ScienSage

Journal of Advanced Scientific Research

Available online through http://www.sciensage.info

ISSN
0976-9595
Research Article

LOW TEMPERATURE SYNTHESIS, CHARACTERIZATION AND SOME PHYSICAL STUDIES ON ALKALINE EARTH METAL VANADATES

Teotone Vaz*[1], A. V. Salker[2]

[1]*Department of Chemistry, St. Xavier's College, Mapusa, Goa, India*

[2]*School of Chemical Science, Goa University, Goa, India*

**Corresponding author: teovaz18@gmail.com*

ABSTRACT

Alkaline earth metal ceramics MV_2O_6 (M = Ba, Sr and Ca) were prepared via sol-gel chemical technique at low temperatures. The phase formation and their crystal structure were confirmed by X-ray powdered diffraction measurement. The BaV_2O_6 and SrV_2O_6 are found to have orthorhombic and CaV_2O_6 with monoclinic structure. Impurity checks were done by FTIR spectrometry. The temperature dependence of electrical resistivity of these vanadates show semiconducting nature, which is consistent with their electronic band structures. The energy band gaps increase in the order of CaV_2O_6> SrV_2O_6> BaV_2O_6. The photo-catalytic efficiency was investigated by photo-degradation of methylene blue (MB) solutions employing solar light and found to be promising photo-catalyst.

Keywords: Vanadates, Sol-gel, Resistivity, UV-DRS, Photo-catalysis.

1. INTRODUCTION

Vanadate compounds with divalent alkali earth metal atoms having the general formula MV_2O_6 (M = Ca, Ba, Sr etc.) adopt structural types consisting of the frameworks of V-O polyhedral together with interstitial M^{2+} ions. Most of the divalent metal vanadates crystallize in a brennerite like structure. Compounds with a larger divalent metal atoms like SrV_2O_6 and BaV_2O_6 adopts a structure having VO_4 tetrahedral units, consisting of corner sharing VO_4 tetrahedra forming infinite chains, which is similar to alkali metal vanadates MVO_3 [1]. The compounds BaV_2O_6 and SrV_2O_6 adopt an orthorhombic and CaV_2O_6 adopt monoclinic structures at ordinary conditions [2, 3]. They are employed in industrial applications, such as energy materials, gas sensors, optoelectronic materials, rechargeable batteries, microwave dielectric ceramics, LTCC technology, semiconductors, magnetic candidates and catalysis etc. [3 - 7]. In this context, MV_2O_6 (M = Ca, Sr and Ba) are practical and attractive candidates for further comparative investigations of their electrical and photocatalysis. Several traditional methods have been adopted for the synthesis of these metal vanadates, like conventional solid state, hydrothermal, and co-precipitation method [2, 3, 6 - 8]. A more recently, sol-gel precursor method has much advantages of forming pure compound at controlled lower temperatures, less time consumption and good crystallized homogeneous products. Metal carboxylate are good precursors for the synthesis, as these, most of the times decomposes to oxides products with high surface area at comparatively lower temperature [4, 5, 9]. Recently, nano-catalysis has become an emerging forefront field, due to its exceptionally large surface area to volume ratio, imparting unique properties to materials [10]. Semiconductor photo-catalysts are the most common and useful materials to reduce the pollutants because they illustrate the simple condition to utilize the natural or artificial irradiation. Here, we have chosen a simple, reliable and low temperature sol-gel maliate precursor approach to synthesize CaV_2O_6, SrV_2O_6 and BaV_2O_6 compounds, further investigated their electrical and photo-catalytic performances.

2. MATERIAL AND METHODS

2.1. Low temperature synthesis

MV_2O_6 ceramics (M = Ba, Sr, and Ca) were prepared by low temperature sol-gel precursor route. AR grade purity respective metal nitrates $M(NO_3)_2.nH_2O$ of Ca, Sr and Ba and ammonium vanadate were used as starting materials. Stoichiometric amounts of raw materials were weighed and separately dissolved in minimum quantity of pure water. Malic acid was used, as complexing agent to produce intermediate precursor to each solution

separately maintaining metal-malic acid molar ratio 1:2. All above starting reagents were used as procured without further purification. The two solutions were mixed together maintaining neutral pH on a magnetic stirrer and then slowly evaporated on a hot plate, till a transparent viscous gel was obtained. The gel gets further decomposed to black solid mass, which was heated at 400°C for 5 hrs to free from carbon. The calcined powders were ground again and sintered at 600°C for further 5 hrs to obtain the expected product. The product was furnace cooled, powdered and characterized.

2.2. Sample characterization

Structural and crystallographic analysis of prepared vanadate samples were recorded from X-ray powder diffraction technique using Philips X-ray diffractometer (PW 1820) with Cu K_α radiation at room temperature. The 2θ range used was 20-80°. All the diffraction peaks in the observed XRD patterns can be clearly indexed by the respective I.C.D.D. files.

The Fourier transformed infrared (FTIR) spectra were recorded on a Shimadzu FTIR spectrophotometer (Model 8101A) in the range of 500 - 1500 nm with approximate 1% sample embedded in KBr pellet.

2.3. Physical properties investigation

The Diffuse Reflectance Spectroscopy was carried out to know the band gap energies of the prepared vanadates on a Schimadzu UV-2250 Spectrometer. The spectra of absorbance versus wavelength (nm) were recorded in the range of 200-800 nm at room temperature. The λ_{max} were found out by taking first derivative plot of the reflectance spectra, Band gap were calculated by using the following formula, Band gap (eV) = $1240/\lambda_{max.}$

Electrical conductivity measurements were carried by a simple two-probe conductivity set-up in the temperature range of 425 to 800K. The samples were pelletized under the pressure of 6000 Kg/cm^2, stabilized with a heat treatment at 823K for 12-14 hrs. The pellet was tightly held between two polished and cleaned silver electrodes and the resistivity measurements were carried out heating the assembly and recording point by point measurement. The resistivity (ρ) is then calculated from the resistance (R), surface area (A) and the thickness (l) of the pellet, using the following equation, $\rho = R \times A / l$. In our knowledge, there are scanty literature reports available for resistivity measurements of these class of vanadates.

The photocatalytic activity of samples under investigation, were tested by using Methylene Blue(MB) solutions, as a model reaction representing organic pollutants in waste water. The degradation was carried out with 10^{-5}M dye solution containing optimum amount 0.05g of vanadate compounds. The progress of photocatalytic degradation was monitored by measuring the absorbance at the MB characteristic λ_{max} of 660nm. The experiments were performed in open sunlight. Filtered aliquots of the solutions were taken at the end of 60 min time of the irradiation and analysed with the UV - visible spectrophotometer. The dye degradation percentage was calculated considering initial and final concentrations of MB.

3. RESULTS AND DISCUSSION

The compounds prepared by low temperature sol-gel maliate precursor method were characterized by recording X-ray diffractograms. Fig.1, shows the XRD patterns of the of BaV_2O_6, SrV_2O_6 and CaV_2O_6, all the compounds showed mono-phasic formation.

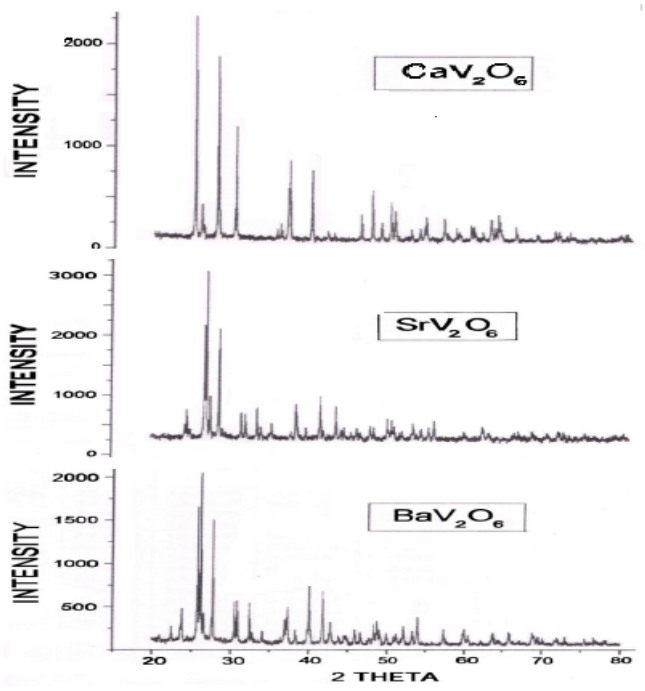

Fig. 1: XRD patterns of CaV_2O_6, SrV_2O_6 and BaV_2O_6.

The obtained d_{hkl} and 2θ values were compared with the respective I. C. D. D. cards. The BaV_2O_6 and SrV_2O_6 are found to have orthorhombic structure matching with I. C. D. D. card no. 26-204 and 27-1444, respectively.

The XRD patterns of CaV_2O_6 could be indexed to I. C. D. D. card no. 23-0137 and also observed as a pure single monoclinic phase. The d_{hkl} and 2θ values obtained were found to be in good agreement, the diffraction peaks were readily indexed and no other peaks of reactants or starting materials found, suggesting that the compounds obtained are monophasic. Also the crystallite particle sizes of these compounds were calculated using Debye Scherrer's formula. The crystallite diameter calculated was 38.22 nm, 62.71 nm and 36.60 nm for CaV_2O_6, SrV_2O_6 and BaV_2O_6 respectively confirming their nano-crystalline nature.

IR absorption bands of CaV_2O_6, SrV_2O_6 and BaV_2O_6 in the range of 500-1500 cm^{-1} shown in Fig. 2. The absorption bands range from 500 to 975 cm^{-1}, which were assigned to stretching and bending vibrations of the V-O and O-V-O groups. No absorption bands in the organic region were observed, confirming the total combustion of the organic acid material during the sol - gel precursor synthesis process. The results are found in agreement with previous result [11].

Electrical resistivity of pelletized vanadates was measured using two-probe method. The temperature dependence of resistivity of CaV_2O_6, SrV_2O_6 and BaV_2O_6 vanadates is shown in Fig. 3. The resistivity measurements were recorded from 425 to 800 K. For all three vanadates, the resistivity decreases exponentially with increasing temperature, indicating typical semiconducting behaviour of the materials at little higher temperatures. At lower temperature, the resistivity pattern of all three vanadates almost remain constant. Resistivity behaviour shown by CaV_2O_6 and SrV_2O_6 vanadates is very similar, changing to intrinsic region in the temperature range of 575 to 600 K and peculiar of semi-conductor material but the trend observed in BaV_2O_6 is slightly different. In BaV_2O_6 compound, the intrinsic behaviour is observed in the region of 615 to 640 K. This shift to slightly higher temperature may be due to larger atomic size of Ba ion, resulting in slight enlarged band gap in BaV_2O_6, which is also observed in our diffused reflectance studies. This is attributed to the strong ionicity in the sample that can enhance the interaction between the anionic group and cation, in agreement with literature [12].

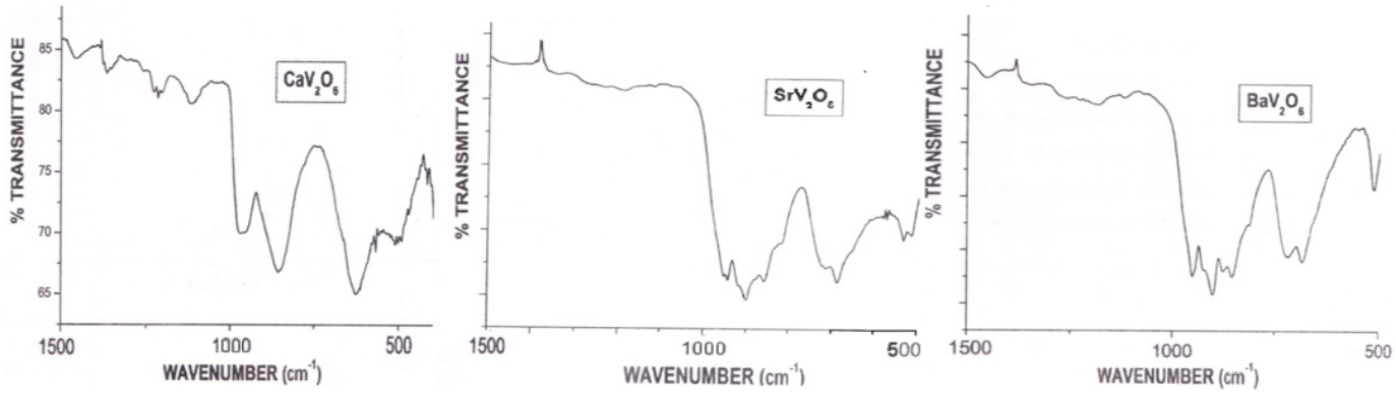

Fig. 2: IR spectra of CaV_2O_6, SrV_2O_6 and BaV_2O_6 in the range of 500 - 1500 cm^{-1}

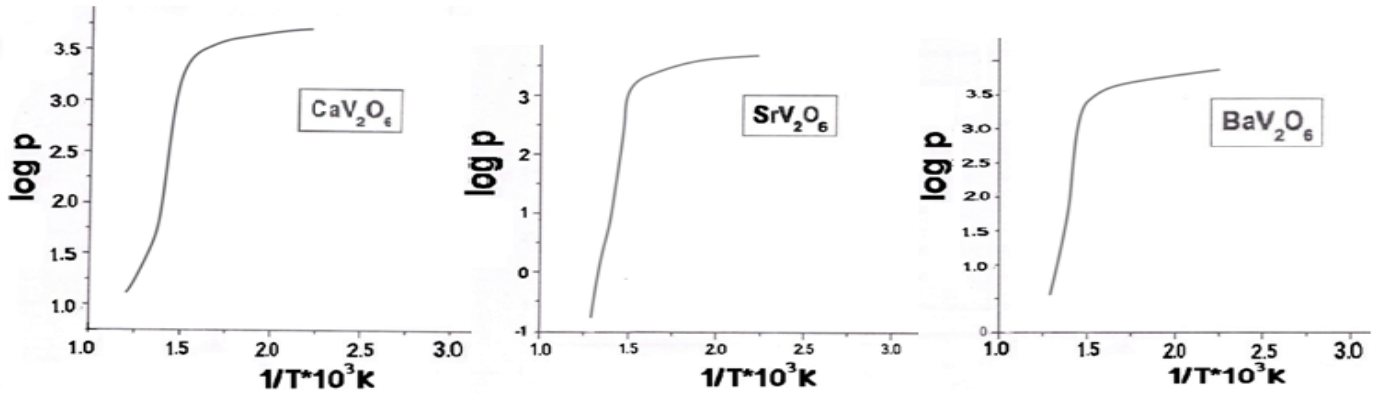

Fig. 3: Temperature dependence of resistivity for CaV_2O_6, SrV_2O_6 and BaV_2O_6

The Diffuse Reflectance Spectroscopy was carried out to know the band gap energies of the prepared vanadates. Fig. 4, shows the spectra of absorbance versus wavelength (nm) for CaV_2O_6, SrV_2O_6 and BaV_2O_6 vanadates. The λ_{max} were found out by taking first derivative plot of the reflectance spectra and the band gap values of 2.67 eV, 3.04 eV and 3.10 eV were obtained respectively. For CaV_2O_6, the observed band gap of 2.67 eV is similar to indirect band gap reported in the literature [3]. For BaV_2O_6, the observed band gap of 3.10 eV is slightly smaller than the reported value of 3.24 eV, in line with the second harmonic generation reported in the literature [11]. Slight higher band gap energy is due to increased ionic size of Ba as compared to Ca and Sr, which increases iconicity that can enhance the interaction between the anionic groups and cations, as reported in the literature [12].

The photo-catalytic activity of prepared vanadates was tested by using methylene blue (MB) solution as model reaction to study the photo-degradation of organic pollutants. Fig. 5, shows the photo-catalytic degradation of MB on CaV_2O_6, SrV_2O_6 and BaV_2O_6 compounds. The degradation reaction were carried out in conical flasks with stoppers containing 50 mL with 10^{-5} M dye solution and 0.050 g of vanadate compounds in the solar light. The photo-catalytic capacity of the vanadates exhibits very high potential for degradation up to 89%. Their corresponding photo-degradation efficiencies within 60 min were determined to be 83%, 85 % and 89% for CaV_2O_6, SrV_2O_6 and BaV_2O_6 respectively. It was clearly seen that under identical conditions, BaV_2O_6 have superior photo-catalytic activity over SrV_2O_6 and CaV_2O_6. In order to examine the photo-catalytic stability of these compounds, the experiment was repeated next day on the same catalyst materials, the results obtained were consistent.

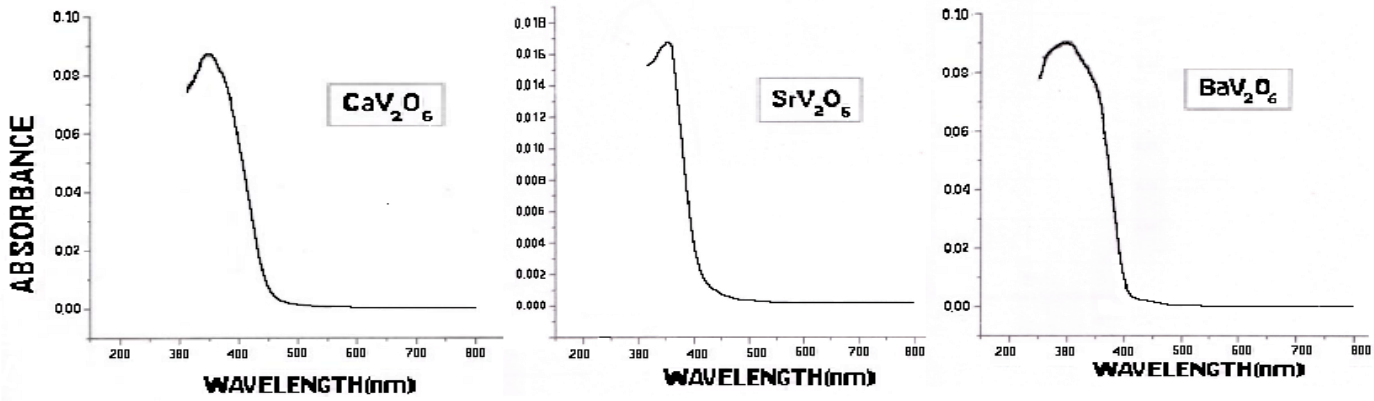

Fig. 4: Diffuse Reflectance Spectra for CaV_2O_6, SrV_2O_6 and BaV_2O_6

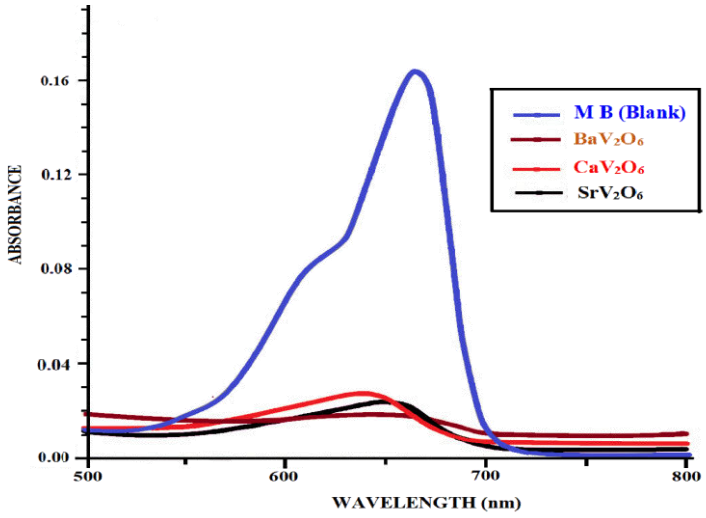

Fig. 5: Photocatalytic degradation of methylene blue on CaV_2O_6, SrV_2O_6 and BaV_2O_6

The higher photo-catalytic activity of BaV_2O_6 could be attributed to its stronger Visible light absorption. As observed in Fig. 5, the MB degradation percentage on vanadates increased rapidly, after the reaction mixture kept in direct sunlight between 11.00 am to 12.00 noon and within 60 min, it was noted almost degradation of all, as indicated by fading of dye colour, almost too colourless. These results indicate that prepared alkaline earth vanadates have potential and efficiency for photo-catalytic applications. The heterogeneous photo-catalytic process involves many stages, such as diffusion, adsorption and reaction. Large surface area of these materials, owing to finer crystallite particle size, as observed from XRD patterns prepared by low temperature sol-gel precursor technique using malic acid has a straight forward enhance effect on the reaction rate and may be also a reasonable explanation for high photo-catalytic capacity of these materials. In addition, the larger band gap energies of these vanadates resulting in better chemical activity are significantly favouring their suitability for photo-catalytic degradation of organic pollutants.

Table 1: Summary of the investigated work on CaV_2O_6, SrV_2O_6 and BaV_2O_6 vanadates

Compound	Structure indexed	Crystallite diameter (nm)	Band gap energy (eV)	Degradation of MB (%)
CaV_2O_6	Monoclinic	38.22	2.67	83
SrV_2O_6	Orthorhombic	62.71	3.04	85
BaV_2O_6	Orthorhombic	36.60	3.10	89

4. CONCLUSION

Alkaline earth vanadates MV_2O_6 ceramics with M = Ca, Sr and Ba have been successfully prepared through sol-gel maliate precursor method. The phase purity of the samples was confirmed by powder X-ray diffraction technique. The BaV_2O_6 and SrV_2O_6 are found to have orthorhombic and CaV_2O_6 having monoclinic structure. No organic impurities were observed in IR spectra. These vanadates showed typical semi-conductor type behaviour, increased band gap energies were observed with increase in the size of alkali metal atom in the vanadates. The photocatalytic behaviour of these vanadates shows that all vanadates have efficient degradation capacity for methylene blue resembling organic pollutants, with superior activity of BaV_2O_6.

5. ACKNOWLEDGEMENT

The authors are grateful to Ms. Daya Adonkar, for the help in this investigation.

Conflict of Interests

The authors declare that they have no conflicts of interests.

6. REFERENCES

1. Yao T, Oka Y, Yamamoto N. *Inorg. Chim. Acta*, 1995; **238:**165-168.
2. Schnuriger B, Enjalbert R, Savariault JM, Galy J. *J. Sol. St. Chem*, 1991; **95:**397-402.
3. Islam MS, Kabir H, InagakiY, Sarker AR. *J. Alloys Compd.*, 2020; **829:**154499.
4. Li Y, Tang R, Li N, Li H, Zhao X, Zhu P, et al. *J. Appld Phys.*, 2015; **118:**035902.
5. Tang R, Li Y, Xie S, Li N, Chen J. *Sci. Rep.*, 2016; **6:** doi: 10.1038/srep38566.
6. Yao G, Ren Z, Liu P. *J. electroceram*, 2018; https://doi.org/10.1007/s10832-018-0113-6.
7. Neelakantan UA, Kalathil SE, Ratheesh R. *Eur.J. Inorg. Chem.*, 2014; doi: 10.1002/ejic.201402844.
8. Cheng J, Xiang H, Tang Y, Fang L.*Mater. Res. Bull.*, 2017; doi.org/10.1016/j.materresbull.2017.12.053.
9. Hossain MK, Sotelo P, Sarker HP, Galante MT, Kormanyos A, Longo C, et al. *ACS Appld. Energy Mater.*, 2019; doi: 10.1021/acsaem.9b00179.
10. Singh SB, Tandon PK.*J. Energy Chem. Engg.*, 2014; **2(3):**108-115.
11. ChenW, Zhang W, Lee M, Jing Q, Lu X, Chen Z, *Opt. Mater.*,2019; **68:**642-647.
12. Huang Y, Meng X, Gong P, Yang L, Lin Z, Chen X, et al. *J. Mater. Chem. C*, 2014; **2:**4057-4062