power from n - type to p - type semiconductors with increasing Na-content. The electrical conductivity shows that all samples are semiconductor and it increases with increasing Na-content and the activation energy decreases with increasing Na-content. From the best fits, reasonable values of various small polaron hopping parameters were obtained. The electrical conduction at $T > \theta_D/2$ was due to non-adiabatic SPH.

1. Introduction

Vanadium oxide gels have been known for a long time. They can be described as nanocomposites made of water molecules trapped within a vanadium oxide network. They exhibit a wide range of electronic and ionic properties [1]. The vanadium oxide network can be partially reduced allowing an electron hopping process between vanadium ions in different valence states, namely V^{4+} and V^{5+}. Conduction is achieved by electrons hopping from low valance, vanadium (V^{4+}), to high-valance vanadium (V^{5+}), sites and depends upon the average distance between vanadium ions (R) the relative fraction of vanadium (V^{4+}) and vanadium (V^{5+}) ions [2, 3]. The charge transfer is usually termed a 'small polaron hopping' (SPH) [4, 5]. Thin films can be easily deposited by dip-coating or spin coating. The main concerns are due to the following numerous factors: homogeneous mixing at the atomic level, lower synthesis temperature, shorter heating time, better crystallinity, uniform particle distribution and smaller particle size at the nanometer level. The advantages of this method include simplicity of the equipment involved, and the purity of initial reagents, which ensures high quality and reproducibility of the resulting layers [6–8]. Various

physical and chemical methods are used to obtain V2O5 films such as thermal and magnetron sputtering, chemical vapor deposition and sol–gel technology [2]. Electrical properties of alkali-intercalated vanadium pentoxide nanocrystalline films were studied and reported in a number of publications and the results were due to the existence of two different valance states of vanadium ions namely V4+ and V5+. The electrical conductivity of these nanocrystalline films showed that all samples were semiconductor and increased with increasing alkali content. The conductivity of these systems was primarily determined by hopping carrier mobility. Also, conduction was confirmed to obey the non-adiabatic SPH [9–11]. Alternatively, bronzes sodium-doped vanadium pentoxide, -Na$_x$V$_2$O$_5$, was a subject of a number of studies. Specifically, when, x = 0.33, which was extracted initially from xerogel Na0.33V$_2$- O$_5$.1.6 H$_2$O precursor by heat treatment at 550°C. Magnetic susceptibility, electron paramagnetic resonance and electrical conductivity measurements were the topics of the study. On the other hand, Na$^+$ doped V$_2$O$_5$ thin film specimens, were prepared first by the melt quench technique in NaCl solution [12,13]. Thermopower and electrical conductivity were studied. Significant increase in the electrical conductivity was attributed to the increase in the small polaron concentration by 50 times, and a decrease in the activation energy by a half. The power factor was increased up to 350, demonstrating that this technique improved the thermoelectric properties of the V$_2$O$_5$ thin films [13].

In this study, Na-doped molybdenum and vanadium oxide nanocrystalline thin films were synthesized by sol–gel method. We have investigated the structural and electrical properties of xNa-(80-x)V$_2$O$_5$ 20MoO$_3$.nH$_2$O as prepare xerogel nanocrystalline thin films.

2. Experimental

Five different compositions, of xNa-(80-x)V$_2$O$_5$ 20MoO$_3$.nH$_2$O (where 8 ≤ x ≤ 26 mol.%) have been proposed for the present investigation. These compositions were synthesized from highly pure vanadium pentoxide (V$_2$O$_5$) (99.99), molybdenum oxide (MoO$_3$) (99.99) and sodium carbonate (NaCo$_3$) (99.99). Films of the investigated compounds were prepared by sol–gel technique (colloidal route). V$_2$O$_5$ and MoO$_3$ were dissolved in hydrogen peroxide (H$_2$O$_2$) and NaCo$_3$ was dissolved in distilled water at room temperature. The formed solution was stirred continuously by using magnetic stirrer. and heated at 60 ^{o}C, with continuous stirring. xNa-(80-x)V$_2$O$_5$-20MoO$_3$.nH$_2$O gels can be synthesized via the condensation of aqueous solutions of xNa-(80-x)V$_2$O$_5$ -20MoO$_3$.nH$_2$O. The obtained gels were deposited on Pyrex substrates by dip coating method. The samples were made in coplanar geometry and dried spontaneously in room temperature[1,2]. The surface morphology of the films was observed using a High resolution transmission electron microscope (JEOL 200 CX). The film thickness was measured by an optical based technique using Shimadzu-240 double beam spectrophotometer[14]. The density was measured by Archimedes method using

toluene as the immersion liquid [1]. The dc electrical conductivity was measured by the two-point probe method using silver electrodes in the temperature range of 300–500 K. The ohmic behaviour of the films was ascertained from the linearity of the current–voltage curves. A thermoelectric power (S) measurement above room temperature was also measured where the type of conduction was found to be changed from n - type to p - type semiconductors.

. The general expression for S in the case of nanocrystalline semiconductors is $\Delta V/\Delta T$ where ΔV is the voltage developed between two points of the material is maintained at temperature ΔT [15].

3. Results and discussion
3.1. TEM

Morphology of the film surface on the other hand was evaluated using transmission electron micrograph (TEM). Figure 1 shows the TEM image of $12Na-68V_2O_5-20MoO_3.nH_2O$ nanorod film. It were found that the films surface was relatively smooth. Fig. 2 shows the TEM image of $26Na-54V_2O_5$ $20MoO_3.nH_2O$ nanorods. The TEM image in Figs. 1,2 show the overall features of the product under high magnification with an average nanocrystalline size of 10.1 nm.. Each nanorod is straight and has a uniform diameter along its entire length. Examination by TEM
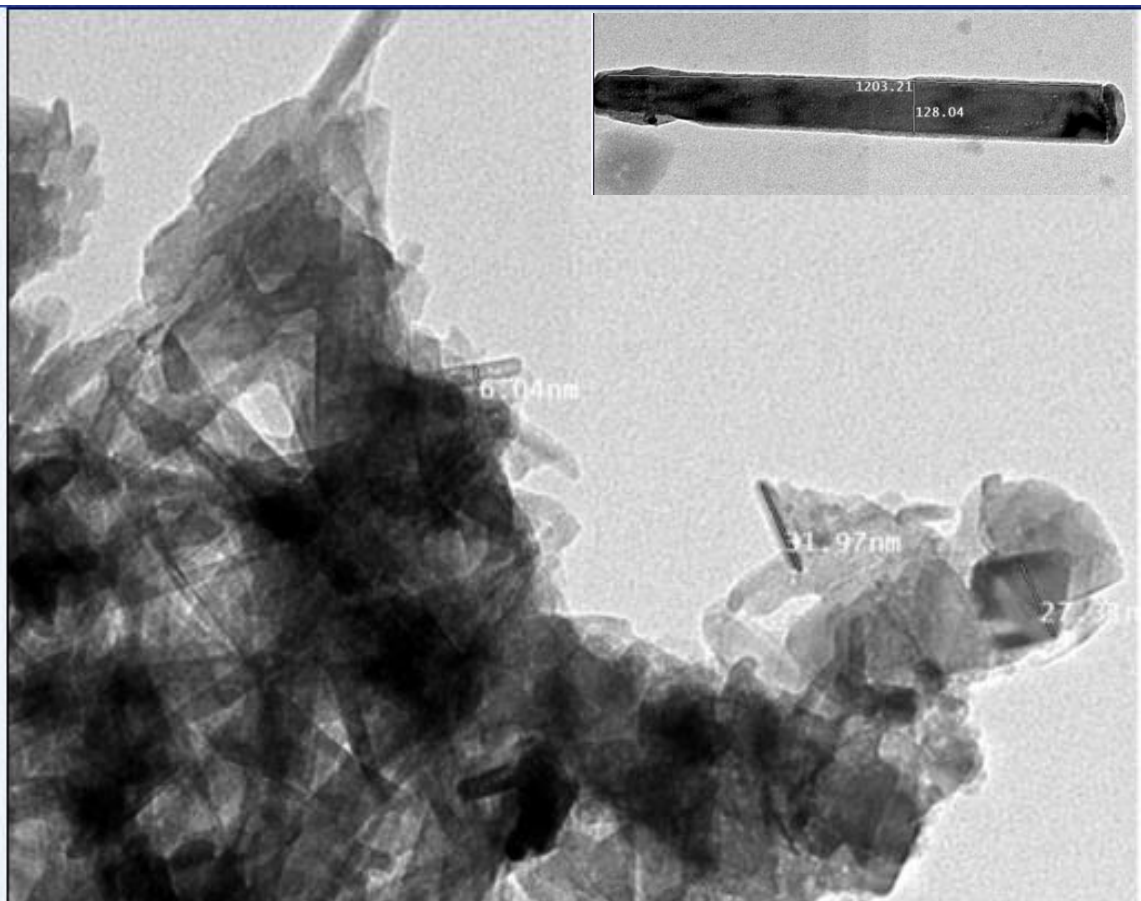
Fig. 1 TEM image of $12Na-68V_2O_5–20MoO_3. nH_2O$ nanorod film

Fig. 2 TEM image of $26Na-54V_2O_5–20MoO_3. nH_2O$ nanorod film

(Fig. 1, 2) shows those nanorods with an approximate widths range between 6.04 and 128.04 nm and the lengths range between 31.97 and 1203.21 nm are formed, which exhibits an interesting morphological feature: high magnification TEM micrographs reveal that they indeed form bundles of agglomerated smaller filaments. This interesting shape in the nanoscale dimension leads to the exposure of a large fraction of the atoms to the surface, making these materials promising candidates for the development of new functionalized materials.

3.2. Density

Fig. 3 shows the composition dependence of density (d) of the present $xNa-(80-x)V_2O_5-20MoO_3.nH_2O$ nanocrystalline system. It may be observed that the density (d) increases gradually with the increase of the sodium content in the present $xNa-(80-x)V_2O_5-20MoO_3.nH_2O$ nanocrystalline samples. In the present system the densities varies from 2.412 to 2.805 g/cm^3 (Table 1). The measured density is in good agreement with that observed by M.M. El-Desoky et al. [16]. This indicates that our sample structure follows the bilayer model proposed M.M. El-Desoky et al. [16]. On the other hand, the increase in the density with increasing sodium content may be due to the loss of intercalated water molecules, of less molecular weight, Na ions of higher molecular weight on the average. This

is together with the increase of the attractive interactions between the positively charged sodium ions and the negatively charged V_2O_5 layers [2,10,17]. The concentration of composition N (cm^{-3}) may be evaluated using the density by the relation:

$$N = \rho p N_A / A_W \qquad\qquad (1)$$

where ρ is the density of the sample as evaluated above and presented in Table 1, p is the weight percentage of atoms, N_A is the Avogadro's number and A_W is the molecular weight. While the relationship between N and the mean distance R is generally described as:

$$R = \acute{C}(1/N)^{1/3} \qquad\qquad (2)$$

The calculated values of R and N are summarized in Table 1.

Table 1
Chemical composition and physical properties of xNa-(80-x)V_2O_5-20MoO_3.nH_2O nanocrystalline thin films.

X(mol%)	d (g cm^{-3})	N(x10^{21}cm^{-3})	R(nm)	W (eV)
8	2.412	0.83	1.06	0.282
12	2.521	0.86	1.05	0.263
16	2.634	0.89	1.04	0.244
20	2.742	0.92	1.03	0.225
26	2.805	0.95	1.02	0.211
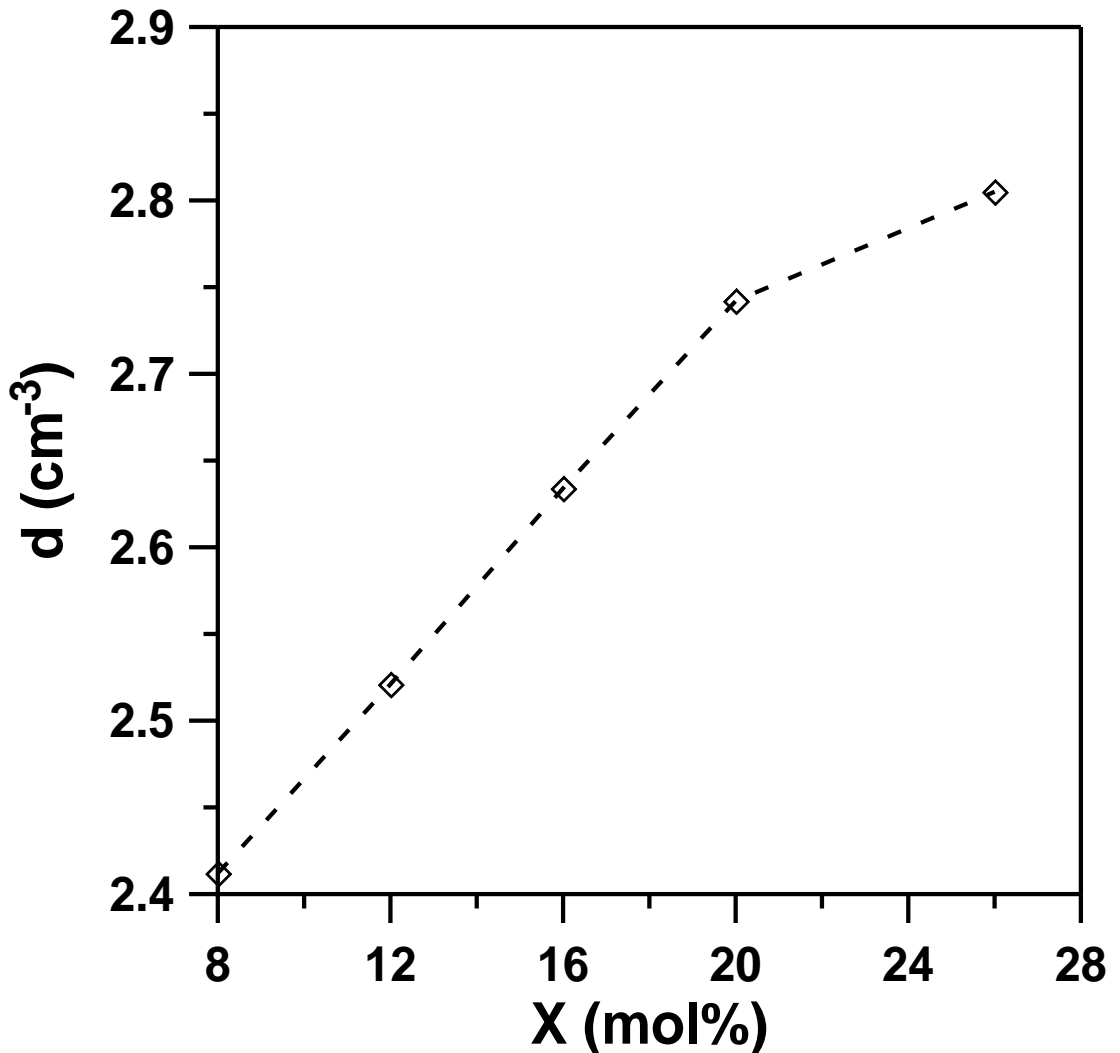
Fig. 3. Composition dependence of density for xNa-(80-x)V_2O_5-20MoO_3.nH_2O
nanocrystalline samples

3.3. Electrical conductivity

Fig.4 shows a temperature dependence of the electrical conductivity $\sigma(T)$, for xNa-(80-x)V_2O_5-20MoO_3.nH_2O nanocrystalline thin films system, which is the best being described by Mott formula [4,5].

$$\sigma = \sigma_o \exp(-W/kT) \tag{3}$$

where σ_o is a pre-exponential factor and includes the charge carrier mobility and density of states, k is the Boltzmann's constant, T is the absolute temperature and W is the conduction activation energy which is a function of the energy band gap. The activation energy (W) and pre-exponential factor (σ_o) were obtained from the least square straight line fits of the data above 342 K..
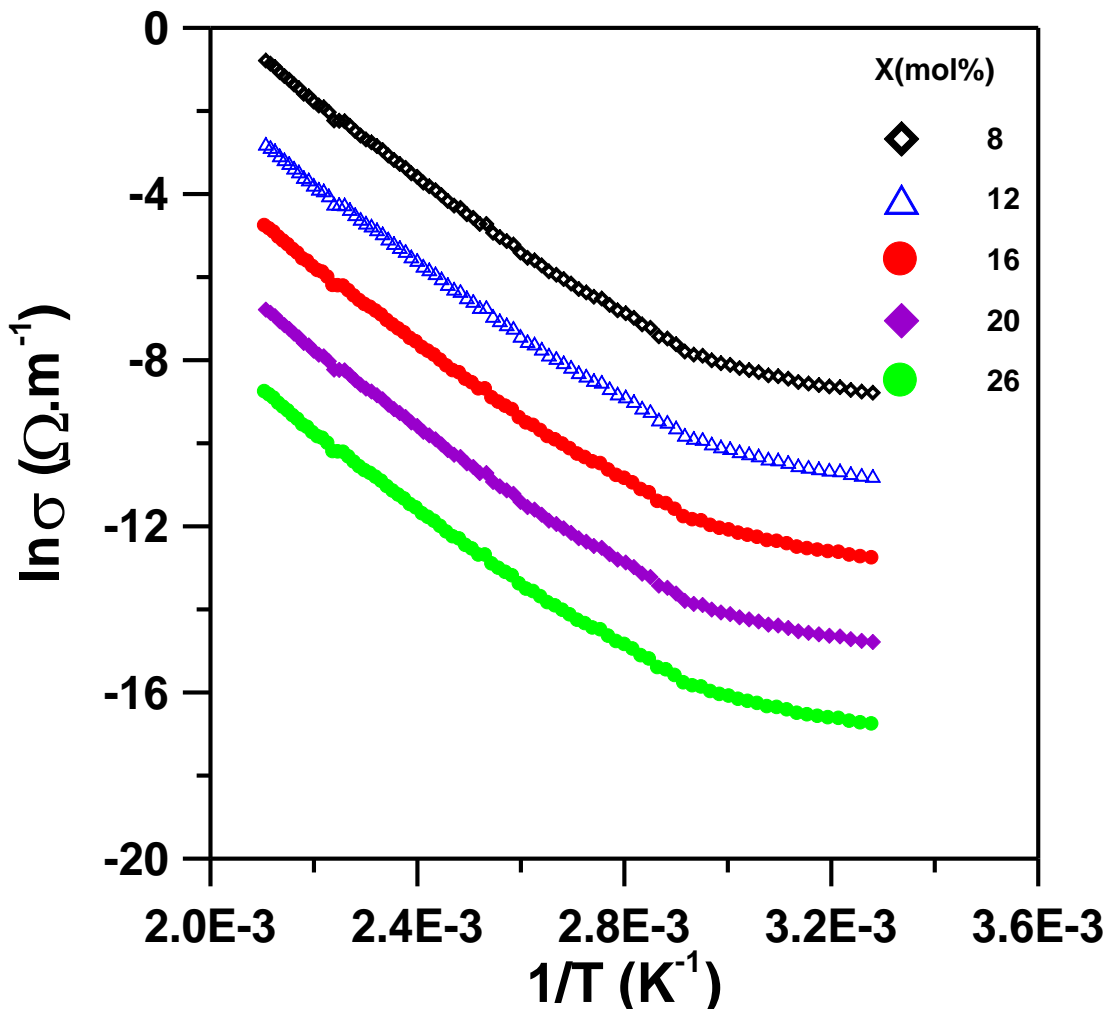
Fig. 4. Temperature dependence of dc conductivity (σ) for xNa-(80-x)V_2O_5-20MoO_3.nH_2O nanocrystalline thin films

It shows linear temperature dependence up to a critical temperature $\theta_D/2$ (θ_D Debye temperature) and then the slope changes with deviation from linearity and the activation energy (W) is temperature dependent. Such a behavior is a feature of SPH [4,5]. However, above this temperature range, the variation of activation energy with temperature is negligibly small so that the behavior may be treated as thermally activated process.

The compositional dependence of the activation energy (W) is shown in Fig. 5. It was observed in this figure that the magnitude of activation energy is small, which is consistent with SPH mechanism [4,5].
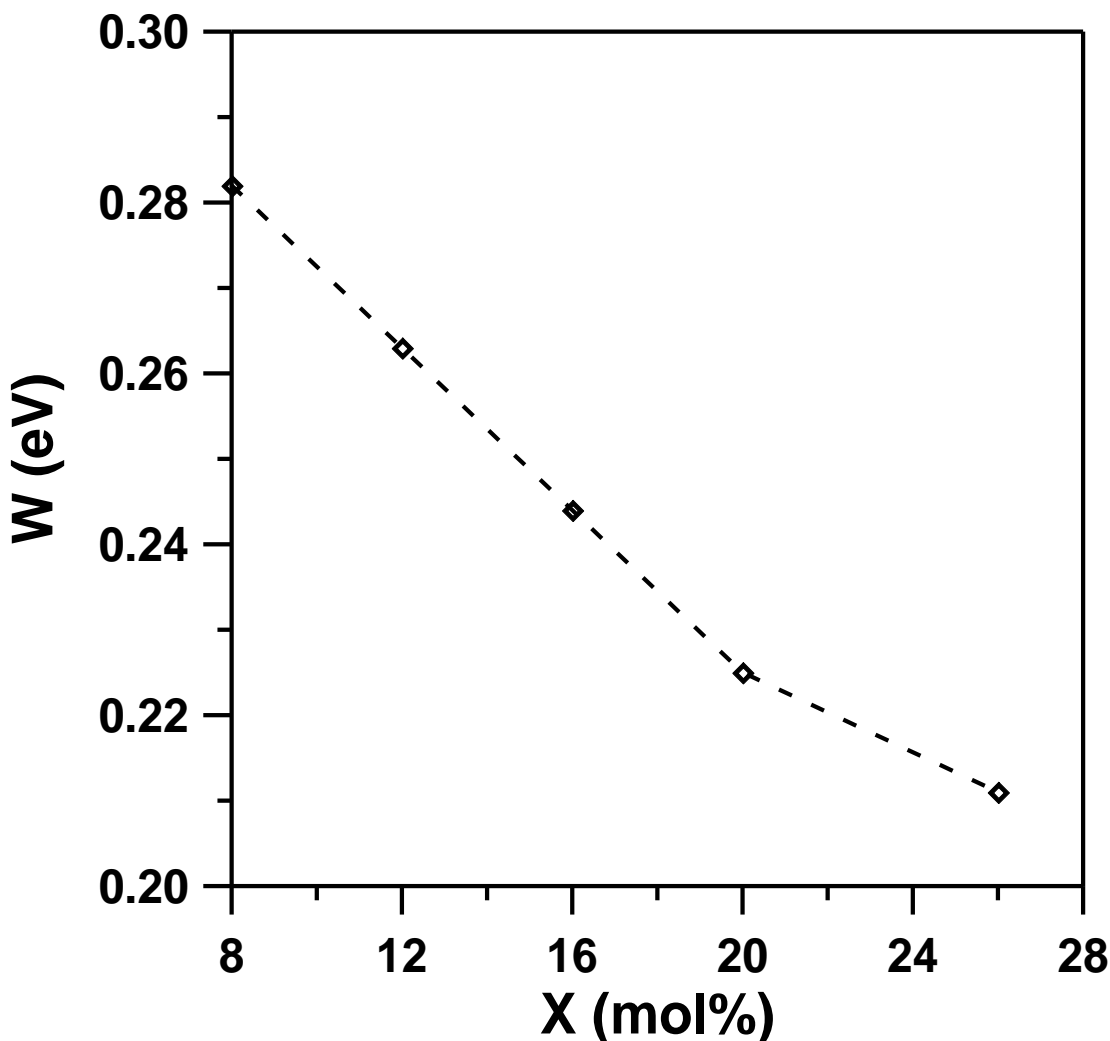
Fig. 5. Effect of Na-content on the activation energy (W) for $xNa-(80-x)V_2O_5-20MoO_3.nH_2O$ nanocrystalline thin films

The electrical conduction in nanocrystalline materials, containing, transition metal oxide (TMO) such as V_2O_5, have been proved to be electronic in nature [4, 5]. The conduction process is believed to occur by electron hopping between the ions existing in different valance states (such as V^{4+} and V^{5+}) in the nanocrystalline materials. We therefore favor the possibility of electronic conductivity as a possible mechanism in the present system for the observed conductivity [16]. On the other hand, the

nature of the conductivity observed in Fig. 4 corresponds to a steadily increase with addition of Na ions in the vanadium framework. Addition of sodium ions is believed to higher the valence state of vanadium ions by transfer of electrons [2].

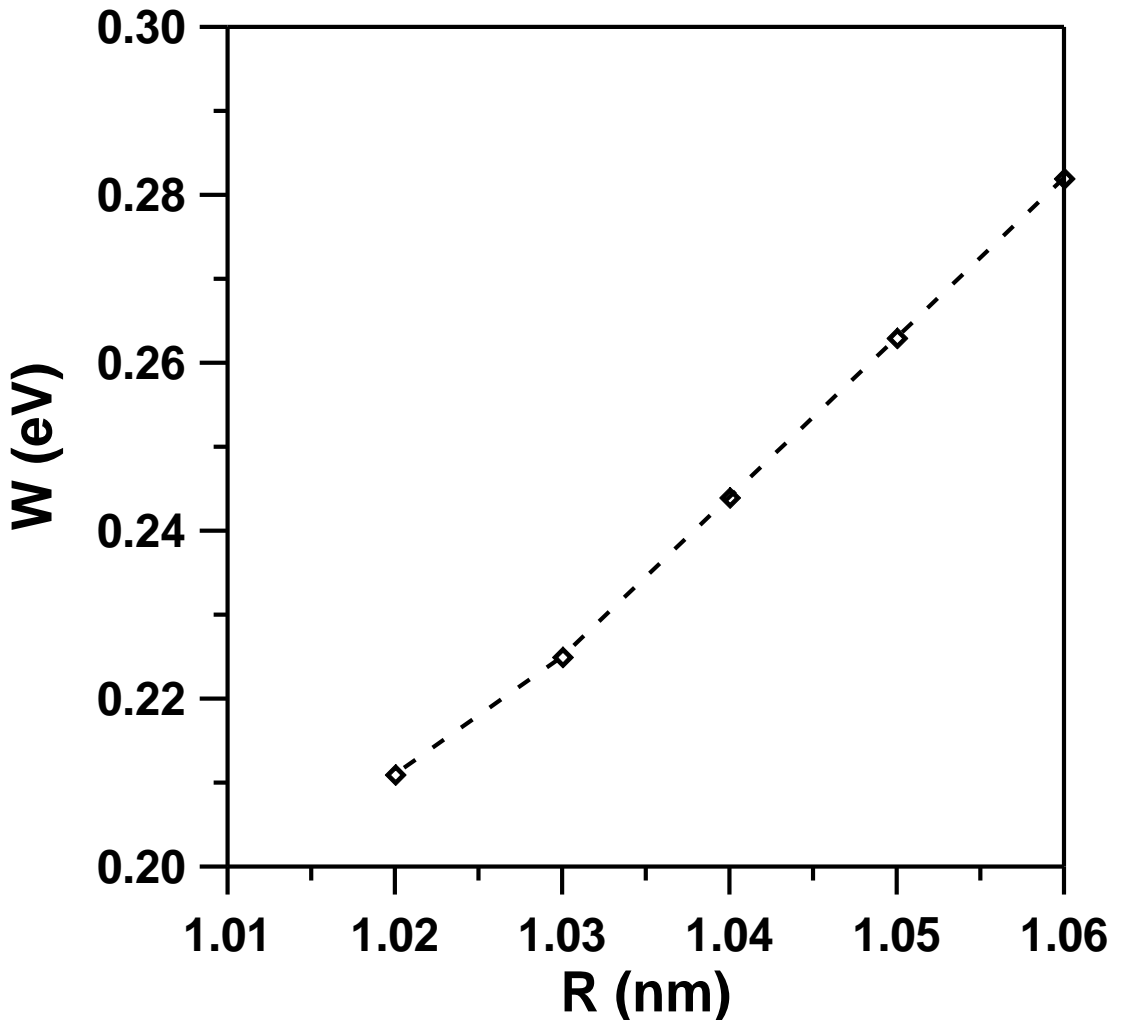Similar results were obtained recently on comparable thin films samples of the compositions $xNa-V_2O_5.nH_2O$ [16].

Fig. 6. Effect of mean distance (R) on activation energy (W) at 400 K for xNa-$(80-x)V_2O_5-20MoO_3.nH_2O$ nanocrystalline thin films

Fig. 6 Shows, the activation energy (W) as a function of the mean distance (R) between V ions at 400 K. In the range of measurements, W depends on the site-to-site distance R. These results show that there is a prominent positive correlation between W and R between vanadium ions. The effect dependence of σ upon the sodium content in a $xNa-(80-x)V_2O_5-20MoO_3.nH_2O$ nanocrystalline thin films can be explained by changes in the distance between the vanadium ions, R. With increasing sodium content the calculated distance between the vanadium ions decreases from 1.06 to 1.02 nm and the increase in σ is attributed to decrease

in the distance R between vanadium ions. It is concluded, therefore, that the tunneling transfer between V^{4+} and V^{5+} ions depends strongly on R which is important to the conduction mechanism of these $xNa-(80-x)V_2O_5-20MoO_3.nH_2O$ nanocrystalline thin films. This agrees with the results obtained recently on comparable nanocrystalline thin films samples of $V_2O_5.nH_2O$ and $Nax-V_2O_5.nH_2O$ [2,16].

Mott [4] has investigated the hopping conductivity in oxide amorphous and nanocrystalline materials containing transition metal ions. The conductivity of the nearest neighbor at high temperatures (T > $\theta_D/2$) is given by Eq. (4), where [2,16];

$$\sigma_o = \frac{v_o Ne^2 R^2}{kT} C\,(1-C)\exp(-2\alpha R)$$

(4)

here v_o is the optical phonon frequency, α is the tunneling factor (the ratio of wave function decay), N the transition metal density, C the fraction of reduced transition metal ion and W is the activation energy for hopping conduction. Assuming a strong electron–phonon interaction in non-adiabatic hopping regime, Austin and Mott [5] have shown that;

$W=W_H + W_D/2$ *(for T > $\theta_D/2$)* (5a)
$W= W_D$ *(for T < $\theta_D/4$)* (5b)

where W_H is the hopping energy and W_D is the disorder energy defined as the difference of electronic energies between two hopping sites.

In the adiabatic hopping regime αR in Eq. (3) becomes negligible [4, 5]. The σ_o is then given as,

$$\sigma_o = v_o Ne^2 R^2 C(1-C)\,/kT$$

(6)

Thus σ gives log σ = log σ_o - W/(2.303 kT), indicating that the slope of σ at a fixed temperature versus activation energy of different glasses should be -1/(2.303 kT). Fig. 7 presents the effect of sodium content on the pre exponential factors (σ_o) obtained from the least squares straight line fits ofthe data indicating a decrease in σ_o with sodium content from 8 to 26 mol%. These results indicate that σ depends on W and σ_o in Eq. (3) in non-adiabatic regime. From both these results, we conclude that the conduction mechanism in the present system is to be due to non-adiabatic hopping of the polarons [2,16].
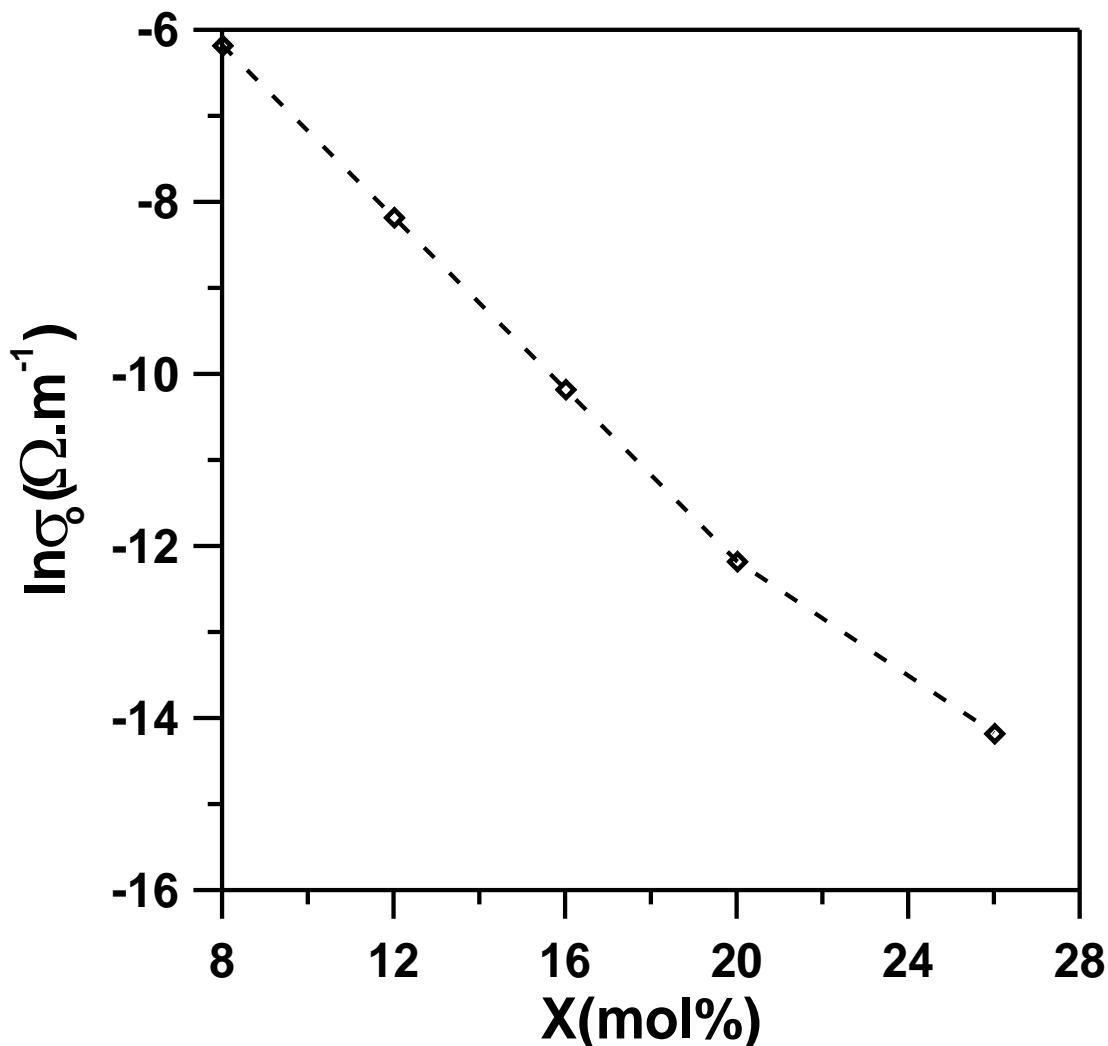
Fig. 7. Effect of Na-content on pre-exponential factor (σ_o) for xNa-(80-x)V$_2$O$_5$-20MoO$_3$.nH$_2$O nanocrystalline thin films

Emin and Holstein [18] have suggested a method for calculating the polaron hopping energy WH;

$$W_H = (1/4N)\Sigma_p \left[\gamma_p\right]^2 \hbar\omega_p \tag{7}$$

where $[\gamma_p]^2$ is the electron–phonon coupling constant and ω_q is the frequency of the optical phonons. Bogomolov et al. [19] on the other hand have calculated the polaron radius r_p for a non-dispersive system of frequency ν_o for Eq. (4):

$$r_p = \left(\frac{\pi}{6}\right)^{1/3} \frac{R}{2}$$

$$\text{(8)}$$

The values of the polaron radii calculated from Eq. (8), using R from Table 1 is shown in Table 2 for the present system. Although the possible effect of disorder has been neglected in the above calculation, the small values of polaron radii suggest that the polarons are highly localized [19].

The polaron hopping energy W_H is given by [19];

$$W_H = \frac{e^2}{4\varepsilon_P}\left(\frac{1}{r_P} - \frac{1}{R}\right)$$

$$\text{(9)}$$

where

$$\frac{1}{\varepsilon_P} = \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_S}$$

$$\text{(10)}$$

ε_S and ε_∞ are the static and high frequencies dielectric constants of the present samples. An estimate of W_H can be made from Eq. (9) from the known values of R and r_P, while ε_P were estimated from cole–cole plot [20,21]. The values of W_H and ε_P are given in Table 2. The density of state at Fermi level can be estimated from the following expression [17];

$$N(E_F) = 3/4\pi R^3 W$$

$$\text{(11)}$$

The results for the present samples are listed in Table 2. The values of $N(E_F)$ are reasonable for localized states.

We estimate the optical phonon frequency, (v_o) in Eq. (4) using the experimental data from Table 1.

Table 2
Polaron hopping parameters of xNa-(80-x)V$_2$O$_5$-MoO$_3$.nH$_2$O nanocrystalline thin films system.

X(mol%)	W_H (eV)	r_P (nm)	ε_P	$N(E_F)$ ($x10^{21}$ eV^{-1} cm^{-3})	v_o ($x10^{13}$ s^{-1})	γ_p
8	0.127	0.523	3.23	1.834	1.98	0.76
12	0.124	0.512	5.31	2.011	1.76	0.65
16	0.121	0.505	6.53	2.342	1.56	0.57
20	0.117	0.498	6.98	2.536	1.38	0.44
26	0.113	0.481	7.46	2.771	1.13	0.35

The values of small polaron coupling constant γ_p, a measure of electron–phonon interaction, given by the formula $\gamma_p = 2W_H/h\nu_o$ [4, 5] were also evaluated for the present samples. The estimated value of γ_p is 0.35–0.76 (Table 2). The value of $\gamma_p < 4$ usually indicates a weak electron phonon interaction [20,21].

3.4. Thermoelectric power

Thermoelectric power (S) of $xNa-(80-x)V_2O_5-20MoO_3.nH_2O$ nanocrystalline thin films have been investigated as a function of temperature. Fig. 8 shows the temperature dependence of thermoelectric power of the present nanocrystalline thin films. The general expression for S in the case of nanocrystalline semiconductors, where carriers are excited to extended states beyond the mobility edge, is assumed by [15]:

$$S = \pm(k/e)\left[(\Delta E_s / kT) + A\right] \tag{12}$$

where A is a small constant which represents the thermal energy transported by carriers, e is the electronic charge k Boltzmann's constant and ΔE_s is the activation energy associated with conduction.
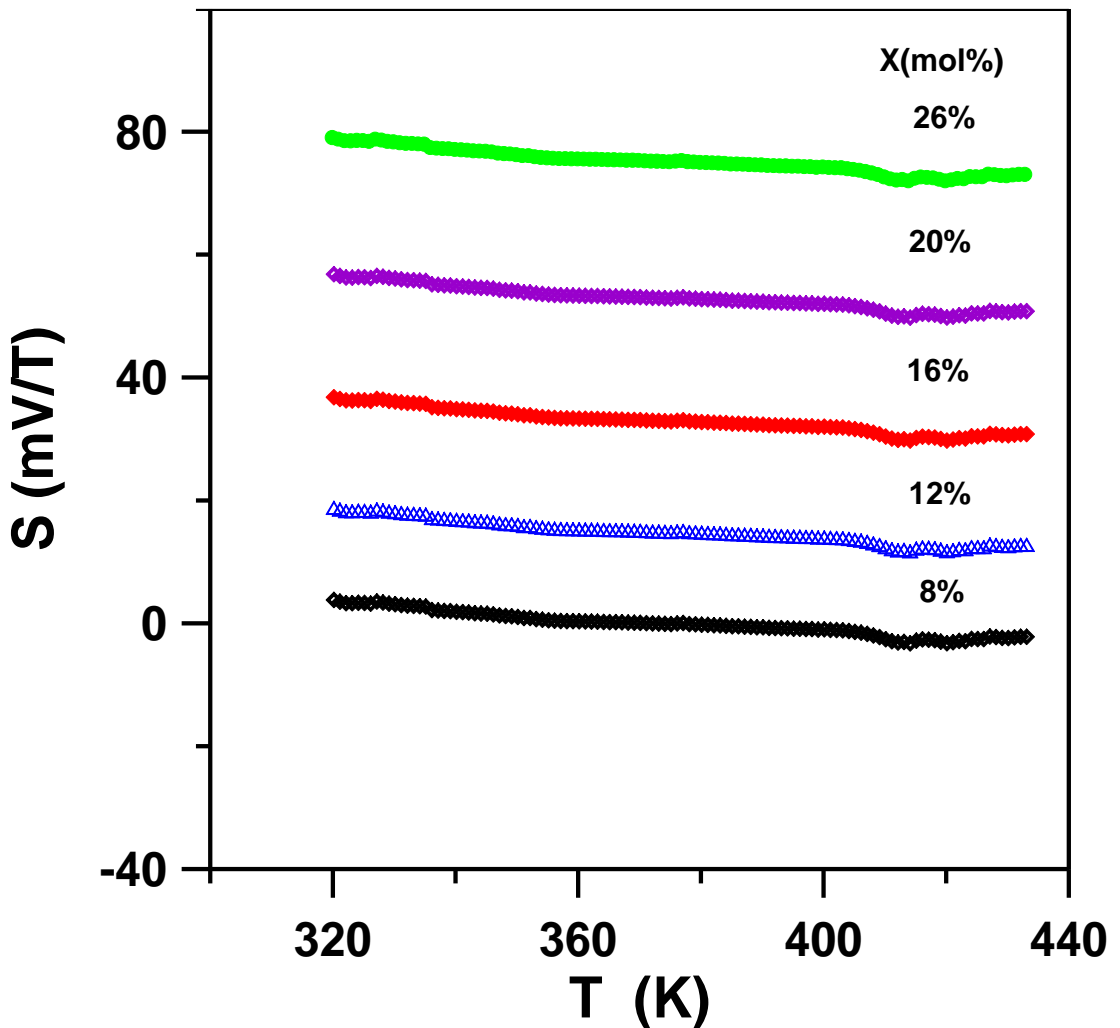
Fig. 8 Thermoelectric power(S) as a function of temperature for
xNa-(80-x)V_2O_5-20MoO_3.nH_2O nanocrystalline thin films

Fig. (8) shows the different thermoelectric power, TEP, measurements corresponding to the as the different content of Na. The temperature dependence of thermoelectric power *S* measures the energy difference between the Fermi energy and the energy level where charge transport occurs. It is found that ΔE_s=0.196- 0.225 eV in agreement with the activation energy, (W), obtained from the electrical conductivity. It is found that the activation energy ΔE_s calculated from the slope of *S* vs. *T* curve (Fig.8) is consistent with the obtained results of electrical conductivity measurements. On increasing Na content in the system x xNa-(80-x)V_2O_5-20MoO_3.nH_2O, gradual changes in thermoelectric power from n - type to p - type detected as shown in Figs. 8. This is a planned advantage aiming for different practical applications.

4. Conclusion

The aim of the present system was to determine an effect of sodium excess in nanocrystalline xNa-(80-x)V_2O_5-20MoO_3.nH_2O thin films ($8 \leq x \leq 26$ mol%) on their electrical and structural properties. The density of the samples increases with increasing sodium content. The electrical conductivity shows that all samples are semiconductor and decreases with increasing sodium content. From the best fits, reasonable values of various small polaron hopping parameters were obtained. The density of state $N(E_F)$ values were evaluated and found to vary from 1.834 to 2.771 eV^{-1} cm^{-3}. The values of optical phonon frequency (ν_o) were obtained to be 1.13–1.98 x 10^{13} s^{-1}. The values of small polaron coupling constant $\gamma_p < 4$ usually indicate a weak electron phonon interaction. The electrical conduction at high temperature was due to non-adiabatic SPH. The thermo-electric power measurements show that: the samples are changes from n - type to p - type semiconductors.

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