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Optical properties of chemically synthesized nanostructured strontium tungstate

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Abstract

Nanostructured materials differ from conventional materials in terms of its tunable physical properties. The optical properties of nanostructured materials are grain size dependent and this gives an opportunity to engineer these properties to develop materials to suit specific needs. Strontium tungstate (SrWO_4) is employed as solid state scintillators and in optoelectronic devices. In the present study, nanocrystalline SrWO_4 of three different grain sizes were synthesized using chemical precipitation technique. The crystal structure, phase and the grain size of the samples were found from X-ray diffraction spectra. The Fourier transform Infrared spectra of the sample was recorded and analysed for phase purity. The UV-Visible absorption, photoluminescence and Raman spectra of the samples were recorded and the features of the spectra are discussed in detail.

Key words: Nanostructured materials, Optical absorption spectra, Photoluminescence, Raman spectra, Strontium tungstate.

Introduction

Nanostructured materials are new class of materials that have properties often superior compared to conventional bulk solid. Unique properties exhibited by these materials have attracted extensive studies and find potential applications in different fields of science and technology (L. Tian et. al., 2018 and A. M. Abadalla et. al., 2018). The reduction of crystalline size to nanoscale often involves spectacular changes in optical properties of materials through charge and phonon confinement (D.M. Sagar et. al., 2015 and E. Nazek et. al., 2016). One of the distinct features of nanostructured materials is that a large percentage of atoms are associated with interface such as surfaces and grain boundaries. Therefore with the decrease in average particle size, the characteristics of surface atoms will become increasingly sharper and contribution from these atoms should be taken into account when attempting to describe strange properties exhibited by materials with nanograin size (C. Zhou et. al., 2012 and MD. P Ahmaed et. al., 2019).

Metal tungstates and molybdates are two important families of inorganic materials that have high application potential in various fields, such as in photoluminescence, microwave applications, optical fibers, scintillator materials, humidity sensors, magnetic properties and catalysis (W. Van Loo, 1975, T.T. Basiev et. al., 2000, D. Chen et. al., 2003, M.A.M. A. Maurera et. al., 2004, G. Jia et. al., 2004,



S.K. Arora and B. Chudasama, 2006, L. Sun et. al., 2007, J.C. Sczancoski et. al., 2015, H. Hossainian et. al., 2016, E. A. Potanina et. al., 2019). Strontium tungstate crystal belongs to the tungstate family. Alkaline-earth tungstates, MWO_4 ($M = Ba, Ca, Sr, Pb$) are important because of their scientific and technological applications. These compounds are employed as solid-state scintillators and optoelectronic devices. Tungstate divalent scheelite compound strontium tungstate ($SrWO_4$) finds use in solid state laser applications and various other technological applications. Strontium Tungstate crystallizes in a tetrahedral structure with four molecules in each crystallographic unit. Several reports of synthesis and characterization of crystals of $SrWO_4$ are available in the literature (W. Van Loo, 1975, T.T. Basiev et. al., 2000, M.A.M. A Maurera et. al., 2004, G. Jia et. al., 2004, S.K. Arora and B. Chudasama, 2006, L. Sun et. al., 2007, J.C. Sczancoski et. al., 2015, H. Hossainian et. al., 2016, E. A. Potanina et. al., 2019). Rare-earth doped strontium tungstate crystals and their optical properties were also reported in the literature (S. K. Gupta et. al., 2016, Y. Zhang et. al., 2018). In the present work, the synthesis and evolution of optical properties of nanostructured $SrWO_4$ are attempted. The structural characterization of the samples were done using x-ray diffraction, Fourier transform Infrared spectroscopy, UV-Visible spectroscopy, photoluminescence spectroscopy and Fourier transform Raman spectroscopy.

Materials and Methods

Nanocrystalline $SrWO_4$ was synthesized by chemical precipitation technique. Strontium chloride hexahydrate ($SrCl_2 \cdot 6H_2O$) and Sodium Tungstate dehydrate ($Na_2WO_4 \cdot 2H_2O$) are the reactants. The equation for the reaction could be given as



Aqueous solutions of the reactants were added to the reaction medium under rigorous stirring. The resulting precipitate is washed and dried. Three different samples of strontium tungstate were prepared by changing the reaction medium, pH and the preparation conditions. The samples were given codes ST1, ST2 and ST3. The powder samples were then characterized using X-ray diffraction technique to identify crystal structure, phase and grain size. The X-ray diffraction patterns of all the powder samples were recorded using Philips XPERT PRO diffractometer with $Cu K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) source. Fourier transform Infrared (FTIR) spectrum of the sample was recorded in the range 400 to 1200 cm^{-1} using Bruker IFS FTIR spectrometer. 10 mg of each powder sample is finely dispersed in ethanol using ultrasonicator and the absorption spectra of the dispersed sample were recorded in the UV-Visible range using CARY 100 BIO UV-Visible spectrometer from 200 – 700 nm range, The photoluminescence (PL) spectra of the dispersed samples in ethanol medium were recorded for an excitation wavelength of 240 nm using SPEX Fluorolog Spectrometer. The Fourier Transform Raman spectrum of the sample with smaller grain size (Sample Code:ST2) was recorded using Bruker FT Raman spectrometer.



Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) spectrum of one of the as prepared sample of nanocrystalline SrWO₄ (sample code: ST1). The XRD spectrum showed distinct peaks indicating that the samples are crystalline in nature. The 2θ values of three major peaks are 27.8°, 45.3° and 55.9° correspond respectively to the three crystal planes (112) (204) (312) of crystalline SrWO₄. All the diffraction peaks in the spectrum can be indexed to ICDD data file 85-0587 which corresponds to SrWO₄ belonging to scheelite structure. The average grain size of the sample was determined from the broadening of diffraction peaks using Debye - Scherrer equation

$$D = k\lambda / \beta \cos\theta \quad (1)$$

where, k is a constant equal to 0.9, λ is the wavelength of X-rays equal to 1.5406 Å, β is the full width at half maximum of the diffraction peak and θ is the diffraction angle. The sizes calculated by using Debye - Scherrer equation for the samples ST1, ST2 and ST3 are 21, 16 and 25 nm respectively.

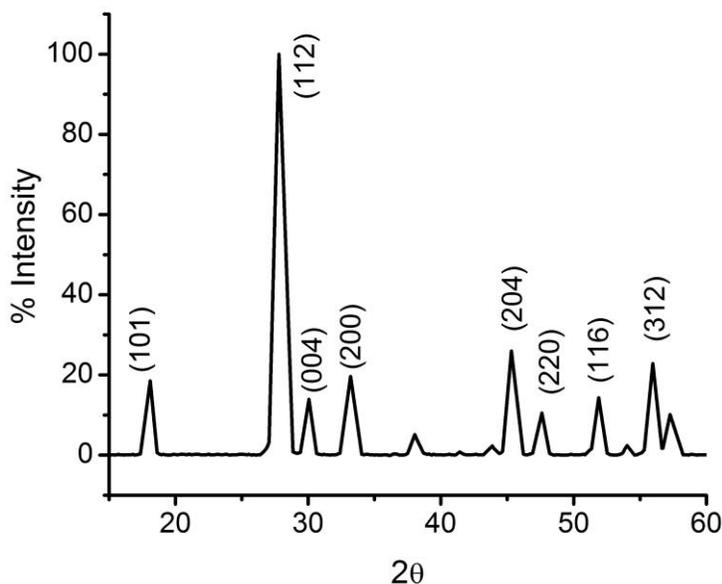


Figure 1 XRD spectrum of nanostructured SrWO₄ (sample code: ST1)

Figure 2 shows the Fourier Transform Infrared (FTIR) spectrum of nanocrystalline SrWO₄ recorded in the range 400 to 1200 cm⁻¹. The spectrum showed a sharp absorption peak at 410 cm⁻¹ and a broad peak around 820 cm⁻¹. Out of the 8 allowed modes only two modes are recorded in this range. Tungstates of scheelite type has allowed 8 stretching and bending vibrations in the IR region. The strong and sharp absorption band seen at 410 nm can be attributed to the $\nu_2(A_u)$ mode of vibration of



WO_4^{2-} tetrahedra corresponding to bending vibrations. The strong and broad band found around 820 cm^{-1} may be related to the anti-symmetric stretching vibrations inside WO_4^{2-} clusters belonging to $\nu_3(\text{A}_u)$ mode. Both these peak agree well with that reported for SrWO_4 earlier indicating that the synthesized samples are pure (J.C. Sczancoski et. al., 2015).

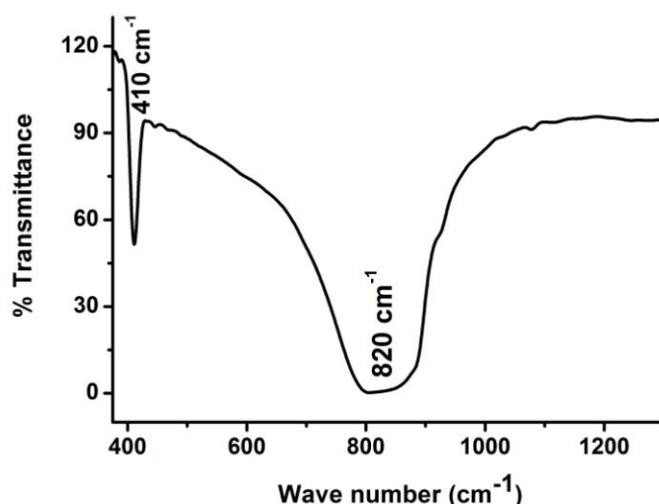


Figure 2 IR spectrum of nanocrystalline SrWO_4 (Sample Code:ST2)

Optical absorption spectra of as prepared nanocrystalline samples of SrWO_4 dispersed in ethanol medium are shown in figure 2. The samples ST1 and ST2 showed absorption onset at around 500 nm and showed a sharp peak around 250 nm. In the case of sample ST3 the absorption becomes significant around 325 nm and showed a peak around 275 nm. The optical properties of single crystals and thin films of SrWO_4 are widely reported in literature (Z. Lou and M. Cocivera, 2002, D. Chen et. al., 2003, G. Jia et. al., 2004, L. Sun et. al., 2007, A. Wang et. al., 2010, J.C. Sczancoski et. al., 2015, E.A. Potanina et. al., 2019). Single crystals of SrWO_4 were synthesized using Czochralski method and pure crystals are found to be transparent up to 2700 nm and has an ultraviolet absorption edge around 300 nm (G. Jia et. al., 2004). Thin films of SrWO_4 were fabricated on glass substrates using spray pyrolysis and study of their optical absorption properties revealed an absorption edge around 255 nm (Z. Lou and M. Cocivera, 2002). Thin films of SrWO_4 were deposited on glass substrates using chemical solution method and the transmittance of these films dropped significantly at around 260 nm (M.A.M. A Maurera et. al., 2004). It was reported that SrWO_4 powders synthesized using co-precipitation method and processed microwave-hydrothermal methods showed absorption maximum around 270 nm (J.C. Sczancoski et. al., 2009). The as prepared nanocrystalline SrWO_4 samples with average grain size 21 and 16 nm showed absorption peak around 250 nm and there is



no significant variation is found in the absorption peak. The early onset of absorption in these samples may be attributed to the defect levels present in the band. But in the case of nanocrystalline sample with average grain size 25 nm, the absorption peak was found to be at around 275 nm. All these samples showed significant blue shift compared to bulk crystals of SrWO₄. Nanostructured systems are confined systems in which the charge carriers get themselves confined. This is manifested as a blue shift in the absorption maximum well reported in semiconductor and ceramic nanoparticles (K. Lin et. al., 2005, I.A. Rahman et. al., 2008, D. Segets et. al., 2009, C. Xia et. al., 2018). In nanocrystalline SrWO₄ also it is observed that the absorption maximum gets blueshifted with reduction in grain size. Thus tuning of grain size can result in blue shift of absorption maxima in the UV-Visible spectra of nanocrystalline SrWO₄.

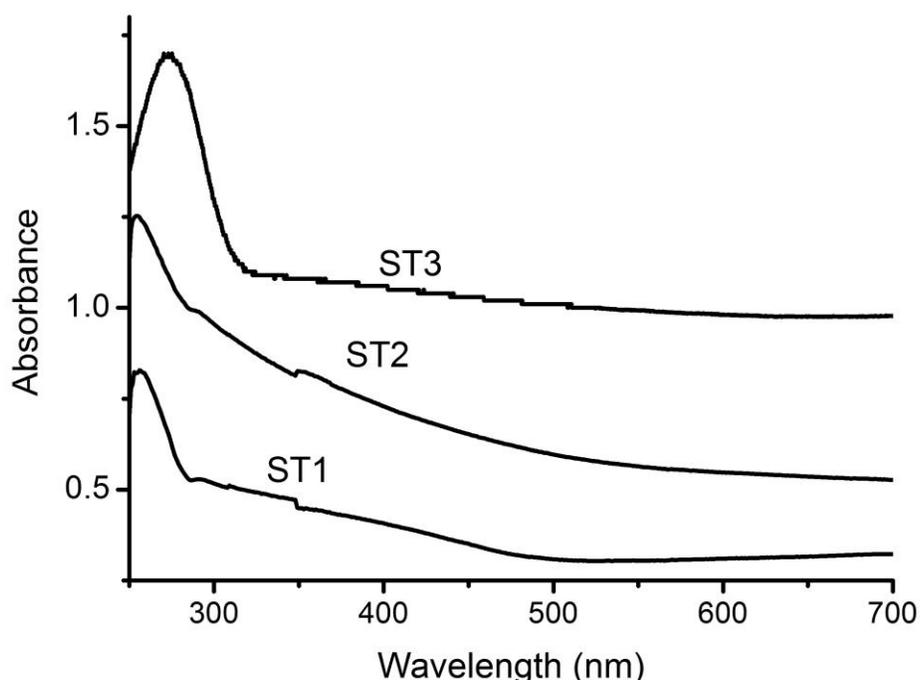


Figure 3 UV-Visible absorption spectra of nanocrystalline SrWO₄
(Sample code: ST1, ST2, ST3)

The room-temperature photoluminescence spectra for an excitation wavelength of 240 nm of nanocrystalline SrWO₄ samples (ST-1, ST-2 and ST-3) are shown in figure 2. The samples ST1 and ST2 showed a sharp peak near 420 nm while the peak shifted to higher wavelength of 430 nm for sample ST3. Hence it is seen that for sample with larger grain size the peak got shifted towards the longer wavelength side. The photoluminescence spectra of as prepared 3D microcrystals of SrWO₄



showed strong emission peaks at 432 and 505 nm (G. Tian et. al., 2014). Photoluminescence emission originates from the radiative return to the ground state upon excitation. The peaks recorded in photoluminescence spectra of SrWO₄ was attributed to the existence of distorted WO₄ clusters within SrWO₄ lattice which create intermediate energy levels in the band gap (J.C Sczancoski et. al., 2015). Thin films of SrWO₄ prepared by spray pyrolysis exhibited a cathodoluminescence at 447 and 487 nm. These peaks were ascribed to the electronic transitions happening within the WO₄²⁻ ions (Z. Lou and M. Cocivera, 2002). Photoluminescent properties of different nanostructures with different morphologies of SrWO₄ prepared using solvothermal mediated microemulsion technique showed peaks at 501 and 468 nm (L. Sun et. al., 2007). Photoluminescence spectrum of nanosized particles in irregular clusters of SrWO₄ using cyclic microwave radiation showed a prominent peak around 420 nm. This peak was attributed to ¹T₂ → ¹A₁ transitions of electrons within WO₄²⁻ ions. This transition is ascribed to be a possible exciton formation (T. Thongtem et. al., 2008, J.C. Sczancoski et. al., 2009) It may be observed that for the sample with average grain size 25 nm the photoluminescence peak got shifted towards higher wavelength. The shape of the nanoparticles, degree of crystallinity, excitation wavelength, presence of impurities, defects and many other factors contribute to emission. The shift of emission maximum to lower wavelength or higher energy may be attributed to quantum confinement effect. As the grain size is reduced to nanosize the charge carriers get confined to nanograins resulting in modification of their energy bands. Usually the band gap widening occurs as a result of lowering of grain size. Hence the emission peak also get shifted towards higher energy side with reduction in grain size.

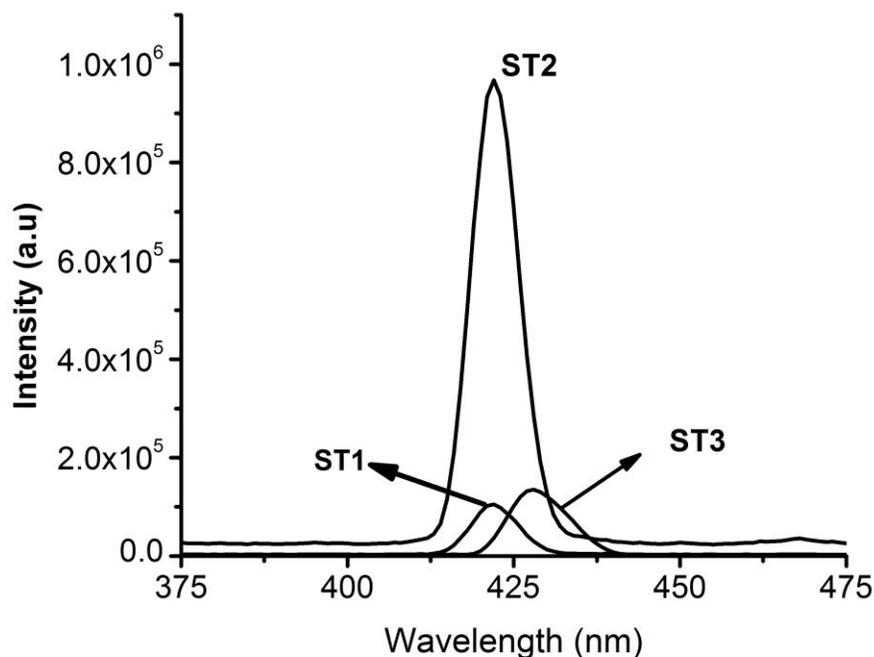


Figure 4 Photoluminescence spectra of nanocrystalline SrWO₄
Excitation wavelength : 240 nm

The figure 5 and 6 show the Fourier transform Raman spectrum of as prepared nanocrystalline SrWO₄ (Sample code: ST2) in the range 50 to 300 cm⁻¹ and 300 to 1000 cm⁻¹ respectively. Sharp peaks were observed at 921, 837, 798, 372, 336, 189, 133, 101 and 75 cm⁻¹. There are 13 zone centre Raman active modes for SrWO₄ crystals given by the equation

$$\Gamma_{\text{Raman}} = 3A_g + 3B_g + 5E_g \quad (2)$$

The vibrational modes of scheelite structured SrWO₄ may be classified as low frequency lattice or external modes and high frequency internal modes. External modes of vibrations arise from lattice phonons which may be resulting from the movement of [SrO₈] clusters and the rigid units. Relatively high frequency internal modes are attributed to the vibrations of the strong bonds inside the sublattice [WO₄] clusters (S.P.S Porto and J.F. Scott, 1967, J.C Sczancoski et. al., 2009, J.C Sczancoski et. al., 2015). First prominent Raman peak was found at 75 cm⁻¹ with a shoulder peak. Up on deconvolution it was found that there are two peaks one at 75 cm⁻¹ and another at 85 cm⁻¹. The prominent Raman peak found at 75 cm⁻¹ was reported as the B_g mode and is attributed to the symmetric bending vibrations O — Sr — O bonds in [SrO₈] clusters. A new peak of weak intensity was found at 85 cm⁻¹ which may be due to the contribution of surface atoms which will be prominent in nanostructured systems. It may be attributed to surface modes prevalent in nanosized systems. The peak found at 101 cm⁻¹ is ascribed to the free motion of [SrO₈] clusters and the peak at 133 cm⁻¹ is due to the symmetric stretching vibrations of [SrO₈] clusters. The Raman peaks 189 and 235 cm⁻¹ correspond to free rotations of [WO₄] tetrahedra. Asymmetrical bending vibration of [WO₄] sublattice



results in the Raman peak at 336 cm^{-1} ; The peak recorded at 372 cm^{-1} is characterized with marked asymmetry and hence it was deconvoluted to get two peaks one at 371 cm^{-1} and other at 379 cm^{-1} . These peaks correspond to B_g and E_g modes and are related to the symmetric bending vibrations $[\text{WO}_4]$ sublattice. Asymmetric stretching vibrations of bonds in the $[\text{WO}_4]$ sublattice give rise to Raman peaks observed at 798 and 837 cm^{-1} which match with E_g and B_g modes of symmetry. The strong Raman band observed around 921 cm^{-1} can be assigned to the symmetric stretching vibrations of $[\text{WO}_4]$ sublattice correspond to A_g mode of symmetry. It may be noted that the reduction of grain size to nanometer do not alter the frequencies of internal modes of vibrations. The surface to volume ratio of nanoparticles is very large and the contribution of surface atoms will become significant compared to that of bulk material. These surface atoms will collectively oscillate to give new low frequency surface modes of vibration. The high surface to volume ratio can create a surface stress which may be compressive or tensile. This strain also can shift the frequency of the Raman lines.

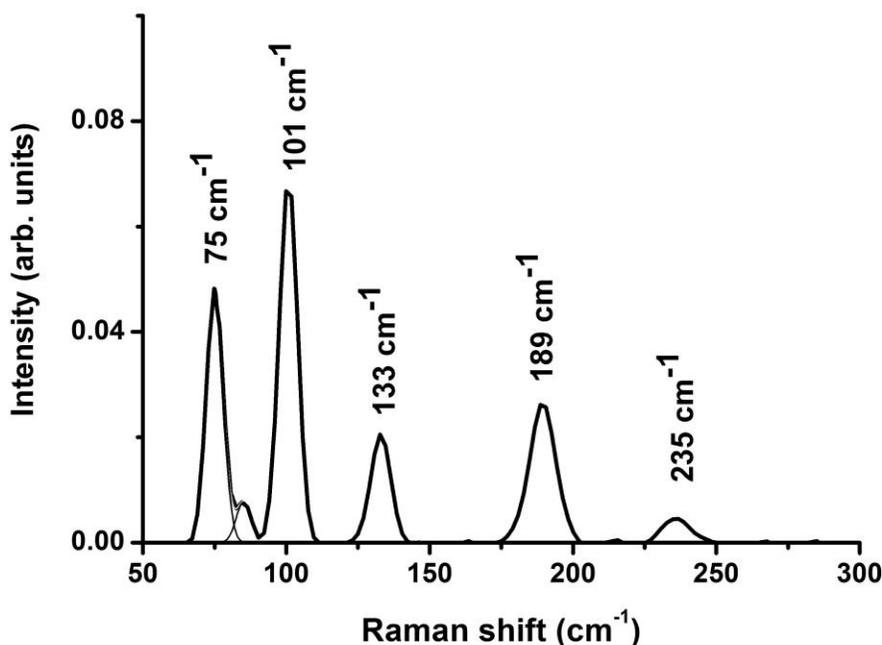


Figure 5 Raman spectrum of nanocrystalline SrWO₄ in the range 50-300 cm⁻¹

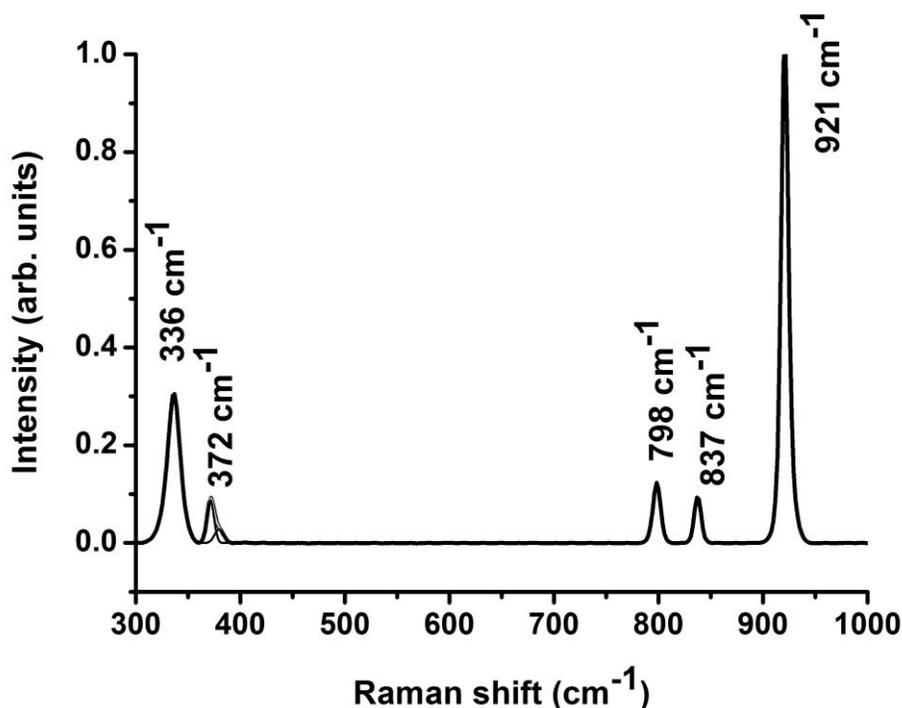


Figure 6 Raman spectra of nanocrystalline SrWO₄ in the range 300 to 1000cm⁻¹

Conclusion

SrWO₄ is an important material having excellent optical properties. They have wide spread applications in various fields, such as in photoluminescence, microwave applications, optical fibers, scintillator materials, humidity sensors, magnetic properties and catalysis. In the present study, nanocrystalline samples of SrWO₄ having three sizes were synthesized using controlled chemical precipitation technique. The crystal structure, phase and the average grain size were calculated by analyzing the X-ray diffraction pattern. The crystal structure is found to be tetragonal with typical scheelite phase. The grain sizes were obtained to be 21, 16 and 25 nm. The FTIR spectrum recorded in the range 400 to 1200 cm⁻¹ showed characteristic peaks at 410 and 820 cm⁻¹ indicating that the synthesized samples are pure. The UV-Visible absorption spectra of the as prepared samples with grain sizes 21 and 16 nm showed a sharp absorption peak around 250 nm while the sample with average grain size 25 nm exhibited a peak around 275 nm. All the absorption peaks of the samples are blue shifted compared to the bulk crystal indicating quantum confinement and it establishes grain size dependence. The photoluminescence spectra of the samples recorded with an excitation wavelength of 240 nm showed peaks at around 420 nm for the samples with lower grain sizes and around 430 nm for sample with grain size 25 nm. The FT Raman spectra of the sample with grain size 16 nm was recorded in the range 50 to 1000 cm⁻¹. It showed characteristic peaks that can be assigned



to internal and external vibrations of SrWO₄. Confinement of phonons in nanosized grains results in broadening and shifting of Raman peaks.

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