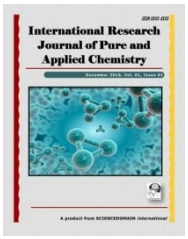


International Research Journal of Pure & Applied Chemistry
3(1): 1-9, 2013

SCIENCEDOMAIN *international*
www.sciencedomain.org

Grinding-Assisted Solid-State Metathetic Synthesis of Divalent Transition Metal Tungstates

U. Sujana Kumari[1*], P. Suresh[1] and A. V. Prasada Rao[1]

[1]Department of Inorganic and Analytical Chemistry, Andhra University, Visakhapatnam, 530003, India.

Authors' contributions

This work was carried out in collaboration with all authors. Author AVPR proposed the study and supervised the work. Author USK performed the experimental work and analysis wrote the first draft and author PS managed literature searches. All the authors read and approved the final manuscript.

Research Article

Received 10th December 2012
Accepted 1st January 2013
Published 8th February 2013

ABSTRACT

A convenient solid state metathetic synthesis has been developed for the preparation of metal tungstates MWO_4 where M = Mn, Fe, Co, Ni and Zn using Na_2WO_4 and respective MCl_2 as reactants. Stoichiometric quantities of respective reactants were mixed and ground for 2hrs. XRD patterns of the homogenised mixture heat treated at 400ºC for 4hrs and then washed free from NaCl bye product were in good agreement with the respective JCPDS data showing the formation of phase pure compounds in each case without any contamination. Microstructural investigation indicated particle size of the order of µm.

Keywords: Solid state metathesis; manganese tungstate; iron tungstate; cobalt tungstate; nickel tungstate; zinc tungstate.

**Corresponding author: Email: sujana.uriti1@gmail.com;*

1. INTRODUCTION

MWO_4 type compounds where M is a divalent transition metal ion have attracted a lot scientific interest in recent times because of their many useful properties. These compounds exist in two different crystal structures namely Scheelite and wolframite. Bivalent metal ions with large ionic radius such as Ca^{2+}, Sr^{2+}, Ba^{2+} and Pb^{2+} prefer to form scheelite type structures whereas metal ions with smaller ionic radius viz. Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+} tend to crystallize in wolframite type of structure. Crystal structure of Scheelite $CaWO_4$ is tetragonal with calcium surrounded by eight oxygens with isolated tetrahedra of WO_4 being nearly regular, where as in wolframite each W is coordinated to six oxygens unlike scheelite. MWO_4 type divalent transition metal compounds have been reported to be useful for humidity sensors [1], photocatalysts [2], photochromic [3] and as photoanodes [4].

3d transition metal tungstate powders have been synthesized by different techniques such as solid-state reaction [5], chemical synthesis [6-10], hydrothermal [11-13], microwave hydrothermal [14], self propagation [15], template synthesis [16], combustion [17], molten salt [18] and aqueous salt metathetic reaction [19]. Among these methods, solid-state reactions invariably involve higher temperatures of more than 800ºC while solution based chemical methods require special equipment and subsequent annealing of amorphous or nano powders to temperatures above 500ºC for several hours to render them into crystalline form. Compared to these two basic approaches, solid-state metathesis (SSM) offers an easy and convenient route for the synthesis of many mixed metal oxides. These reactions involve double exchange with preferred formation of an alkali halide with large lattice energy which favours the reactions at lower temperatures compared to solid-state reactions between constituent metal oxides. SSM has been successfully employed for the synthesis of perovskite oxides [20], ordered double perovskites [21], $LaAlO_3$ [22], Bi_2WO_6 [23] and molybdates [24].

In continuation of our earlier work relating to room temperature solid-state metathetic synthesis of Ca, Sr, Ba, Pb and Cd tungstates and synthesis of phase pure $BaSnO_3$ and $BaZrO_3$ we now report the solid-state metathetic synthesis of transition metal tungstates MWO_4 where M^{2+} = Fe, Mn, Co, Ni and Zn. Since the transition metal tungstates are potential photocatalysts in the visible region [6] for the degradation of organic pollutants from the industrial exhausts, synthesis of these compounds at lower temperatures so as not to effect the surface area of support is highly essential.

2. EXPERIMENTAL

2.1 Sample Preparation

Metal chlorides, MCl_2 (where M=Fe, Mn, Co, Ni and Zn) along with Na_2WO_4 are used as precursors. All the starting materials were analytical grade and were utilized as received without further purification. Stoichiometric quantities of the reactants were weighed and the mixture was ground in an agate mortar for 2hrs with addition of ethanol as per the reaction given below.

$$MCl_2.nH_2O + Na_2WO_4 \rightarrow MWO_4 + 2NaCl + n.H_2O$$

The homogenised mixture was dried in an air oven and subjected to heat treatment at different temperatures. The resultant solid was washed with water until free from chloride

and the residue after drying was characterized for phase identification by X-ray diffraction (XRD).

2.2. Characterization Techniques

Phase purity of the final calcined powders was investigated with x-ray diffractometer (PANalytical- X' Pert PRO, Japan) at room temperature, using Nickel filter Cu-K_α radiation (λ= 1.54059 Å), over a wide range of $10^o \leq 2\theta \leq 80^o$ with a scanning speed of 2^o min^{-1}. Microstructural investigations of the samples were performed on the fractured surface of the sample using SEM (JEOL-JSM-6610LV, Tokyo, Japan). Energy Dispersive X-ray Spectroscopy (EDS) was used to detect x-rays emitted from the sample during bombardment with an electron beam to identify the elemental composition of the analyzed volume. Raman spectra were recorded using SENTERRA from BRUKER Corporation.

3. RESULTS AND DISCUSSION

XRD patterns obtained for homogenised mixtures of MCl_2+ Na_2WO_4 (where M= Fe, Mn, Co, Ni and Zn) subjected to heat treatment at 400ºC for 4hrs followed by washing with water until free from chloride and dried are given in Figures 1 to 4. XRD patterns of homogenised mixture of $NiCl_2$ + Na_2WO_4 at room temperature and heat treated at 300ºC and 400ºC for 4hrs followed by washing are shown in Fig. 1. XRD patterns indicate formation of well crystalline $NiWO_4$ only for the sample heat treated at 400^0C for 4hrs. All the peaks in the XRD pattern could be indexed as the observed pattern is in good agreement with that of $NiWO_4$ given in JCPDS file no.15-0755. No extra peaks were noticed which indicates the formation of phase pure sample. Observed XRD patterns below 400ºC does not match with the highest intensity peaks of $NiCl_2$, Na_2WO_4 and NaCl. Hence these peaks may be ascribed to amorphous precursor with some partially crystalline $NiWO_4$.((002), (022) and (220) peaks).

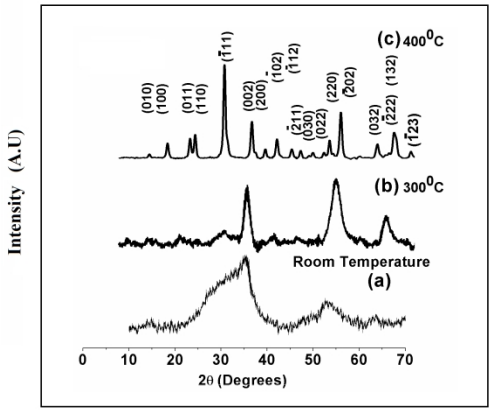


Fig. 1. XRD patterns of stoichiometric mixture of $NiCl_2$ + Na_2WO_4 ground for 2hrs a) room temperature b) heat treated at 300ºC for 4hrs c) heat treated at 400ºC for 4hrs and washed free of chloride.

Fig 2 shows the XRD patterns of homogenised mixture of stoichiometric amounts of $ZnCl_2$ and Na_2WO_4, ground for 2 hrs at room temperature and subjected to heat treatment of 400ºC for 4hrs, both washed free of chloride and dried. The washed product of $ZnWO_4$ at

room temperature did not indicate any sharp peaks characteristic of the reactants or NaCl bye product. The broad peak coincides with the 100% intensity peak of $ZnWO_4$ and this can be attributed to $ZnWO_4$ in the amorphous form. However, when subjected to heat treatment at 400ºC, characteristic peaks due to formation of well crystalline phase pure $ZnWO_4$ were obtained and the data is in agreement with that reported in JCPDS file no.73-0554.

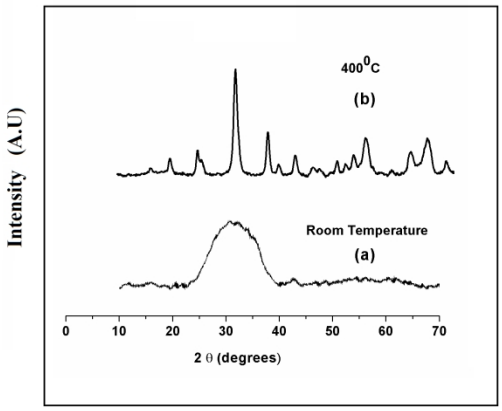


Fig. 2. XRD patterns of stiochiometric mixture of $ZnCl_2$ + Na_2WO_4 ground for 2hrs a) room temperature, b) heat treated at 400ºC for 4hrs.

Fig 3 shows the XRD patterns obtained for mixtures of $MnCl_2$+Na_2WO_4 and $CoCl_2$+ Na_2WO_4 ground for 2hrs and heated at 400ºC for 4hrs followed by washing to remove NaCl. The observed XRD patterns are in good agreement with the reported data for $MnWO_4$ and $CoWO_4$ of JCPDS files 80-0134 and 72-0479 respectively. Miroslaw Maczka et al [25] reported two different synthesis routes for $MnWO_4$ (i) a hydrothermal method using ethanolamine and CTAB and (ii) by annealing a precursor obtained by co-precipitation. In their second method, XRD patterns were indicative of nanocrystalline $MnWO_4$ formation with crystallite size smaller than 20 and 26 nm when the synthesis was performed at 250 and 400ºC, respectively. In the present method sharp peaks characteristic for large and well-crystallized $MnWO_4$ particles were revealed for annealing at 400ºC for 4 hrs.

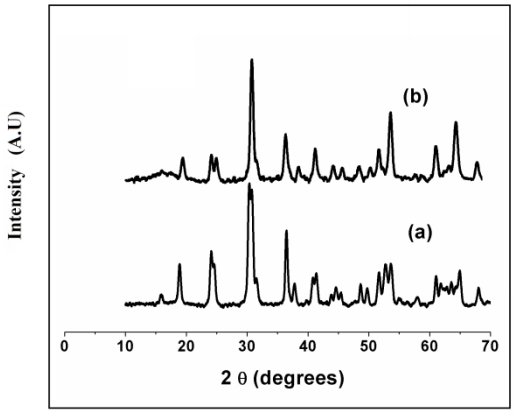


Fig. 3. XRD patterns of stoichiometric mixture of a) $MnCl_2$ + Na_2WO_4 ground for 2hrs and heat treated at 400ºC for 4hrs washed and dried. b) $CoCl_2$ + Na_2WO_4 ground for 2hrs, heat treated at 400º C at 4hrs washed and dried.

Fig 4 shows the XRD patterns obtained for mixture of $FeCl_2$+Na_2WO_4 ground for 2hrs and heat treated at 400ºC for 2hrs and at 600ºC for 3hrs and washed free from NaCl bye product. Though the formation of $FeWO_4$ is evident at 400ºC, for unambiguous indexing of peak positions, the sample is subjected to heat treatment at 600ºC for 3hrs to render it more crystalline. All peaks for the resultant sample could be indexed in accordance with JCPDS file no. 71-2391.

Synthesis of MWO_4 powders was reported by solution based metathesis reaction using equimolar solutions of metal nitrates and sodium tungstate, with subsequent heating of the precipitate to 800ºC for 15hr [19]. Parhi et al [26] reported synthesis of $ZnWO_4$, $NiWO_4$ and $MnWO_4$ by microwave assisted solid-state metathesis using 2.45 GHz microwave frequency and a power of 1100 W for 10 minutes duration. Though crystalline $ZnWO_4$ was obtained at room temperature by this process, crystalline $MnWO_4$ and $NiWO_4$ were obtained only after heat treatment at 500ºC for 6hrs. Angana sen etal [8] reported the synthesis of Co, Ni, Cu and Zn metal tungstates from the complete evaporation of polymer based metal-complex precursor solution subjected to heat treatment. Rajagopal [27] reported the hydrothermal synthesis of $FeWO_4$ and $CoWO_4$ using sodium tungstate with ferrous ammonium sulphate and cobalt chloride solutions as precursors respectively. Recently Garcia-Perez et al. [7] reported the synthesis of Co, Cu, Mn and Ni tungstates by co-precipitation method at 400ºC. Tiziano Montini etal reported the synthesis of transition metal tungstates $M^{II}WO_4$ (M = Co^{II}, Ni^{II}, $Cu^{II,}$ Zn^{II}) by reaction of transition metal nitrates with sodium tungstates and then subjected to heat treatment at 500ºC. The SSM synthesis reported in the present study is the lowest synthesis temperature reported for solid-state synthesis. It is less cumbersome and could be performed at ambient pressure.

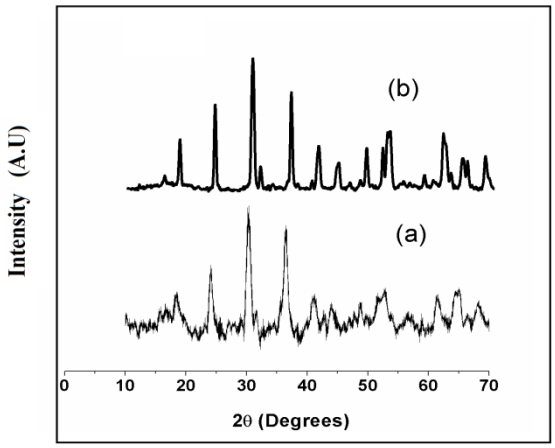


Fig. 4. XRD patterns of stoichiometric mixture of $FeCl_2$ + Na_2WO_4 ground for 2hrs and heat treated at a) 400ºC for 4hrs b) 600ºC for 3hrs and washed free of chloride.

Fig 5 shows Raman spectra of $MnWO_4$, $FeWO_4$, $CoWO_4$, $NiWO_4$ and $ZnWO_4$ In terms of group theoretical analysis, wolframite structure belonging to P2/c (z = 2) monoclinic structure is expected to give 18 ($8A_g$ + 10 B_g) Raman-active bands out of 36 possible lattice modes [28]. Raman spectra for all samples revealed peaks due to $8A_g$ (breathing of tungstate tetrahedra) vibrations while some peaks due to $10B_g$ were not resolved. Based on the previous reports, the most intense band in $ZnWO_4$ was ascribed to antisymmetric bridging mode associated with the tungsten chain [13]. In MnO_4 the band at 127 cm^{-1} accompained

by two weak bands in the range 160 and 180 cm^{-1} were ascribed to interchain deformation and torsion modes [14]. Though extensive studies on Raman spectra of some of these tungstates were reported in the literature subsequently [29], we at this stage did not make an elaborate interpretation of Raman spectra as our interest is limited to show the phase formation of tungstates only. Our data is in agreement with those reported earlier [13],[14],[28].

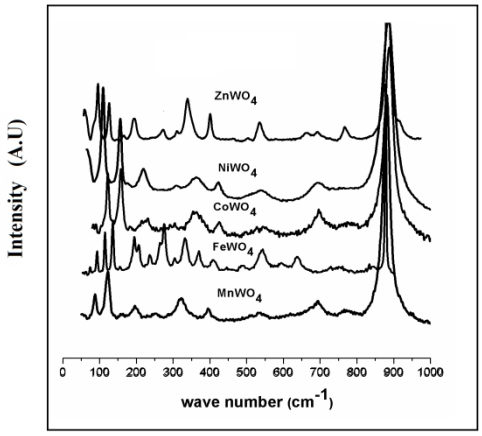
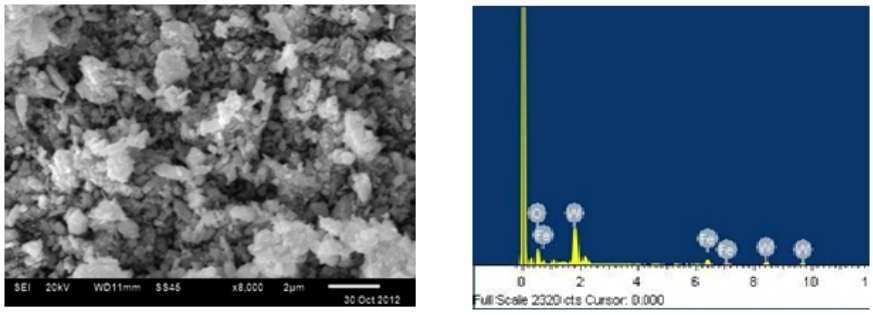


Fig. 5. Raman spectra of $MnWO_4$, $CoWO_4$, $NiWO_4$ and $ZnWO_4$ heat treated at 400^{0}C and $FeWO_4$ heat treated at 600^{0}C .

SEM micrograph of a representative sample $FeWO_4$ powder heat treated at 600^{0}C is shown in fig. 6 which shows particles of different sizes due to aggregation. Elemental analysis of the sample confirms the presence of Fe, W and O, with no extra lines due to any contamination.



(a) **(b)**

Fig. 6. a) SEM image of $FeWO_4$ powder and b) EDS of the $FeWO_4$ powder under SEM investigation.

4. CONCLUSION

A simple low temperature solid state metathetic synthesis is reported for the preparation of MWO_4 (M = Fe, Mn, Co, Ni and Zn) powders using respective metal chlorides and sodium tungstate as precursors. XRD patterns of respective powders obtained by mixing

stoichiometric quantities of the reactants, ground for two hours followed by heat treatment at 400ºC for 4hrs, and washed free of chloride indicated formation of respective phase pure metal tungstates. Reaction temperatures reported for the synthesis of transition metal tungstates are less compared to these solid-state methods. The process is costeffective and simple. Microstructural investigation indicated particle aggregation.

ACKNOWLEDGEMENTS

One of the authors (Sujana Kumari) gratefully acknowledges the research supervisor Prof. A. V. Prasada Rao for the constant encouragement throughout research work.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Bhattacharya AK, Biswas RG, Hartridge A. Environment sensitive impedance spectroscopy and DC conductivity measurements on $NiWO_4$. J. Mater. Sci. 1997;32(2):353-356.
2. Huang G, Zhu Y. Synthesis and photocatalytic performance of $ZnWO_4$ catalyst. Mater Sci. Eng.B. 2007:139(2/3):201-208.
3. Kuzmin A, Purans J, Kalendarev R, Pailharey D, Mathey Y. XAS, XRD, AFM, and Raman studies of nickel tungstate electrochromic thin films. Electrochim. Acta 2001;46:2233-2236.
4. Pandey PK, Bhave NS, Kharat RB. Structural, Optical, electrical and photovoltaic electrochemical characterization of spray deposited $NiWO_4$ thin films. Electrochim. Acta. 2006;51(22):4659-4664.
5. Bhaskar Kumar G, Sivaiah K, Buddhudu S. Synthesis and characterization of $ZnWO_4$ ceramic powder. Ceram. Inter. 2010; 36:199-202.
6. Tiziano Montini, Valentina Gombac, Abdul Hameed, Laura Felisari, Gianpiero Adami, Paolo Fornasiero. Synthesis, Characterization and photocatalytic performance of transition metal tungstates. Chem. Phys. Lett. 2010;498:113-119.
7. Garcia Perez UM, Martinez-de la Cruz A, Peral J. Transition metal tungstates synthesized by co-precipitation method: Basic photocatalytic properties. Electrochim. Acta. 2012;81:227-232.
8. Angana Sen, Panchanan Pramanik. A chemical synthetic route for the preparation of fine-grained metal tungstate powder (M= Ca, Co, Ni, Cu, Zn). J. Eur. Ceram. Soc. 2001;21:745-750.
9. Kalinko A, Kuzmin A. Raman and Photoluminesence spectroscopy of Zinctungstate powders. J. Lumin. 2009;129:1144-1147.
10. Aleksandr Kalinko, Alexey Kotlov, Alexei Kuzmin, Vladimir Pankratov, Anatoli I. Popov, Liana Shirmana. Electronic excitations in $ZnWO_4$ and $Zn_xNi_{1-x}WO_4$ (x=0.1-0.9) using VUV synchrotron radiation. Cent. Eur. J. Phys. 2011; 9(2):432-437.
11. Fu-Shan Wen, Xu Zhao, Hua Huo, Jie-Sheng Chen, E. Shu-Lin, Jia- Hua Zhang. Hydrothermal Synthesis and photoluminescent properties of $ZnWO_4$ and Eu^{3+}-doped $ZnWO_4$. Mater. Lett. 2002;55:152-157.
12. Qiang Wang, Mingming Sun, Chunhong Li. Hydrothermal synthesis and photoluminescent properties of zinc tungstate Nano/Micro structures. Adv. Mater. Res. 2011;328-330:1580-1584.

13. Hongbo Fu, Chengsi Pan, Liwu Zhang, Yongfa Zhu. Synthesis, Characterization and photocatalytic properties of nanosized Bi_2WO_6, $PbWO_4$ and $ZnWO_4$ catalysts. Mater. Res. Bull. 2007;42:696-706.
14. Theo Kloprogge J, Matt L. Weier, Loc V. Duong, Roy L. Frost. Microwave-assisted synthesis and characterisation of divalent metal tungstates nano crystalline minerals: ferberite, hubnerite, sanmartinite, scheelite and stolzite. Mater. Chem. and Phys. 2004;88:438-443.
15. Tiaotiao Dong, Zhaohui Li, Zhengxin Ding, Ling Wu, Xuxu Wang, Xianzhi Fu. Characterizations and properties of Eu^{3+}-doped $ZnWO_4$ prepared via a facile self-propagating combustion method. Mater. Res. Bull.2008;43:1694-1701.
16. Hongjun Zhou, Yuen Yiu, Aronson MC, Stanislaus S. Wong. Ambient template synthesis of multiferroic $MnWO_4$ nanowires and nanowires arrays. J. Solid State Chem. 2008;181:1539-1545.
17. Larisa Gigorjeva, Donats Millers, Janis Grabis, Dzidra Jankovica. Photoluminecence and photocatalytic activity of zinc tungstate powders. Cent. Eur. J. Phys. 2011;9(2):510-514.
18. Yakubovskaya AG, Katrunov KA, Tupitsyna IA, Starzhinskiy NG, Nagornaya LL, Zhukov AV, Zenya IM, Baumer VN, Vovk OM. Nanocrystalline Zinc and cadmium tungstates: morphology, luminescent and scintillation properties. Funct. Mater. 2011;18 (4):446-451.
19. Sagrario M. Montemayor, Antonio F. Fuentes. Electrochemical characteristics of lithium insertion in several 3D metal tungstates (MWO4, M= Mn, Co, Ni and Cu) prepared by aqueous reaction. Ceram. Int. 2004;30:393-400.
20. Radha Velchuri, Vijaya kumar B, Rama Devi V, Prasad G, Vithal M. Solid State Metathesis of $BaTiO_3$, $PbTiO_3$, $K_{0.5}Bi_{0.5}TiO_3$ and $Na_{0.5}Bi_{0.5}TiO_3$. Ceram. Int. 2010;36: 1485-1489.
21. Siva Kumar T, Lofland SE, Ramanujachary KV, Ramesha K, Subbanna GN, Gopalakrishnan J. Transforming n=1 members of the Ruddlesden-Popper phases to a n=3 member through metathesis: synthesis of a layered perovskite, $Ca_2La_2CuTi_2O_{10}$. J. Solid State Chem. 2004;177:2635-2638.
22. Miroslaw Maczka, Esmeralda Mendoza-Mendoza, Antonio F Fuentes, Karol Lemanski, Przemyslaw Deren. Low-temperature synthesis, luminescence and phonon properties of Er and/or Dy doped $LaAlO_3$ nanopowders. J. Solid State Chem. 2012;187:249-257.
23. Maczka M, Fuentes AF, Kepinski L, Diaz-Guillen MR, Hanuza J. Synthesis and electrical, optical and phonon properties of nanosized Aurivillius phase Bi_2WO_6. Mater. Chem. and Phys. 2010;120:289-295.
24. Thangadurai V, Knittlmayer C, Weppner W. Metathetic room temperature preparation and characterization of scheelite-type ABO_4 (A=Ca, Sr, Ba, Pb; B=Mo, W) powders. Mater. Sci. and Eng. B. 2004;106:228-233.
25. Miroslaw Maczka, Maciej Ptak, Michalina Kurnatowska, Leszek Kepinski, Pawel Tomaszewski, Jerzy Hanuza. Phonon properties of nanosized $MnWO_4$ with different size and morphology. J. Solid State Chem. 2011;184:2446-2457.
26. Purnendu Parhi, Karthik TN, Manivannan V. Synthesis and characterization of metal tungstates by novel solid-state metathetic approach. J. Alloys and Compd. 2008;465:380-386.
27. Rajagopal S, Nataraj D, Khyzhun O Yu, Yahia Djaoued, Robichaud J, Mangalaraj D. Hydrothermal synthesis and electronic properties of $FeWO_4$ and $CoWO_4$ nanostructures. J. Alloys and Compd. 2010;493(1-2):340-345.
28. Kisla PF. Siqueira, Anderson Dias. Incipient crystallization of transition-metal tungstates under microwaves probed by Raman scattering and transmission electron microscopy. J. Nanopart. Res. 2011;13:5927-5933.

29. Maczka M, Ptak M, Hermanowicz K, Majchrowski A, Pikul A, Hanuza J. Lattice dynamics and temperature-dependent Raman and Infrared studies of multiferroic $Mn_{0.85}Co_{0.15}WO_4$ and $Mn_{0.97}Fe_{0.03}WO_4$ crystals. Phys. Rev. B. 2011;83:174439.

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sciencedomain.org/review-history.php?iid=188&id=7&aid=918