Synthesis and Characterization of W^{6+} ions doped Nanocrystals for fabrication of Solid State Batteries

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Abstract: In view of the importance of ionic conductivities and fabrication of solid state batteries W^{6+} ion doped and undoped nanocrystals are synthesized simultaneously by sol - gel method and subjected to characterized by using UV-visible; Fourier transforms infrared spectroscopy, X-ray diffraction, scanning electron microscopy and transmission electron microscopy study. These prepared nanocrystals are found to be essentially ionic conductors. The conductivity (σ) of undoped, 1% and 5% W^{6+} ion doped nanocrystals were measured at various temperatures 33^0C - 330^0C and at frequency of 100 kHz. The results suggested that the conductivity of undoped nanocrystals at 33^0C is found to be 1.12 x 10^{-7} Scm^{1-} while at 330^0C is 1.19 x 10^{-4} Scm^{1-}. The conductivity of 1% W^{6+} ion doped nanocrystals at 33^0C is 7.53 x 10^{-7} Scm^{1-} and at 330^0C is 5.21 x 10^{-4} Scm^{1-}, whereas conductivity of 5% W^{6+} ion doped nanocrystals at 33^0C is 8.26 x 10^{-6} Scm^{1-} and at 330^0C is 8.40 x 10^{-4} Scm^{1-}. The conductivity of doped nanocrystals increases with increasing temperature and concentration of W^{6+} ion dopants both. The results also suggested that conductivities values of W^{6+}ion doped nanocrystals are larger than those of undoped nanocrystals at all temperature respectively. The synthesized nanocrystals are conducting in nature therefore, three solid state batteries of doped and undoped nanocrystals were prepared and their open circuit voltages were also measured at temperature 27^0C and humidity level of 45%.

Keywords: Doped and undoped nanocrystals, X-ray diffraction, Transmission electron microscopy, Conductivity, Solid State Batteries

I. INTRODUCTION

It is interesting to note that the applications of nanotechnology in different fields have distinct different demands, and thus face very different challenges, which need different approaches. Nanotechnology offers an extremely wide range of potential applications from electronics, optical communications and biological systems to new materials [1-3]. Due to these reasons there is great interest of the scientific community toward nanotechnology in recent years. Among them, metal sulphide nanocrystals are structurally and technologically interesting materials which have been greater importance than any other nanomaterials [4-5]. The physico-chemical properties of metal sulphides and doped with metals ions [6-7], exhibit an acute dependence on size. These properties are of special importance because these are related to the industrial uses such as sensors, catalysts, absorbents displays, lighting, and lasers [3-4]. A large number of dopants of transition metal ions such as Co, Mn, Cu and Fe and rare earth ions such as Tb3+, Eu3+, and Ce3+ ions are used in metal oxide and metal sulphide nanocrystals which can lead to an increase of conductivity of nanocrystals [8-11]. It belongs to a class of materials that combines high electrical conductivity with optical transparency and thus constitutes an important component for optoelectronic applications, solid state gas sensor, oxidation catalyst and transparent conductor [12-14]. A survey of literature reveals that no systematic work has been done to study the effect of dopants of W6+ions into the cerium sulphide nanocrystals. Therefore, it was considered worthwhile to study the conducting behavior of W6+ions doped nanocrystals. In view of the importance of ionic conductivity, fabrication of solid state batteries and measurements of their open circuit voltage (OCV) of undoped and W6+ ions doped nanocrystals and their structural characterization were carried out. The conductivity (σ) value of undoped and W6+ ions doped nanocrystals were obtained at different temperature while OCV value of undoped and W6+ions doped nanocrystals were obtained at 270C temperature. In the present investigation the conductivity and OCV of undoped nanocrystals were also measured in order to see the effect of addition of W6+ ions. The undoped and W6+ ion doped nanocrystals have been characterized by SEM (scanning electron microscope) and TEM (transmission electron microscope) indicating crystalline size 35 – 90nm. An attempt has also been made to explain the structure of conducting nanocrystals on the basis of IR and X-ray diffraction pattern. Thus, in this paper for the first time we

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are reporting systematic characterization, electrical conductivity and OCV measurement of undoped and W6+ ion doped nanocrystals and also explain the effect of change of dopants concentration and their structure respectively. The undoped and W6+ ion doped nanocrystals are conducting in nature has large application in industries and solid state batteries [15].

II. EXPERIMENTAL

2.1 Materials

All Chemicals used for preparation of nanocrystals were of analytical grade. Ceric ammonium sulphate $(NH_4)_4Ce(SO_4)_4$ $2H_2O$ (Qualigens), Sodium sulphide $(Na_2S.7H_2O)$ (Qualigens), tungstic acid H_2O_4W(Qualigens) and Ethylene glycol(CH_2OHCH_2OH) were taken from Ranbaxy for preparing the nanocrystals.

2.2 Preparation of undoped and W^{6+} ion doped nanocrystals

Method used for preparing Cr^{3+} ion doped nanocrystals have been described in a previous publication [3]. For preparing W^{6+} ion doped nanocrystals different amount of 1% and 5% of tungstic acid were taken. In all these cases of preparation three round bottle flask were taken. In one round bottle flask appropriate amount of ceric ammonium sulphate and sodium sulphide in 1:1 molar ratio was taken to prepare control (undoped) cerium sulphide nanocrystals while in other two round bottle flask appropriate amount of ceric ammonium sulphate and sodium sulphide in 1:1 molar ratio was taken and the dopants of 1% and 5% of tungstic acid was added in each test tube to prepare the W^{6+} ion doped nanocrystals. The reaction mixture in each case was dissolved in 100ml of distilled water and mixed well with help of magnetic stirrer for 4 hours. The pH value of undoped and doped solution was measured with help of pH-5-25 cw microprocessor pH/mv meter. The reaction mixture in each case was decanted and refluxed in ethylene glycol at 80^0C to obtain undoped and W^{6+} ion doped nanocrystals. The nanocrystals thus obtained were dried in dark and placed in sample tube and stored in desiccator. The purpose of the investigation was to study the changes brought about by the introduction of a metal W^{6+} ion along with control undoped system which were synthesized simultaneously.

2.3 Characterizations

The synthesized undoped and W^{6+} ion doped nanocrystals were characterized by the UV – visible reflectance spectra were recorded on a Shimadzu 160A spectrophotometer. The FT-IR spectra of nanocrystals were run in the range of 4500 - 50 cm^{-1} using KBr discs on a Perkin Elmer FT-IR spectrometer. The XRD patterns of the compound were taken on a Phillips analytical X-ray B.V. diffractometer using Cu α radiation with 2θ = $5\text{-}80^0$ from BARC Kalpakkam. Scanning electron microscope (SEM) and Transmission electron microscopy (TEM) images were taken on Phillips Model – CM200 operating voltages 20 - 200 kv with resolution 2.4A° from IIT Bombay.

2.4 Electrical conductivity measurements

In these method pellets of undoped, 1% and 5% W^{6+} ion doped nanocrystals under investigation were prepared by giving pressure of 5t by hydraulic pressure. After measuring the thickness of the pellet with the help of a screw gauge, silver epoxy was coated on the both side. The pellet was allowed to dry completely before measuring the electrical impedance with the help of the LCR Tester. The electrical conductivities of undoped, 1% and 5% W^{6+} ion doped nanocrystals were measured by four probe a.c. impedance method [16] by using HIOKY 3550 LCR Tester. The variations of the conductivity with the temperature of undoped and W^{6+} ion doped nanocrystals were studied in the range of 33- 330^0C at 100 kHz frequency by using equation (1).

$$\sigma = G\, l/A \qquad (1)$$

where G is the impedance, l is the thickness of the pellet and A is cross section area of the pellet.

2.5 Fabrication of Solid State batteries and measurement of Open circuit voltage (OCV)

All chemicals used in the fabrication of solid state batteries were of analytical grade. Iodine (Glaxo), Graphite (Qualigens), Silver (Qualigens) and undoped and W^{6+} ion doped nanocrystals were used as electrolyte without further purification. Three batteries were prepared in the present investigation in which silver was used as anode, synthesized nanocrystals as the electrolyte and a mixture of graphite and iodine in the ratio 9:1 as the cathode. These three materials were powdered separately and successively pressed in a pelletizing die by applied pressure of 5t cm^{-2} to give the desired battery [17]

Ag | $[(H_2O)(OH)Ce(S)_2Ce(OH)(H_2O)]$ | **C+I_2** (Undoped)

Ag | $[(H_2O)(SH)(OH)W\text{-}(O)_3\text{-}W(OH)(SH)(H_2O)]^{2+}$ **C+I_2** | (1%, and 5% W^{6+} ion doped)

The Open circuit voltage (OCV) values of above prepared solid state batteries of undoped and W^{6+} ion doped nanocrystals were measured at temperature (27^0C) with humidity level of 45%.

III. RESULTS AND DISCUSSION

The presence of W^{6+} and S^{2-} ions in doped nanocrystals and $Ce^{3+,}$ S^{2-} ions in undoped nanocrystals were confirmed by elemental analysis. The pH value of 1% W^{6+} ion doped solution is found to 6.65 and the pH value 5% W^{6+} ion doped solution is found to be 5.16 while for undoped solution pH values is 7.21. These pH values decreases from 7.21 to 5.16 clearly indicated that after doping W^{6+}

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ion solution becomes acidic. The UV – vis. spectrum of W^{6+} ion doped $[(H_2O)(SH)(OH)W\text{-}(O)_3\text{-}W(OH)(SH)(H_2O)]^{2+}$nanocrystals indicates broad absorption bands at 326nm, 440nm and 470nm while undoped $[(H_2O)(OH)\ Ce\ S_2\ Ce(OH)(H_2O)]$ show strong and sharp absorption peak at 302nm. IR results of W^{6+}ion doped nanocrystals show absorption bands at 572.64 cm^{-1} and 658.73 cm^{-1} which suggested the υW – S and υW – O stretching. The band at 1462.12 cm^{-1} and 3347.83 cm^{-1} may be due to coordination of H_2O and OH to W metal ion and the coordination occurs through the bridging – O is clearly stipulated in IR-spectra at 2355 cm^{-1} respectively. The absorption peak appeared at 800 cm^{-1} in IR spectra confirmed that undoped nanocrystals are in tetrahedral symmetry and W^{6+} ion doped nanocrystals at 1100 cm^{-1} show hexagonal symmetry[18,19].

The crystallite sizes of undoped and W^{6+} ion doped nanocrystals were calculated by using Debye Scherer equation [20].

$$L = 0.9\,\lambda / \beta\,\mathrm{Cos}\theta \qquad (2)$$

Where L is the average crystallite domain size perpendicular to the reflecting planes, λ is the X-ray wavelength (1.5418A^0), β is the full width at half maximum and θ is the diffraction angle. The crystallite size of undoped and W^{6+}ion doped nanocrystals were calculated by using equation (2). It is clearly indicated that undoped nanocrystals are uniform and range in size from 35 to 47nm while 1% of W^{6+}ion doped nanocrystals are range in size from 65 to 76nm, and 5% of W^{6+} ion doped nanocrystals are range in size from 80 to 90nm respectively. The crystallite size of W^{6+}ion doped nanoparticles are found to be larger than those of undoped nanocrystals. XRD results further suggested that when concentration of dopants increases size of nanocrystals also increase. It is clearly reveals that after doping W^{6+} ions, these ions goes in to crystal lattice and expansion of crystals lattice takes place due to larger coordination and clustering tendency of W^{6+}ion. The XRD studies of W^{6+} ion doped nanocrystals show the three sharp and well defined diffraction lines at $2\theta = 28.43^0$, 47.29^0 and 56.13^0 respectively which can be assigned to the (1 0 1),(1 1 1) and (0 0 4) reflection planes of the hexagonal lattice with metallic cluster shown in Fig.2. The broadening of peaks in X – ray diffraction patterns after addition of different amount of W^{6+}ions ascertain that W^{6+} ion goes into the crystal lattice and occupied the place of Ce^{3+} ion to obtained hexagonal symmetry**.**

Fig.1 show the scanning electron microscope (SEM) of 5% W^{6+} ion doped nanocrystals which indicated that size of W^{6+}ion doped nanocrystals is 2μm.

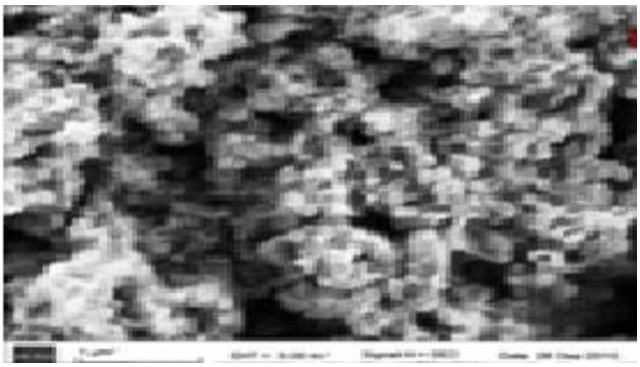

Fig.1. SEM of 5% W^{6+}ion doped nanocrystals

Fig.2 represent the typical TEM image of 5% W^{6+} ion doped nanocrystals which is in size 90nm.The diffraction rings have been indexed in the figure are clearly due to a hexagonal lattice which is prior to the X– ray diffraction measurements.

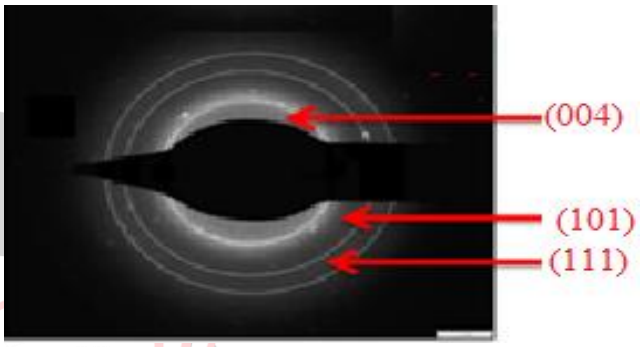

Fig.2. TEM image of 5% W^{6+} ion doped nanocrystals.

The conductivity (σ) of 1%, 5% W^{6+} ion doped and undoped, nanocrystals were measured at various temperatures (i.e.33-330^{0}C) at frequency of 100 kHz given in Table 1. The results given in table 1 suggested that the conductivity of undoped nanocrystals at 33^{0}C is found to be 1.12 x 10^{-7} Scm^{1-} while at 330^{0}C is 1.19 x 10^{-4} Scm^{1-}. The conductivity of 1% of W^{6+}ion doped nanocrystals at 33^{0}C is 7.53 x 10^{-7} Scm^{1-} and at 330^{0}C is 5.21 x 10^{-4} Scm^{1-} which is greater than those of undoped nanocrystals. The conductivity of 5% W^{6+}ion doped nanocrystals at 33^{0}C is 8.26 x 10^{-6} Scm^{1-} and at 330^{0}C is 8.40 x 10^{-4} Scm^{1-} which is greater than those of 1% W^{6+} ion doped nanocrystals. The results presented in Table 1 also suggested that conductivity values of 1% and 5% of W^{6+} ion doped nanocrystals are greater than those of undoped nanocrystals at all temperature respectively. Due to Conducting nature of undoped and W^{6+} ion doped nanocrystals which are used as electrolytes for fabrication of solid state batteries. The three different batteries were also fabricated by using undoped, 1% and 5% W^{6+}ion doped nanocrystals as electrolytes and their corresponding OCV values are measured given in Table 2. The OCV values for 1% and 5% of W^{6+} ion doped cells II and III are 0.635 and 0.734V respectively, whereas OCV value for undoped nanocrystals used as electrolyte (cell I) is 0.325V. The results of OCV suggested that the addition of percentage of W^{6+} ions increases markedly the

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OCV value increases in the order; OCV (5% W^{6+}) > OCV (1% W^{6+}) > OCV (undoped). On comparing the results obtained from Cr^{3+} ion doped nanocrystals [3] and W^{6+} ion doped nanocrystals shows that conductivity and OCV values of the W^{6+} ion doped nanocrystals are higher than those of Cr^{3+} ion doped nanocrystals. This is because of the fact that upon addition of W^{6+} ion, enhance expansion of crystal lattice more than Cr^{3+} ions doped nanocrystals. Therefore, large number of ions trape in to the crystal lattices and these ions easily migrate towards the electrodes and consequently causes larger conductivity and OCV values. The conductivity of undoped nanocrystals at 33^0C is ~10^{-7} Scm^{-1} and OCV is 0.325V which is much less than Cr^{3+} and W^{6+} ions doped nanocrystals. This is probably undoped nanocrystal is not able to provide sufficient mobile of H^+, OH^- and SH^- ions. If these nanocrystals doped with W^{6+} ions the conductivity and OCV values increases continuously with increasing concentration of dopants of W^{6+} ions and temperature both respectively. The increase in conductivity and OCV values with increase in concentration of dopants of W^{6+}ion may be simply due to the expansions of crystal lattice resulting in a more opened – up structure and suitable for conduction [16]. However, this increase of conductivity and OCV values may also be explained by the possible two reasons.

The first possibility is that when dopants of W^{6+}ion added to undoped nanocrystals which are reduced to Ce^{3+} ion and consequently causes expansion of crystal lattice through which movement of electrons and ions occurs readily. Thus increase in conductivity and OCV values due to increase in mobility of electrons and ions across the crystal lattice.

The second possible reason for increase in conductivity and OCV values is that during the nanocrystals formation undoped nanocrystals react with dopants of W^{6+} ion to form $[(H_2O)(SH)(OH)W\text{-}(O)_3\text{-}W(OH)(SH)(H_2O)]^{2+}$ nanocrystals in which W^{6+} ion has strong coordination power than Ce^{3+} ion. Therefore, Ce^{3+} ion is replaced by W^{6+} ion. The results of conductivity and OCV measurements indicated that the prepared undoped and W^{6+} ion doped nanocrystals are used as solid state batteries [15]. On the basis of IR and X-ray diffraction studies it has been shown that undoped nanocrystals contain Ce – S, Ce – O and Ce – OH_2 bonds while the dopants of W^{6+} ions are used to it, Ce^{3+} ions get replaced by W^{6+}ions resulting in formation of W – $(O)_3$ – W bonds and Ce^{3+} ions gets free in the crystal lattice which are responsible for ionic conduction. When more and more W^{6+} ions added to undoped nanocrystals more and more Ce^{3+} ions replaced due to larger coordination ability of W^{6+} ions and consequently increases conductivity and OCV values. On the basis of above discussion a proposed possible structure for undoped and W^{6+} ion doped nanocrystals are given in Fig.3.

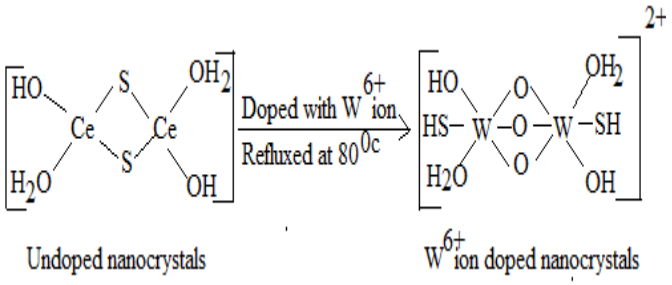

Fig.3. Proposed structure for undoped and W^{6+}ion doped nanocrystals.

These results shows that lattice sites are occupied by W^{6+} ions, therefore, broadening of peaks in X- ray diffraction pattern occur, which clearly indicated that when concentration of dopants of W^{6+} ions increases broadening of X- ray diffraction patterns also increase consequently size of nanocrystals increases. This increase in size with increase of dopants concentration also ascertained by scanning electron microscope (SEM), transmission electron microscope (TEM), electrical conductivity and OCV studies. All these studies also provide support to the size of nanocrystals respectively. The expansions of crystal lattice after addition of dopants of W^{6+} ions are also explained by UV- visible spectrum through the splitting peaks. Thus the synthesized W^{6+} ions doped nanocrystals are much more importance in solid state batteries.

IV. CONCLUSIONS

We have prepared a more useful doped and undoped nanocrystals and measured their electrical conductivity and open circuit voltage. On the basis of their results it can be found that electrical conductivity and OCV values of W^{6+}ion doped nanocrystals are higher than those of undoped nanocrystals and corresponding values increases with increasing concentration W^{6+}ions. The W^{6+} ion doped nanocrystals are potential electrolytes for the fabrication of solid state batteries.

V. ACKNOWLEDGEMENT

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Table1. Conductivity (σ) values for undoped and W^{6+} ion doped nanocrystals at different Temperature

Nanocrystals	Temperature °C	1/T x 10^3 K^{-1}	Conductivities(σ) Scm^{-1}
Undoped	33	3.26	1.12 x 10^{-7}
	330	1.65	1.19 x 10^{-4}
1% W^{6+} ion	33	3.26	7.53 x 10^{-7}

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doped	330	1.65	5.21×10^{-4}
5% W^{6+} ion doped	33	3.26	8.26×10^{-6}
	330	1.65	8.40×10^{-4}

Table2. Open circuit voltage (OCV) values of solid state batteries using W^{6+} ion doped and undoped nanocrystals as electrolyte

Cells	Anode	Electrolytes	Cathode	OCV (V)
I	**Ag**	$[(H_2O)(OH)\mathbf{Ce}(S)_2\mathbf{Ce}(OH)(H_2O)]$ (Undoped)	**C + I_2**	0.325
II	**Ag**	$[(H_2O)(SH)(OH)W\text{-}(O)_3\text{-}W(OH)(SH)(H_2O)]^{2+}$ (1% W^{6+} ion doped)	**C + I_2**	0.635
III	**Ag**	$[(H_2O)(SH)(OH)W\text{-}(O)_3\text{-}W(OH)(SH)(H_2O)]^{2+}$ (5% W^{6+} ion doped)	**C + I_2**	0.734

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