Preparation, characterization and properties of LnSmWO_6 ($\text{Ln} = \text{Nd}$ and Dy) nanofunctional ceramics

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Abstract. Isovalent substitution of lanthanide ions in Ln_2WO_6 ($\text{Ln} = \text{lanthanides}$) nanoceramics can probe into multifunctional applications due to their unique structural and electronic properties. In this work Sm^{3+} ions in the Sm_2WO_6 nanoceramics were partially replaced with Nd^{3+} and Dy^{3+} ions and their structural, optical and ionic transport properties were studied. The size and structure of the nanocrystalline LnSmWO_6 ($\text{Ln} = \text{Nd}$ and Dy) compounds prepared through a combustion method were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy and transmission electron microscopy (TEM). UV–Visible spectroscopy and photoluminescence spectroscopy were used for the investigation of optical and electronic properties of the nanoceramics. Bulk ceramics prepared from the nanoparticles achieved high-density during the sintering process and the surface morphology of the dense NdSmWO_6 was imaged using scanning electron microscopy. The electrical properties of the dense ceramics were analysed using impedance spectroscopy. XRD analysis carried out on the prepared materials showed a single-phase monoclinic structure for the nanoceramics. A combined analysis of FTIR and Raman studies showed the presence of Ln-O and O-W-O vibrations, which confirm the monoclinic structure. Particulate properties investigated through the TEM imaging showed that the prepared materials are polycrystalline aggregates. Optical studies carried out on the nanoparticles showed absorption in the UV region and emission in the visible region. Impedance spectroscopic studies conducted on bulk ceramics imply that these are good oxide ion conductors at high-temperature.

Keywords. Combustion; band gap; photoluminescence; Cole–Cole plot.

1. Introduction

Nanomaterials with a particle diameter ranging from 1 to 100 nm exhibit unique physical and chemical properties that are totally different from their bulk materials. They have novel optical and electronic properties, which mainly comes from their high-surface to volume ratio and the quantum size effect. In materials science research community, materials exhibiting better dielectric and optical properties have gained interest in the recent years. The oxides based on $\text{Ln}_2\text{O}_3\text{--MO}_3$ ($\text{Ln} = \text{La, Nd, Sm, Gd}$ and Dy and $\text{M} = \text{W}$ and Mo) compounds were attracted by the researchers due to their optical, catalytic, ferroelectric and ionic transport properties [1–4]. Tungsten-based ceramics have self-activated luminescence properties, so that they are used in the field of phosphors, scintillators and laser host materials [5,6]. The intrinsic emission shown by the self-activated hosts such as tungstates, molybdates and vanadates is due to the transitions of electrons between the conduction and valence bands [7]. The luminescence observed in the blue-green region in these materials is mainly originated from the charge transfer transitions, defect luminescence and exciton recombination [8].

Tungsten oxide reacts with rare-earth oxides and forms a series of isomorphous rare-earth tungstates with the general

formula RE_2WO_6 and monoclinic symmetry [9]. Generally, metal tungstates can be divided into two groups depending on the co-ordination of tungsten, the first one is a scheelite type structure which consists of regular $(\text{WO}_4)^{2-}$ tetrahedra and the other one is a wolframite structure in which W^{6+} ions are six-fold co-ordinated to form distorted $(\text{WO}_6)^{6-}$ octahedra [10–16]. The Ln_2WO_6 family of compounds belongs to the second group. These rare-earth tungstates were known in the literature from 1902 when Cleve prepared Yb_2WO_6 [17]. Chen *et al* [18] studied the structure stability, sintering behaviour and microwave dielectric properties of Ln_2WO_6 ($\text{Ln} = \text{La, Nd, Sm, Eu}$ and Gd) ceramics prepared by the conventional solid state method; the dielectric studies conducted on Sm_2WO_6 show a dielectric constant (ϵ_r) of 18.75. However, the microwave dielectric studies conducted on the Nd_2WO_6 ceramics sintered at 1500°C show the dielectric constant (ϵ_r) value of 15.6 [19]. There are also few reports on the magnetic and electrical properties of RE_2WO_6 ($\text{RE} = \text{Nd, Sm, Eu, Gd, Dy}$ and Ho) ceramics. The magnetic studies performed on RE_2WO_6 ($\text{RE} = \text{Nd, Sm, Eu, Gd, Dy}$ and Ho) within the temperature range of 4.2–280 K show that $\text{RE} = \text{Nd, Gd, Dy}$ and Ho tungstates are the paramagnetic substance whereas $\text{RE} = \text{Sm}$ and Eu exhibit more complex behaviour [20,21]. The rare-earth ions were characterized by a partially

filled 4f shell shielded by $5s^2$ and $5p^6$ orbitals. The unfilled 4f electronic structure of the rare-earth elements makes them to exhibit special properties in luminescence, magnetism and electronics, which could be used to develop many new materials for various applications such as phosphors, magnetic materials, hydrogen storage materials and catalysts. The rare-earth ions have nearly the same electric charge and ionic radii, so that they can be easily replaced by each other in the host materials. In this study, the parent compound is selected as Sm_2WO_6 , Sm^{3+} is partially substituted by isovalent rare-earth ions Nd^{3+} and Dy^{3+} . So far, to the best of our knowledge, no work has been reported for the optical and dielectric properties of partially substituted LnSmWO_6 ($\text{Ln} = \text{Nd}$ and Dy). So, an attempt has been made to prepare LnSmWO_6 ($\text{Ln} = \text{Nd}$ and Dy) ceramics and to study its structural, optical and electrical properties.

The controlled synthesis of inorganic nanomaterials with a specified size, shape and structure is of fundamental significance in materials science and engineering because these factors could not only affect the optical, electrical and magnetic properties but also will determine the performance of these material-based devices. Among the reported synthesis techniques, combustion synthesis has an advantage of preparing ultra-fine particles due to its low-cost, time saving and high-yield. The combustion method occurs at a lower-temperature, shorter reaction time and lesser steps than the solid-state reaction and modified Pechini method [22]. In this work an auto-igniting combustion technique is used to prepare the fine nanoceramics.

2. Experimental

2.1 Preparation of nanoceramics

An auto-igniting combustion method was used for the synthesis of LnSmWO_6 ($\text{Ln} = \text{Nd}$ and Dy) nanoparticles, hereafter abbreviated as NSW and DSW. In this synthesis, the stoichiometric ratio of high-purity chemicals of ammonium tungsten oxide hydrate ($[\text{NH}_4]_6\text{W}_{12}\text{O}_{39} \cdot x\text{H}_2\text{O}$) and rare-earth oxide of Nd_2O_3 , Sm_2O_3 and Dy_2O_3 are used. Rare-earth oxides are dissolved in nitric acid and ($[\text{NH}_4]_6\text{W}_{12}\text{O}_{39} \cdot x\text{H}_2\text{O}$) in double distilled water. Urea is used as the fuel (reducing agent) and citric acid as the complexing agent [23]. The proportion between the complexing agent and salts is calculated according to the valency of reacting elements in order to supply the maximum energy for the reaction. The product is stirred well until a clear solution with no sedimentation or precipitate is obtained. The solution is heated using a hot plate maintained at 250°C in a ventilated fume hood and undergoes dehydration followed by decomposition producing dark foam. As temperature increases the foam gets auto-ignited due to self-propagating combustion, resulting in a voluminous fluffy powder. In order to eliminate few traces of black organic impurities, the powder thus obtained is annealed at 800°C for one hour in an oxygen atmosphere.

2.2 Characterization methods

The structure and phase purity of the prepared samples are characterized using an X-ray diffractometer (XRD) (D8 advance, Bruker, Germany) with $\text{CuK}\alpha$ radiation in the 2θ range of 20 – 60 in steps of 0.02 . The infrared spectra of the samples are recorded in the range of 400 – 1100 cm^{-1} on a Fourier transform infrared (FTIR) spectrometer (Spectrum2, Perkin-Elmer, Singapore) using the attenuated total reflection method. The Raman spectra of the samples are recorded in the wavenumber range of 100 – 1000 cm^{-1} at room temperature using a confocal Raman spectrograph (Alpha 300 RA, WITec GmbH, Ulm, Germany) with a 532 nm DPSS laser. The transmission electron microscopy (TEM) image of the prepared nanoparticle of DSW is recorded using high-resolution transmission electron microscopy (HRTEM) (Joel/JEM 2100, USA) operating at 200 KV . The TEM image is obtained by sonicating a pinch of sample using acetone as the dispersing solvent for half an hour and then is taken on copper grid of 300 mesh which is coated with carbon. The UV–Visible absorption spectrum of the sample is recorded in the range of 200 to 700 nm using a UV–Vis spectrometer (Lambda 35, PerkinElmer, Singapore) with an integrated sphere accessory (RSA-PE-20, Labsphere, USA). The photoluminescence (PL) spectrum of the prepared samples is recorded using a spectrofluorometer (FP-846 JASCO, Japan). The phase pure nanopowder is pressed into a circular pellet by mixing with solution of polyvinyl alcohol, which is used as a binder, ground well and dried. Then the powder is uniaxially pressed using a hydraulic press with a pressure of 20 MPa at room temperature. The pellet of LnSmWO_6 ($\text{Ln} = \text{Nd}$ and Dy) is sintered with the help of high-temperature resistive heating furnace and sintering temperature is optimized and is shown in table 1. The density of the sintered pellet is measured using Archimedes' principle. The surface morphology of the thermally etched pellet of NSW at a temperature of 1150°C for one hour is subjected to scanning electron microscopy (SEM) analysis using JEOL 6390 LV. For dielectric measurements the sintered pellets are made in the form of disc capacitor by polishing the flat surfaces and silver paste is applied as the electrode on both sides of the pellet.

The electrical conductivity studies of sintered pellets are performed using an LCR meter (LCR HiTester 3532-50, Hioki, Japan) in the frequency range of 50 Hz to 5 MHz at temperature varying from 450 to 750°C for NSW and 500 to 700°C for DSW. The dielectric constant of the pellet is measured using the equation:

$$C_p = \epsilon_0 \epsilon_r A/d, \quad (1)$$

where ϵ_r is the dielectric constant, ϵ_0 is the permittivity of free space, A is the cross-sectional area and d is the thickness of the disc. The dependence of microstructure on electrical behaviour is analysed using impedance spectroscopy.

Table 1. Crystallite size, lattice parameter, density, percentage of density attained and sintering temperature of LnSmWO₆ (Ln = Nd and Dy) ceramics.

Name of samples	Crystallite size (nm)	Lattice parameter (Å)			Density (g cm ⁻³)	Percentage of density attained (%)	Sintering temperature (°C)
		<i>a</i>	<i>b</i>	<i>c</i>			
NSW	34.78	15.8959	11.3914	5.3853	7.82	95	1250
DSW	21.10	15.8791	11.2734	5.2579	8.12	95	1225

Figure 1. XRD pattern of (a) prepared LnSmWO₆ (Ln = Nd and Dy) and (b) sintered pellets of LnSmWO₆ (Ln = Nd and Dy).

3. Results

3.1 XRD studies

XRD studies are used to investigate the structure, phase and average crystallite size of nanoparticles. Figure 1a and b shows the XRD patterns of the as-synthesized compounds

at two different temperatures, one at 800°C and other at a sintering temperature of 1250°C for NSW and 1225°C for DSW. All the diffraction peaks of NSW and DSW can be indexed using the ICDD file of Sm₂WO₆ (file no. 23-1401) monoclinic with the space group *I2/a* (15). Chen *et al* [18] studied the XRD of the Sm₂WO₆ sample prepared by the conventional solid-state method at a temperature of 1100°C. In this study, NSW and DSW samples are prepared by the combustion method and we have obtained the XRD diffraction pattern of NSW and DSW similar to Sm₂WO₆. The XRD diffractograms of sintered pellets show sharp peaks compared to the powder XRD pattern. Comparing figure 1a and b, it is inferred that the highest intensity reflection in the XRD pattern (figure 1a) of NSW has two distinctly visible peaks whereas the XRD pattern of DSW shows a single merged high-intensity peak. The merging of peaks in DSW is due to nano-nature of the prepared samples. The (−321) and (321) reflections occur separately and are clearly visible in the sintered pellet XRD diffractogram of DSW. From figure 1b, it is also obvious that the crystal structure does not change during sintering. Depending on the ionic radius of the lanthanide ions, the Ln₂WO₆ ceramics can generally adopt any one of the monoclinic, tetragonal and orthorhombic structures. Recent studies on lanthanide ceramics show that Ln₂WO₆ with a lanthanide ionic radius value less than 0.964 Å will stabilize in the monoclinic structure whereas greater than this value will be in a mixed phase. As the ionic radius of Nd³⁺ (0.983) is higher than the above reported value, the partial substitution of it may affect the stability of the monoclinic structure. However, it is obvious from the XRD pattern of the prepared materials that the partial replacement of the Sm³⁺ ion by Nd³⁺ and Dy³⁺ ions does not affect the stability of the structure, since these show similar peaks with the reference pattern of Sm₂WO₆. That is there is no evidence for secondary phases in the pattern, implying the single-phase monoclinic form of LnSmWO₆ (Ln = Nd and Dy) nanoceramics. The slight shift observed in the relative position of the peaks in the diffractograms with respect to the reference pattern validates the replacement of isovalent ions. The broad peaks in the XRD pattern are the indication of nanocrystalline nature of the samples. The average crystallite size of the prepared nanoparticles can be estimated from the full-width at half maximum (FWHM) of the XRD peaks using the Scherrer formula:

$$D = K\lambda/\beta \cos \theta, \quad (2)$$

Figure 2. FTIR spectra of LnSmWO_6 ($\text{Ln} = \text{Nd}$ and Dy).

where D is the crystallite size, $K = 0.9$ a correction factor, β is the FWHM and λ is the wavelength of X-ray ($\text{CuK}\alpha = 1.5405\text{\AA}$). The lattice parameter values are calculated by the least squares method. The calculated values of the crystallite size and lattice parameters are shown in table 1.

3.2 FTIR spectroscopy

FTIR is an efficient technique to identify functional groups in the materials through the characteristic vibrational motion of atoms and molecules. In FTIR spectroscopy, each molecule absorbs infra-red (IR) radiation of certain frequencies based on the characteristic vibration of the molecule. Hence it is possible to identify the symmetry of molecules and the amount of each molecule in the materials by studying the IR absorption spectrum. Figure 2 shows the FTIR transmittance spectra of the prepared materials, which are characterized by the appearance of several peaks corresponding to the mid-IR vibrational modes of the metal–oxygen bonds. The compound Sm_2WO_6 shows IR bands at 875, 790, 765, 690, 530, 520, 480, 460, 425 and 410 cm^{-1} , respectively [24]. The bands observed for DSW are at 420, 474, 525, 674, 695, 760 and 880 cm^{-1} and NSW are at 410, 444, 508, 639, 674, 880 and 927 cm^{-1} . The bands observed at 927 cm^{-1} is due to WO_6 polyhedra, $881\text{--}878\text{ cm}^{-1}$ are due to the corner-sharing W–O–W and $786\text{--}746\text{ cm}^{-1}$ are due to the edge-sharing W–O–W bonds. Bands below 500 cm^{-1} are due to the deformation modes of W–O bonds in WO_6 octahedra or due to the deformation modes of W–O–W bridges. All the other observed bands are due to the Ln–O stretching vibrations. The vibrational modes obtained in FTIR are in good agreement with the literature [25–34]. It is also observed that the FTIR spectrum of DSW is shifted to a higher wavenumber region as compared to the spectrum of NSW, which confirms the replacement of Sm^{3+} ion by Nd^{3+} and Dy^{3+} ions.

Figure 3. Raman spectra of LnSmWO_6 ($\text{Ln} = \text{Nd}$ and Dy).

3.3 Raman spectroscopy

Another vibrational study tool, Raman spectroscopy is used for the determination of the structure and chemical properties of materials. Raman spectra of the prepared nanoceramics are shown in figure 3. Both the samples show similar patterns irrespective of replacement of Ln^{3+} ions which confirms the monoclinic structure of LnSmWO_6 . From the spectra it is clear that DSW is shifted to higher wavenumber. The main peaks of Raman spectra are observed between $820\text{--}880\text{ cm}^{-1}$ which are due to the stretching vibrations of tungsten (O–W–O), which confirms the monoclinic structure of the compounds [35].

3.4 TEM analysis

The particle size and morphological properties of the as-prepared nanoparticles of DSW are studied using TEM. From figure 4a, it is clear that the particles are nearly spherical in shape, slightly agglomerated and the observed particles are in the nanometre range. ImageJ software is used to measure the size of particles and from the measured data a histogram is constructed. The average particle size is calculated from Gaussian fit to this histogram. Figure 4b shows the histogram distribution of the particle size of DSW nanoparticles and the mean size obtained is $88.09 \pm 0.45\text{ nm}$. The particle size measured from TEM analysis is much higher than the crystallite size measured from XRD analysis, which indicates that the prepared nanoparticles are polycrystalline aggregates [36]. Figure 4c shows the HRTEM image of the prepared sample. The d -spacing marked on the HRTEM image is comparable with corresponding hkl planes obtained from the XRD data.

Figure 4. (a) TEM image of DSW, (b) particle size distribution histogram of DSW and (c) HRTEM of DSW.

3.5 Optical spectral analysis

The absorption of UV light may cause the excitation of electrons in atoms and molecules to higher energy states and this causes each molecule to undergo electronic excitation. The wavelength of light absorbed depends on its chemical structure. So, the absorption spectra can be used to study atomic and molecular species. The rare-earth ions have partly filled 4f electron ($4f^n 5s^2 5p^6 6s^2$), as a result they show absorption peaks from the infrared to ultraviolet region. The absorption spectra of visible and near infra-red belong to the transition between f–f and energy level in the $4f^n$ configuration, while UV absorption is caused by the transition from the low-energy level 4f to the high-energy level 5d configuration [37,38]. Figure 5a shows the absorption spectra of the prepared nanomaterials in the range of 200–700 nm. These materials heavily get absorbed in the UV region and decrease with an increase in the wavelength towards the visible region. The maximum absorbance in the UV region and moderate absorbance in the

visible region make it an excellent material in screening of the UV portion of the electromagnetic spectrum which is dangerous to human health. The wavelength at which absorption starts for NSW and DSW is 346 and 361 nm, respectively. The broad absorption observed in the UV region depends on various factors such as band gap, oxygen deficiency and surface roughness. As the size of the particles decreases the surface to volume ratio increases, which in turn increases the distribution of defects on the surface of nanomaterials [39,40]. The observed absorption spectra exhibit the optical behaviour of a wide band gap semiconducting oxide. Therefore, these samples can be used as UV filters and sensors in optical applications. A common peak observed at 405 nm in the absorption spectra of DSW and NSW is due to the ${}^6\text{H}_{5/2} \rightarrow {}^4\text{F}_{7/2}$ transition of Sm^{3+} [41]. Several other absorption peaks are visible in the absorption spectra of NSW, which is due to the optical absorption of Nd^{3+} .

The Wood and Tauc's equation are used to estimate the band gap of the above synthesised nanopowders. The band

Figure 5. (a) Absorption spectra of LnSmWO₆ (Ln = Nd and Dy). (b) Tauc's plot of NSW. (c) Tauc's plot of DSW.

gap in the nanomaterials is the energy difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital. For semiconductors the absorption co-efficient near the fundamental edge depends on the photon energy which is expressed by Tauc's equation. The measured reflectance is converted into the Kubelka–Munk function:

$$F(R) = (1 - R)^2 / (2R), \quad (3)$$

where $F(R)$ is the Kubelka–Munk function, R is the reflectance which is proportional to the absorption co-efficient α in Tauc's equation. According to this relation $F(R)$ is related to the band gap of a material by the relation:

$$(F(R) \cdot h\nu) = B(h\nu - E_g)^n, \quad (4)$$

where B is the energy independent constant, h is the Planck constant, ν is the frequency of incident radiation and n is the constant which varies with the nature of electronic transition responsible for optical transition. The value of

$n = 1/2$ and $3/2$ correspond to direct allowed and forbidden transitions and $n = 2$ and 3 correspond to indirect allowed and forbidden transitions. The band gap can be obtained by extrapolating Tauc's plot to $(F(R) \cdot h\nu) = 0$. Tauc's plot for the prepared materials is shown in figure 5b and c. The estimated band gaps for NSW and DSW are 3.63 and 3.74 eV, respectively. By comparing the band gap values corresponding to different n values with absorption energy values (from the absorption spectra) $n = 1/2$ suitably fits for DSW whereas $n = 2$ fits for NSW. Therefore, DSW may be a direct band gap material whereas NSW is an indirect band gap material.

PL occurs when an external source of energy in the form of electromagnetic radiation is absorbed by an atom or molecule resulting in the emission of photons. The room temperature PL spectra of NSW and DSW excited at 404 nm are shown in figure 6. The PL emission bands of NSW and DSW occur in visible regions of electromagnetic spectra. Defect levels inside the band gap known as trap levels are responsible for emission in the visible region. The emission peaks of NSW

Figure 6. Photoluminescence spectra of LnSmWO_6 ($\text{Ln} = \text{Nd}$ and Dy).

occur at 486 (blue) and 600 nm (orange), which may be due to $^4\text{I}_{9/2} - ^2\text{G}_{9/2} + ^4\text{G}_{11/2} + ^2\text{K}_{15/2}$ and $^2\text{G}_{7/2} + ^4\text{G}_{5/2}$ of Nd^{3+} and $^6\text{H}_{5/2} - ^4\text{M}_{17/2}$ and $^4\text{G}_{5/2} - ^6\text{H}_{7/2}$ of Sm^{3+} . The observed emission peaks of DSW may be due to the combined action of Dy^{3+} and Sm^{3+} . Peaks at 456, 489 (blue) and 606 nm (orange) may be due to $^6\text{H}_{15/2} - ^4\text{I}_{15/2}$, $^4\text{F}_{9/2} - ^6\text{H}_{15/2}$ and $^6\text{H}_{11/2}$ of Dy^{3+} and $^6\text{H}_{5/2} - ^4\text{I}_{11/2}$, $^4\text{I}_{15/2}$ and $^4\text{G}_{5/2} - ^6\text{H}_{7/2}$ (partly magnetic and partly electric dipole) of Sm^{3+} [42–45]. The 489 nm emission of Dy^{3+} is magnetically allowed transition and 606 nm is forced electric dipole transition [46].

3.6 SEM analysis

The compounds are sintered to their maximum density at different temperatures. The high-surface area and surface energy of nanoparticles lead to good sintering characteristics. Chen *et al* [18] optimized the sintering temperature of Sm_2WO_6 , as 1170°C. In the present study, ceramics are sintered at slightly higher temperature as compared to the above study. This is due to the partial replacement of Sm^{3+} by Ln^{3+} ions. The percentage of density obtained and sintering temperature are shown in table 1. The SEM image of the thermally etched NSW pellet is shown in figure 7a. The grains are well separated by grain boundaries. It is also evident from figure 7a that the sample has achieved high densification with minimum porosity. Using the data obtained from the SEM image, the grain size histograms are drawn and are shown in figure 7b. The mean size of the grain obtained is about $0.98 \pm 0.04 \mu\text{m}$.

3.7 Dielectric studies

The study of the dielectric constant provides an insight into the nature of atoms, ions and bonding in the material. The variation of the dielectric constant with temperature and frequency

Figure 7. (a) SEM image of NSW. (b) Grain size distribution of NSW.

gives different polarization mechanisms in solids. The variation of the dielectric constant of the prepared dense ceramics as a function of frequency is shown in figure 8a and b. From the graph, it is clear that the dielectric constant decreases with an increase in the frequency. The value of ϵ_r is high for different temperatures in the low-frequency region and reaches a constant value in the high-frequency region. The value of the dielectric constant at higher frequencies is important for the fabrication of materials for ferroelectric, photonic and electro-optic devices. The values of the dielectric constant at 10 kHz and at a temperature of 700°C for samples NSW and DSW are 80 and 166, respectively. These values of the dielectric constant obtained are high as compared with Sm_2WO_6 prepared by the conventional solid state method [18]. The large value of the dielectric constant at a low-frequency is due to space charge polarization of the charged lattice sites. Space charge polarization which is generally active at high temperature and low-frequency indicates the purity and perfection of samples [47].

The complex impedance spectrum, Nyquist plot or Cole–Cole plot clearly indicates the charge transport behaviour of the samples. The pattern of semi-circular arc, their extent of intercept on the real axis and the number of semicircles in it provide important information regarding electrical behaviour of the sample. In general, the arc at the high-frequency end

Figure 8. (a) Variation of the dielectric constant with the frequency of NSW. (b) Variation of the dielectric constant with the frequency of DSW.

refers to grain, in the mid-frequency region corresponds to the grain boundaries and the arc at the low-frequency end is due to the space charge–electrode interaction [48]. The effect of temperature on impedance and related parameters can also be analysed by the Cole–Cole plot. At lower temperatures the plots show almost semicircular structures, due to the hopping of thermally activated ions. The Cole–Cole plots for the samples, plotted in a linear scale are shown in figures 9a and b. For NSW at a temperature of 450 to 550°C a single semicircle is observed. The absence of the second semicircle indicates that the electrical behaviour in the sample is basically due to grain. At high-temperature a depressed semicircle is observed which can be resolved into two semicircles. The first semicircle is due to the grain and second is due to the grain boundary effect. Also, as temperature increases the arc is shifted towards the left side which is the indication of a decrease of grain and grain boundary resistance. This also shows the negative temperature coefficient of resistance behaviour of the samples.

Figure 9. (a) Cole–Cole plot of NSW. (b) Cole–Cole plot of DSW.

The variation of the real part (Z') of impedance with frequency at different temperatures of NSW and DSW is shown in figure 10a and b. As temperature increases the magnitude of Z' falls off with an increase in the frequency and merges at the high-frequency. This is due to the reduction of barrier properties and space charge release of the material when temperature is increased. This may be the cause in the magnification of total conductivity of materials when temperature increases (discussed later). This also confirms the negative temperature co-efficient of resistance behaviour of the materials similar to the semiconductors. The entire curve at different temperatures coincides in the high-frequency region, reaches a constant value for Z' , indicating the release of space charge with the rise in temperatures. The variation of the imaginary part (Z'') of the impedance with frequencies at different temperatures for NSW and DSW is shown in figure 11a and b. The peak shift with an increase in temperature towards the high-frequency side is caused by the variation in the relaxation process. This indicates that

Figure 10. (a) Variation of the real part of impedance with the frequency of NSW. (b) Variation of the real part of impedance with the frequency of DSW.

the relaxation time decreases with an increase in temperature because of the increased mobility of space charges at high-temperature.

The ionic conductivity of materials varies with temperature and shows Arrhenius behaviour:

$$\sigma = \sigma_0 \exp(-E_a/K_B T), \quad (5)$$

where σ_0 is the pre-exponential factor, E_a is the activation energy, K_B is the Boltzmann constant and T is the absolute scale working temperature. The conductivity of Sm_2WO_6 at 550 °C (in air) is reported to be $2.62 \times 10^{-8} \text{ S cm}^{-1}$ and activation energy as 1.40 eV, respectively [49]. The Arrhenius plot of the materials is shown in figure 12 and activation energies are marked on it. These materials show almost linear behaviour with a deviation at particular temperature, for NSW this deviation occurs at 650 °C whereas it appears at 600 °C for DSW. Compared with the low-temperature activation energy values, the high-temperature activation energy values are

Figure 11. (a) Variation of the imaginary part with the frequency of NSW. (b) Variation of the imaginary part with the frequency of DSW.

Figure 12. Arrhenius plot of LnSmWO_6 (Ln = Nd and Dy).

slightly high, this indicates the change of the conduction mechanism in the materials. The high-temperature activation energy values support the ionic conducting nature of the materials with predominant oxide ion migration [50]. The maximum value of conductivity observed in this study is $1.65 \times 10^{-4} \text{ S cm}^{-1}$ at 700°C for the dense DSW ceramic.

4. Conclusion

LnSmWO_6 ($\text{Ln} = \text{Nd}$ and Dy) nanocrystalline materials have been successfully prepared by an auto-igniting combustion method. XRD analysis confirms the monoclinic structure of the prepared nanoparticles. The particle size of DSW is found to be in the range of 80 nm. FTIR and Raman analysis support the XRD results. The high-absorbance in the UV region and low-absorbance in the visible region of samples suggest that they are good materials for the fabrication of UV filters. The PL spectra of the samples show the ability of visible emission. The value of the dielectric constant is found to be high for DSW as compared to NSW. The electrical properties indicate that conduction is due to grain and grain boundary effects. The analysis of real and imaginary parts of the impedance shows that they are frequency and temperature dependent. The prepared nanomaterials can be used for optical and electronic applications.

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