Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2018, 7 (1): 264-271

(International Peer Reviewed Journal)

Synthesis, Characterization and thermal behavior of An amorphous phase of stannic molybdosilicate ion exchanger

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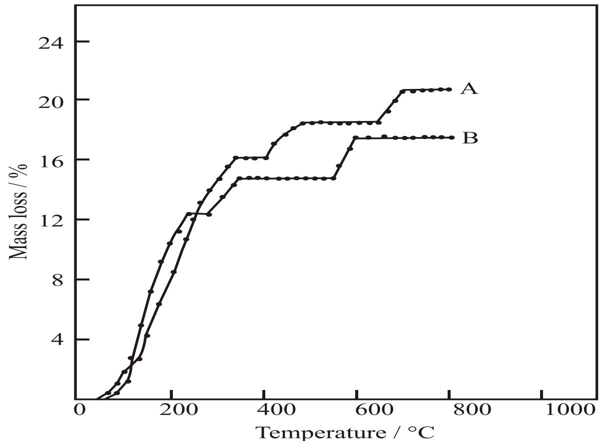
Accepted on 23rd January 2018, Published online on 27th January 2018

ABSTRACT

A new amorphous, reproducible and monofunctional stannic molybdosilicate ion exchanger has been synthesized, which possesses a promising ion exchange behaviour. The gain/ loss of ion exchange capacity has been studied in the temperature range 40°C to 800°C and compared with stannic molybdates to establish the role of silicate in the structure with temperature rise vis-a-vis its ion exchange capacity. Characterization of the material has been done by the chemical and instrumental methods of analysis like X-ray, TGA, IR and pH titrations. Based on these studies, the empirical formula of the material has been suggested. Analytical applications of the product have also been explored by achieving some quantitative binary separations involving Zn^{2+}, Cu^{2+}, Pb^{2+} and Mg^{2+} on its column, based on the distribution studies.

Graphical Abstract:



TG curves for stannic molybdosilicate
A-xchanger in H^+form,B- Exchanger in K^+ form

Keywords: Characterization, TG; IR; X-ray, thermal stability, stannic molybdosilicate, Distribution Coefficients.

INTRODUCTION

Tin based double salts as inorganic ion exchangers [1, 2] have been found to be quite stable, reproducible and compatable with the Zirconium based materials which have found extensive attention in earlier studies [3,4]. Addition of silicon in their structure has decidedly increased their thermal stability [5-9]. Some other thermally stable double salts of Zr, Th, and Ti [10-13] with silicon have been synthesized, characterized and their analytical applications studied. Recently, we have synthesized some inorganic ion exchangers based on Sn and Si and also studied their thermal behaviour [14-16].

Present study summarizes the synthesis and ion exchange characteristics of a new material stannic molybdosilicate which has been found as a promising material for column operations. Some analytically important separations have been found feasible by this ion exchanger.

MATERIALS AND METHODS

Reagents: Stannic chloride pentahydrate (PPH, Poland 98%), sodium molybdate (BDH 99%) and silica gel coarse (BDH) were used. All other chemicals were of analytical grade.

Apparatus: X-Ray, I.R., T.G. and pH-measurements were performed on a Debar- Scherer powder X-ray diffractometer, Perkin-Elmer spectrophotometer model 157, F.C.I. (Sindri, India), Stanton H 4 thermobalance and a Systronics (India) digital pH- meter respectively. T.G. measurements were carried out using a 500mg sample in a silica crucible. Shaking was done with the Toshniwal (India) electric shaker. An electric muffle furnace was used for the heat treatments.

Synthesis: Stannic molybdosilicate was synthesized by adding with constant shaking, a 0.25M aqueous solution of $SiO_2.H_2O$ prepared in a minimum quantity of NaOHto a 0.25 M aqueous solution of $SnC1_4.5H_2O$, followed by the addition of a 0.25M aqueous solution of $Na_2MoO_4.2H_2O$.

Ten samples, shown in Table 1, were obtained by varying the parameters such as mixing ratios, molarity of the reactants, precipitation pH,and refluxing time. In all cases, awhite gelatinous precipitate was obtained. The product was allowed to settle down for 24h before filtration. It was then washed with demineralized water (DMW), dried at 40°C and converted into the H^+ from by treating with 1M HNO_3 and finally washing with DMW to the pH 6-7.

Physical appearance: The product was obtained as light greenish– yellow granules. The K^+ ion- exchange capacities (Table 1) of all the samples was determined by the column method. Sample1was selected for further studies due to its maximum IEC.

Table 1. Conditions of preparation, original and regenerated ion exchange capacity of stannic molybdosilicate samples

Sample No.	Molarity	Mixing ratios (V/V) Sn:Si:Mo	Precipitation pH	Refluxing time (h)	Colour of the beads	Ion Exchange Capacity for K^+ (meq g^{-1})	
						Original	Regenerated
1	0.25	3:1:2	2.0	–	Greenish Yellow	0.80	0.80
2	0.25	2:1:1	2.0	–	–do–	0.76	0.65
3	0.25	1:1:1	2.0	–	–do–	0.60	0.60
4	0.25	1:1:2	2.0	–	–do–	0.68	0.68
5	0.25	3:1:2	0.5	–	Yellow	0.48	0.40
6	0.25	3:1:2	10.0	–	Greenish Yellow	0.45	0.40

7	0.25	3:1:2	2.0	24	–do–	0.60	0.50
8	0.05	3:1:2	2.0	–	–do–	0.75	0.72
9	0.10	3:1:2	2.0	–	–do–	0.75	0.75
10	0.50	3:1:2	2.0	–	–do–	0.70	0.60

Chemical Composition: 300 mgof the exchanger was heated with conc. HCl and the insoluble silica was filtered out, washed, dried and weighed as such, retaining only a small water content (0.18 mole of H_2O/SiO_2) [17]. Molybdenum in the filtrate was precipitated with α–benzoin–oxime [18] and weighed as MoO_3. Tin, in the filtrate, obtained after the precipitation of molybdenum, was determined by iodometric titration. The Sn: Si:Mo ratio was found to be 1.8:1:1.2.

Reproducibility: The reproducible nature of the material (Sample 1) was checked by preparing it again several times under the same conditions of temperature, volume ratios and concentrations. A variation of nearly 5% in the IEC was observed while the composition varied by 4%. The results of the X-ray and TG measurements of the different samples were in conformity with the original sample.

Chemical stability: The exchanger was stable in dilute mineral acids, water, electrolytes and organic solvents. Only a small portion of the exchanger was found dissolved in 0.1N NaOH when kept for 10 days.

Regeneration studies: Samples in the K^+ form was re-converted into the H^+ form by passing 50 mL of a 1M HNO_3solution through the exchanger column. The column was again washed with DMW after the acid treatment till all the unused acid was removed. The IEC of these regenerated samples were measured by the usual method (Table 1).

Heat Treatment: Different 1 gm portions of sample1in the H^+ form were heated at various temperatures in a muffle furnace up to 800°C for 1h each, and the ion exchange capacity was determined in each case. The results reported for stannic molybdate were included for comparison as shown in Figure 1 and Table 2.

X-ray study: X-ray diffraction patterns obtained by the powder method were obtained with nickel-filtered Cu-K_α radiations. No line was observed.

pH-titration: Titration was carried out by the method of Topp and Pepper as reported earlier [19].

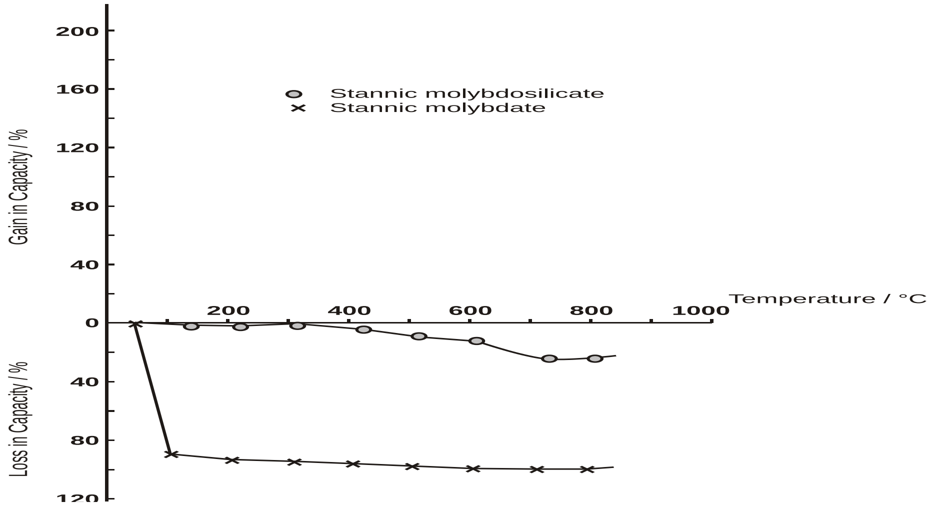


Fig 1. Loss in ion exchange capacity of stannic molybdosilicate and stannic molybdate as a function of temperature

Table 2. Change in colour and ion exchange capacity of stannic molybdosilicate and stannic molybdate on heating

SnMoSi			**SnMo (Ref 21)**
Temp. (°C)	Colour	IEC meq g^{-1}	IEC meq g^{-1}
40	Greenish yellow	0.80	1.00
100	Yellow	0.80	0.10
200	Yellow	0.80	0.07
300	Yellow	0.78	0.07
400	Grey	0.75	0.04
500	Grey	0.70	0.04
600	Grey	0.68	0.04
700	Grey	0.60	0.04
800	Grey	0.63	0.04

Thermogravimetry: Sample 1 in H^+ and K^+ forms was subjected to TG measurements in the range 40°C to 800°C, rate of heating was 10°C min^{-1}. TG at a heating rate of 6°C min^{-1} for the H^+ form of the exchanger gave identical results. Results are shown in Fig. 2.

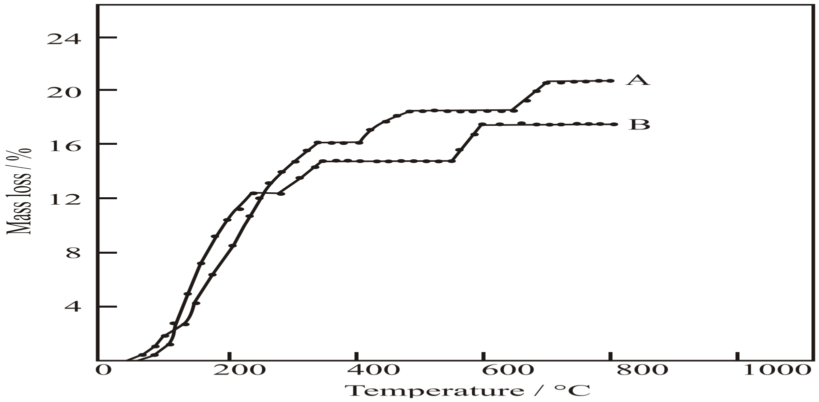


Fig. 2 TG curves for stannic molybdosilicate
Exchanger in H^+form,B- Exchanger in K^+ form

Infra-red studies: Infra-red spectra (Fig.3) of the exchanger in H^+ form was obtained by the KBr disc method.

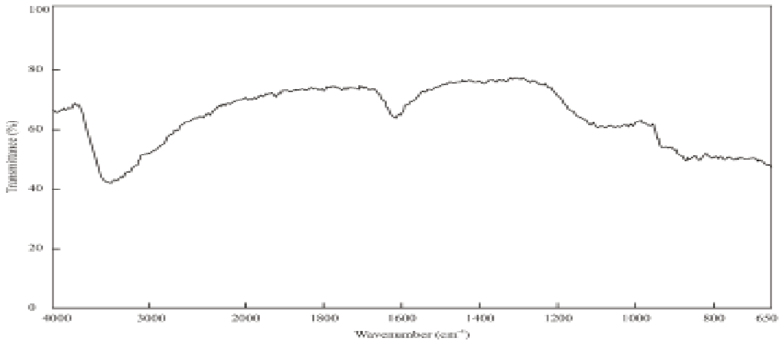


Fig 3. Infra-red spectrum of stannic molybdosilicate

Distribution studies: The distribution coefficients for 10 common metal ions in DMW were determined by using a loading of the cation not more than 3% of the ion-exchange capacity as stated earlier [20]. The total volume of the solution was 50 ml and the amount of the exchanger was 0.5 gm. All the cations were determined by titration with 0.001 M EDTA. Results are given in Table 3.

Table 3. Distribution coefficients of metal ions on stannic molybdosilicate in DMW

Metal Ion	**Kd Value (mlg^{-1})**
Mn^{2+}	14.0
Zn^{2+}	136.4
Cu^{2+}	12.4
Ni^{2+}	5.2
Co^{2+}	6.0
Pb^{2+}	10.2
Mg^{2+}	4.2
UO_2^{2+}	7.6
VO^{2+}	6.9
Al^{3+}	5.7

Separations: Quantitative separations of Zn^{2+} from Pb^{2+}, Cu^{2+} and Mg^{2+} were achieved on a glass column containing 2 gm of the exchanger (H^+ form) on a glass-wool support. The column was washed with DMW and the amount of the cation loaded on the column was <3% of the total exchange capacity of the material. The flow-rate was 0.6 to 0.8 mlmin^{-1}. The adsorbed cations were eluted with suitable solvents and determined by EDTA titration. Results are shown in Fig. 4.

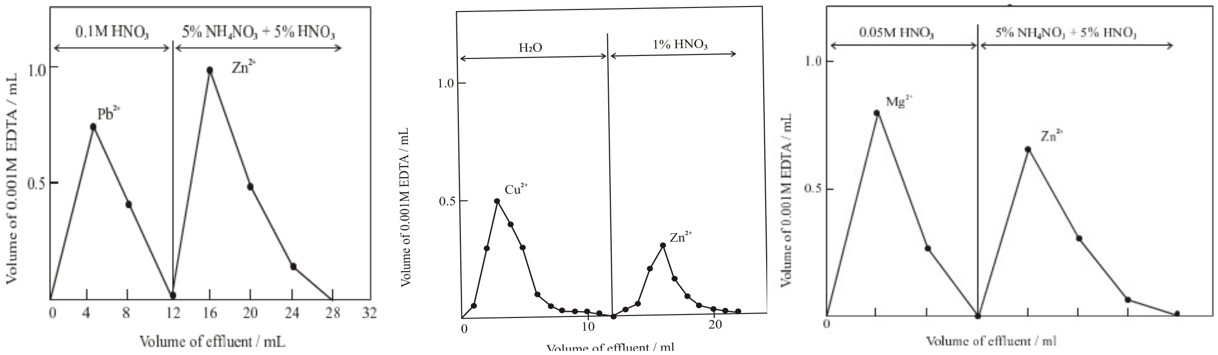


Fig 4. Separations of Zn^{2+} from Pb^{2+}, Cu^{2+} and Mg^{2+}

RESULTS AND DISCUSSION

The main advantage of this material is its fairly high thermal stability and almost total regain of its ion-exchange capacity on regeneration at room temperature (Table 1). Further, there is no significant loss in its ion-exchange capacity on heating upto 800°C (Fig. 1) showing its thermal stability. On the other hand, stannic molybdate prepared earlier [21] has a poor thermal stability (Table 2). It clearly shows the advantage of adding silica in the parent exchanger stannic molybdate. The exchanger can be synthesized over a wide range of pH from 0.5 to 10.0 (Table1). The pH titration curve shows that the exchanger is monofunctional while its amorphous nature is verified by the x-ray diffraction pattern.

Infra-red spectra (Fig.3) confirm the presence of water and OH^- groups in the exchanger. The stretch from 1000-1110 cm^{-1} shows the presence of Si-O-Si bonding in its structure.

The thermal stability of stannic molybdosilicate can be studied by knowing the TG behavior of the exchanger. It is evident from fig. 2 that the mass loss in the exchanger (H^+ form) is greater than in the K^+ form obviously because the condensation is not possible in the K^+ form and hence the mass loss is only due to the removal of external water molecules. The figure indicates a marked inflexion (both in H^+ form and K^+ form) at 350°C, may be due to the removal of the external water molecules upto 350°C. Beyond this temperature condensation appears to have started. It is supported by the change in appearance and ion exchange capacity at different temperatures. The TG curve is horizontal for both forms ($H^+$and K^+) upto 400°C and 540°C respectively. On further heating both the curves exhibit mass loss upto 500°C and 600°C respectively. Beyond 600°C, TG curve for the K^+ form remains horizontal throughout whereas the one for the H^+ form shows a mass loss upto 650°C. Above this temperature the curve remains horizontal showing no further loss of mass. Interestingly, at 600°C or above, the x-ray of stannic molybdate was found to be the same as that of SnO_2 pointing out that above 600°C, MoO_3 is completely lost [21].

It has been supported by the dehydration studies of titanium molybdate [20]. Above 600°C, volatilization of MoO_3occurs which is responsible for the complete loss of molybdenum. In TG curves of stannic molybdosilicate, the total percent loss upto 600°C in the H^+ form is always higher than in the K^+ form, indicating the fact that the water present in the exchanger is in two forms.

(a) As OH groups with the exchangeable H^+ ions, and
(b) As hydrated water molecules within the structure, which do not play any role in the exchange process but are responsible for the cavity size.

With the percent mass loss upto 600°C in the K^+ and H^+ form, the following calculations are made.

$(SnO_2)_{1.8}.SiO_2(H_2MoO_4)_{1.2}$ (mol. mass = 507.67) …(1)

Composition data given in Table 4.

Now, the H_2O molecules whose hydrogen is exchangeable = Total % mass loss in H^+ form upto 600°C-Total % mass loss in K^+ form upto 600°C = 1.0% (as from Fig. 2) … … (2)

From ALBERTI's equation

% mass loss in exchanger is = $\dfrac{1800n}{507.67+18n} = 1$ … … (3)

Where n = no. of external water molecules as from Fig. 2)

Therefore, n = 0.29… … (4)

Now, the proposed formula will be

$SnO_2)_{1.8}.SiO_2(H_2MoO_4)_{1.2}(H_2O)_{0.29}$ (mol. mass = 512.89)… … (5)

The H_2O molecules whose hydrogen is un-exchangeable

= Total % mass loss in K^+ form upto 600°C = 17.5%… … (6)

Therefore, using ALBERTI's equation

$$\frac{1800n}{512.89+18n} = 17.5\% \quad \text{… …} \quad (7)$$

n = 6.04

Thus, the empirical formula of SnMoSi will be

$(SnO_2)_{1.8}.SiO_2(H_2MoO_4)_{1.2}(H_2O)_{0.29}.\ 6.04\ H_2O$ … … (8)

(Mol. mass = 621.61)

Therefore, the I.E.C. per dry gm of exchanger

$$= \frac{0.29 \times 2 \times 10^3}{621.61} = \frac{580}{621.61} = 0.93 \text{ meq/gm} \qquad \dots \dots \qquad (9)$$

The saturation ion exchange capacity determined experimentally (as given in Table 1 and 2) is lower than the theoretical ion exchange capacity (Table 4) because of the amorphous nature of the samples, as the replacement of all hydrogen ions by other cations is not possible.

Table 4. Thermogravimetric results of stannic molybdosilicate

Composition	Molar mass	Water molecules in the form of OH group	Water molecules in the form of H_2O	ion exchange capacity $meqg^{-1}$
$(SnO_2)_{1.8}.SiO_2.(H_2MoO_4)_{1.2}$	507.67	0.29	6.04	0.93

Analytical importance of the material has been illustrated by the separation of Zn^{2+} from Pb^{2+}, Cu^{2+} and Mg^{2+}on the basis of Kd values (Table 3). Further, the regeneration capability of the exchanger was experimentally verified by achieving these separations on regenerated exchanger columns as well. The results for both the original and regenerated samples were found to be almost same (Fig. 4).

APPLICATIONS

Stannic molybdosilicate shows greater selectivity for Zn^{2+} ion and thus can be utilized for the removal and recovery of the metal ion from dilute water samples and industrial effluents. It can be used as packing material in ion chromatography for the environmental analysis too. Besides this, the separation of Zn^{2+} from various alloys and rock samples can be achieved using this material.

CONCLUSIONS

The addition of silica during the synthesis of stannic molybdosilicate results in a higher thermal stability of the exchanger as the IEC is retained to a considerable extent even at elevated temperatures. The heating effect shows a greater percent loss in the H^+ form than in the K^+ form of the material. On the basis of percent mass loss upto 600°C in H^+ and K^+ forms of stannic molybdosilicate, and using Alberti's equation, an empirical formula for the exchanger has been evaluated. The material has finally been utilized for the metal ion separations of analytical importance.

REFERENCES

[1] K.G. Varshney, A.A. Khan, Synthesis and ion exchange properties of Sn (IV) and Cr (III) arsenophosphates, *J.Inorg. Nucl. Chem*, **1979**, 41, 241-247.

[2] K.G. Varshney, A.A. Khan, Stability and distribution studies of Sn (IV) and Cr (III) arsenophosphates, *Talanta*, 1978, 25, 528-535.

[3] A. Clearfield, Inorganic ion exchange materials, CRC Press Inc., Boca Raton, **1981**, 1-290.

[4] M. Qureshi, K.G. Varshney, Inorganic ion exchangers in chemical analysis, CRC Press, Inc., Boca Raton,**1991** p. 170-277.

[5] K.G. Varshney, A.Premadas, Silica based double salts as cation exchangers-II: Synthesis and analytical applications of Sn (IV) phosphorsilicate, *J. Liq.chromatog,* **1981**, 4915-4921.

[6] S.D. Sharma, B.C. Lathe, Synthesis and ion exchange properties of thermally stable stannic silico selenite: separation of Cu^{2+} from Zn^{2+} and Mn^{2+}, *J.Ind. Chem. Soc.,* **1984**, 61, 375-377.

[7] S.D. Sharma, S. Misra, A. Agarwal, Synthesis and ion exchange behaviour of stannic tungstate silicate, *Indian J. Chem.,* **1994**, 333A, 696-698.

[8] S.D. Sharma, S. Misra, A. Agarwal, Plannar chromatography of metal ions on stannic selenite silicate in DMSO-HNO_3 systems: quantitative separation of Mo^{6+} from Cr^{3+}, Cu^{2+}, Fe^{3+} and Co^{2+}, J. *Planar Chromatog.*, **1997**, 10, 375-379.

[9] S.D. Sharma, S. Misra, A. Agarwal, Planar chromatography of d-block metal ions on stannic phosphate silicate layers in buffered EDTA solutions: quantitative separation of zirconium from other metal ions, *J. Indian Chem Soc,* **1998**, 75, 410-412.

[10] K.G. Varshney, U. Sharma, Kinetics of exchange of transition metals on Zirconium (IV) and Thorium (IV) phosphosilicate cation exchangers, *Acta chim Hung*, **1984**, 116 (1), 69-75.

[11] K.G. Varshney, S. Agarwal, K. Varshney, Synthesis, ion exchange behavior and analytical applications of a new, crystalline and stable zirconium (iv) arsenosilicate cation exchanger: Analysis of silicate rocks, *Sepn Sci & Tech*, **1983**, 18 (1), 59-72.

[12] K.G. Varshney, V. Sharma, S. Rani, Synthesis and analytical applications of thorium (IV) phosphosilicate, a new mercury selective cation exchanger: Effect of irradiation on its ion exchange behaviour, *J. Ind. Chem. Soc*, **1984**, 61 (3), 220-222.

[13] Z.M.Siddiqui, D. Pathania, Titanium (IV) tungstosilicate and Titanium (IV) tungstophosphate: two new inorganic ion exchangers, *J.Chromatogr. A*, **2003**, 987, 147-158.

[14] S.D. Sharma,K.G. Varshney and S.C.Mojumdar, Synthesis and thermal stability of some inorganic exchangers based on tin and silicon, *J. Therm. Anal.Calorim*, **2012**, 108, 843-850.

[15] S.D. Sharma, K.G. Varshney and S.C. Mojumdar, A new amorphous phase of stannic phosphor silicate,*J. Therm. Anal.Calorim*, **2015**, 119, 837-844.

[16] S.D. Sharma, K.G. Varshney and S.C. Mojumdar, Inorganic ion exchangers based on tin (IV), antimony (V) and silicon, *J. Therm. Anal.Calorim*, **2015**, 119, 899-906.

[17] E. Stahl, Thin layer chromatography— a laboratory handbook, Interscience Publishers, New York, **1969**, P. 20.

[18] N.H. Furman, Standard methods of chemical analysis, Van Nostrand, Princeton, 6th ed., **1963**, 1, 657-677.

[19] K.G. Varshney, A.R. Khan, Synthesis and ion exchange properties of Sn (IV) and Cr (III) Arsenophosphates, *J.Inorg.&Nucl. Chem.*, **1979**, 41, 241-247.

[20] M. Qureshi, H.S. Rathore, R. Kumar, Dehydration studies of Titanium molybdate, *J. Therm. Anal.*, 1971, 3, 371-378.

[21] M. Qureshi, J.P. Rawat, Preparation and properties of stannic molybdate, *J.Inorg.&Nucl. Chem.*, **1968**, 30, 305-309.

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