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

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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 400^0C 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.

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

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reactions invariably involve higher temperatures of more than 800^0C while solution based chemical methods require special equipment and subsequent annealing of amorphous or nano powders to temperatures above 500^0C for several hours to render them into crystalline form. Compared to these two basic approaches, solid-state metathesis (SSM) offers a 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], titanium and vanadium pnictides [22] and molybdates [23].

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

Metal chlorides, MCl_2 (where M=Fe, Mn, Co, Ni and Zn) along with Na_2WO_4 are used as precursors. 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 characterised for phase identification by X-ray diffractometer (panalytical “X” Pert pro) using CuK_α radiation. Microstructural investigation and elemental analysis was done by Scanning Electron Micrograph (JEOL JSM 6610 LV) equipped with an energy dispersive spectrometer. 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 400^0C 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 300^0C and 400^0C 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.

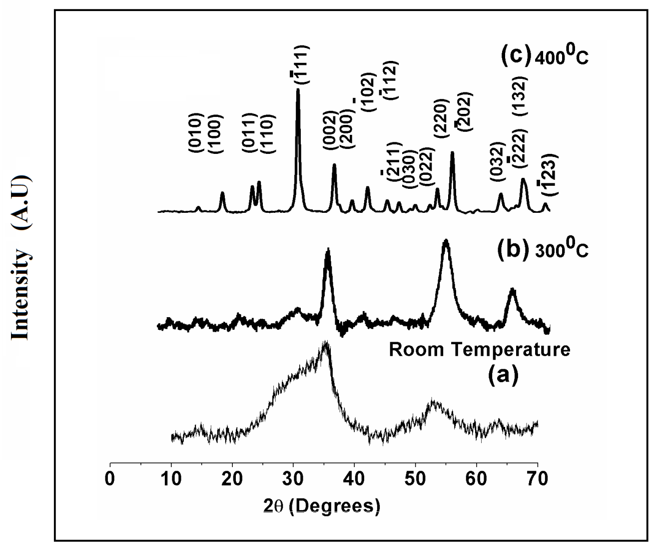

Fig. 1. XRD patterns of stoichiometric mixture of $NiCl_2$ + Na_2WO_4 ground for 2hrs a) room temperature b) heat treated at 300^0C for 4hrs c) heat treated at 400^0C for 4hrs and washed free of chloride.

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 400^0C for 4hrs, both washed free of chloride and dried. XRD pattern of homogenised mixture without heating showed no characteristic peaks indicating only amorphous form of the material. However, when subjected to heat treatment at 400^0C, 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.

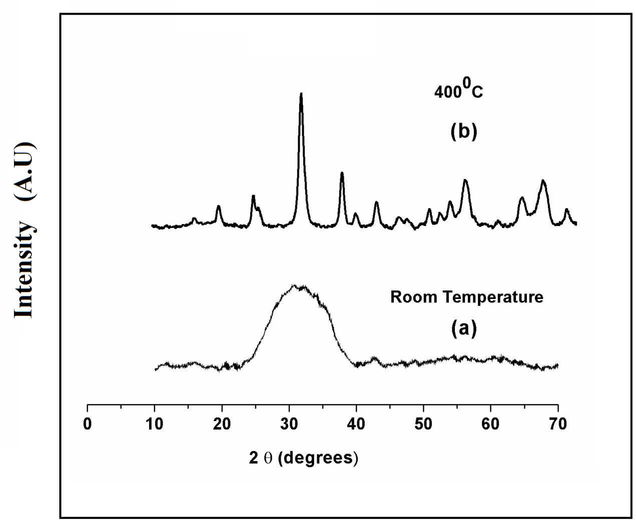

Fig. 2. XRD patterns of stiochiometric mixture of $ZnCl_2$ + Na_2WO_4 ground for 2hrs a) room temperature, b) heat treated at 400^0C for 4hrs

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 400^0C 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.

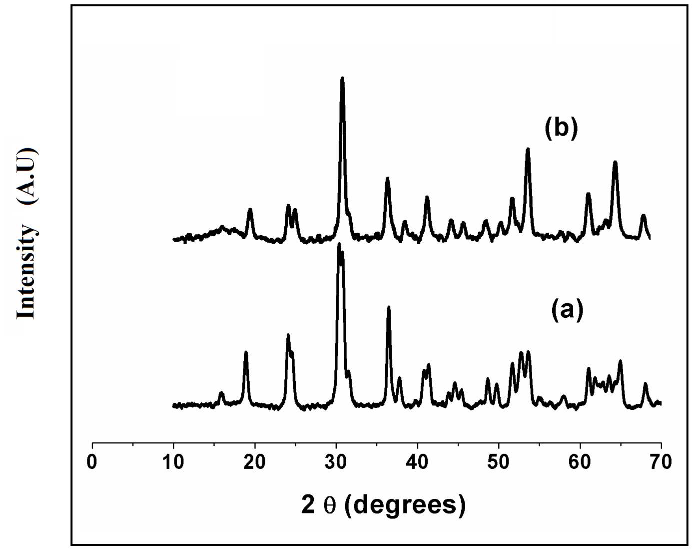

Fig. 3. XRD patterns of stoichiometric mixture of a) $MnCl_2$ + Na_2WO_4 ground for 2hrs and heat treated at 400^0C for 4hrs,washed and dried. b) $CoCl_2$ + Na_2WO_4 ground for 2hrs, heat treated at 400^0 C at 4hrs, washed and dried.

Fig 4 shows the XRD patterns obtained for mixture of $FeCl_2$+Na_2WO_4 ground for 2hrs and heat treated at 400^0C for 2hrs and at 600^0C for 3hrs and washed free from NaCl bye product. Though the formation of $FeWO_4$ is evident at 400^0C, for unambiguous indexing of peak positions, the sample is subjected to heat treatment at 600^0C 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 800^0C for 15hr [19]. Parhi etal [24] 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 500^0C 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 [25] 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 etal [7] reported the synthesis of Co, Cu, Mn and Ni tungstates by co-precipitation method at 400^0C. 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 500^0C . 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.

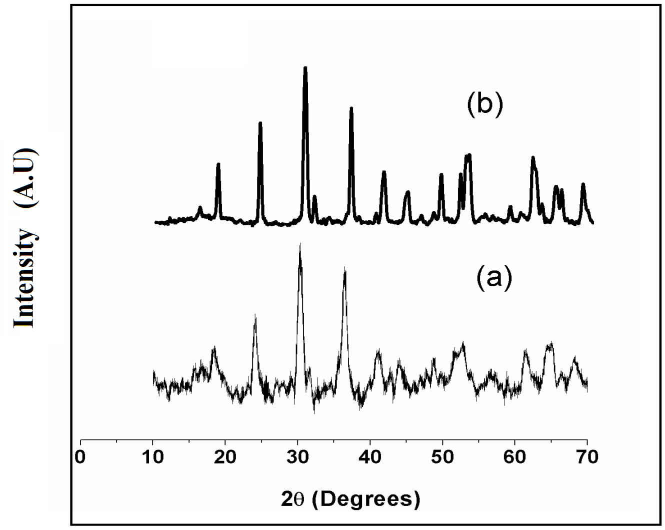

Fig. 4. XRD patterns of stoichiometric mixture of $FeCl_2$ + Na_2WO_4 ground for 2hrs and heat treated at a) 400^0C for 4hrs b) 600^0C for 3hrs and washed free of chloride.

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 [26] out of 36 possible lattice modes. 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.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 were due to interchain deformation and torsion modes [14]. All spectra were in good agreement with literature data.

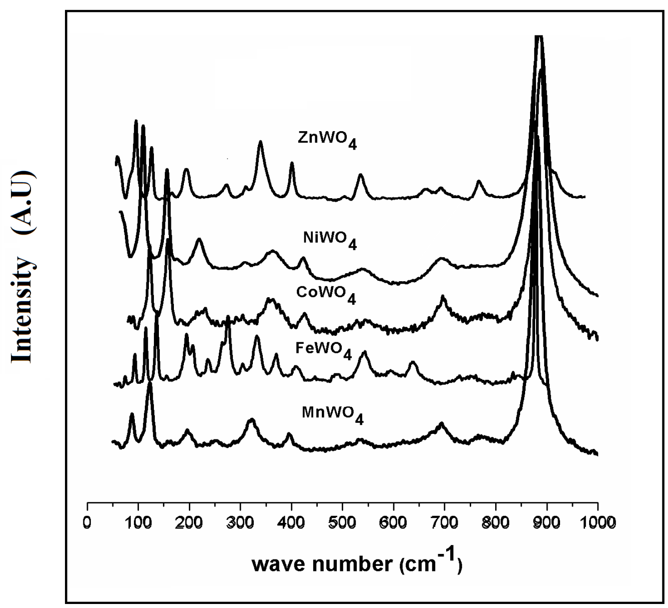

Fig. 5. Raman spectra of $MnWO_4$, $CoWO_4$, $NiWO_4$ and $ZnWO_4$ heat treated at 400^0C and $FeWO_4$ heat treated at 600^0C .

SEM micrograph of a representative sample $FeWO_4$ powder heat treated at 600^0C 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.

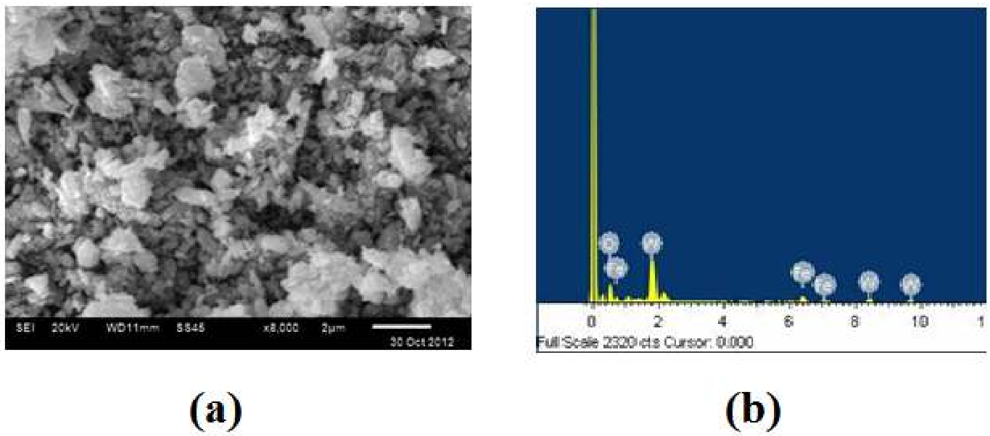

Fig. 6. a) SEM image of $FeWO_4$ powder and b) EDS of the $FeWO_4$ powder under SEM investigation.

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 400^0C 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 method. The process is costeffective and simple. Microstructural investigation indicated particle aggregation.

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