



SDI Review Form 1.6

PART 1:

Journal Name:	International Research Journal of Pure and Applied Chemistry
Manuscript Number:	MS: 2012 IRJPAC 2748
Title of the Manuscript:	Grinding-assisted Solid-State Metathetic Synthesis of Divalent Transition Metal Tungstates

General guideline for Peer Review process is available in this link:

(<http://www.sciencedomain.org/page.php?id=sdi-general-editorial-policy#Peer-Review-Guideline>)

- This form has total 9 parts. Kindly note that you should use all the parts of this review form.



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PART 2: Review Comments

	Reviewer's comment	Author's comment (if agreed with reviewer, correct the manuscript and highlight that part in the manuscript. It is mandatory that authors should write his/her feedback here)
Compulsory REVISION comments	The manuscript reports synthesis of $M^{II}WO_4$ tungstates using metathesis reaction. This route has recently been employed for synthesis of different oxides since it allows obtaining materials at remarkably low temperatures and in a cost-effective way (see for instance Maczka M et al, Materials Chemistry and Physics, 2010;120: 289-295 for synthesis of Bi_2WO_6 or Maczka M et al, Journal of Solid State Chemistry 201; 187: 249-257 for synthesis of $LaAlO_3$). The authors show that $M^{II}WO_4$ tungstates can be obtained after firing the mixture, which was obtained by metathesis reaction, at 400 °C. Thus pure tungstates could be obtained at much lower temperature than typically reported in literature. The authors wrote on page 4 that "The SSM synthesis reported in the present study is the lowest synthesis temperature reported for solid-state synthesis". This statement is not correct. It was reported by Maczka M et al. in J. Solid State Chemistry 2011; 184: 2446-2457 (Phonon properties of nanosized $MnWO_4$ with different size and morphology) that $MnWO_4$ could be obtained already at 250 °C by mixing $MnCl_2$ with Na_2WO_4 in water solution and firing of the obtained precursor at 250 °C. This reference must be added since it reports lower synthesis temperature of $MnWO_4$ (250 °C) than reported in the present manuscript (400 °C).	It is true that $MnWO_4$ was reported to be obtained from $MnCl_2$ and Na_2WO_4 at 250°C. But the synthesis reported is not purely solid state method as it involved mixing of aqueous solutions and firing of resultant powder subsequently. Yes we included the reference 'Maczka M et al. in J. Solid State Chemistry 2011; 184: 2446-2457 (Phonon properties of nanosized $MnWO_4$ with different size and morphology)' in the manuscript.
Minor REVISION comments	Other changes: 1) please delete dot in the "... (8Ag + 10 Bg). Raman-active..." on page 5.	1) Corrected in the manuscript.



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	2) On page 5 the authors write “In MnO_4 the band at 127 cm^{-1} accompanied by two weak bands in the range 160 and 180 were due to interchain deformation and torsion modes [14].” Please add “cm^{-1}” after “180”. Moreover, what means “interchain deformation modes” ? In chain composed of edge-shared WO_6 octahedra ? Recent lattice dynamic calculations showed that these bands should be attributed to translational motions of Mn^{2+} and W^{6+} ions, not deformation modes (see Maczka M et al, Phys. Rev. B 2011; 83: 174439 “Lattice dynamics and temperature-dependent Raman and infrared studies of multiferroic $\text{Mn}_{0.85}\text{Co}_{0.15}\text{WO}_4$ and $\text{Mn}_{0.97}\text{Fe}_{0.03}\text{WO}_4$ crystals”). Deformation modes are observed in Raman spectra above 250 cm^{-1}, according to this reference. 3) Maybe the authors can comment on size of the crystallites ? It is difficult to see this from SEM micrograph. I guess from XRD pattern that crystallites are quite large since broadening seems to be small. But on other hand, Raman bands for MnWO_4, NiWO_4 and CoWO_4 are much broader than for bulk and broader than for synthesized by the authors FeWO_4 or ZnWO_4 (in case of MnWO_4, you can compare your spectra with single crystal spectra presented in the cited above paper). Why such broadening of Raman bands is observed ? Due to small particle size, large particle size distribution, defects or strains ?	2) Corrected in the manuscript. The interpretation of Raman spectra was given in terms of previous reports and the terminology of interchain deformation and torsion modes was from reference [14]. 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. 3) Scanning electron micro graphs clearly indicates large number of smaller particles as well as some bigger particles due to aggregation. The distribution of particle size may be responsible for the observed differences in broadening of peaks in Raman spectra and not so broadening observed in XRD patterns. We have not sieved the product for these studies. Since this is a solid state synthesis, we did not put much emphasis on the particle size distribution.
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<u>Optional/General</u> comments		
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