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Electronic Supplementary Information (ESI)

Directional synthesis of α-$AgFe(MoO_4)_2$ from $\{Mo_{72}Fe_{30}\}$ type Keplerate

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1. General Methods

All the chemicals (Ferric chloride hexahydrate, ammonium heptamolybdate, hydrazine sulfate, ammonium acetate, sodium acetate trihydrate, acetic acid, hydrochloric acid, sodium chloride, silver nitrate, ferric oxide and molybdenum oxide) were of reagent grade, received from commercial sources and used as received. Distilled water was used throughout the synthesis. Fourier transformed infrared spectra (FT–IR) of the solid samples were recorded as KBr pellets on a Varian 7000 FT–IR spectrophotometer at room temperature. The Powder X-Ray diffraction studies of the compounds were carried on a Rigaku X-ray Powder Diffractometer Miniflex-600 using CuKα1 radiation (1.54Å). The transition electron microscopy (TEM) images were obtained on a JEOL 2100F instrument while the scanning electron microscopy (SEM) images were obtained on a Zeiss EVO40 instrument. All these facilities are available in the Advanced Instrumentation Research Facility (AIRF) located within the JNU campus.

2. Experimental Section

2.1. Synthesis of $\{Mo_{72}Fe_{30}\}$-cluster (1)

The cluster was synthesized according to the procedure reported in the literature.[1]

2.2. Synthesis of α-$AgFe(MoO_4)_2$ from $\{Mo_{72}Fe_{30}\}$ cluster (2)

A mixture of aqueous suspension of $\{Mo_{72}Fe_{30}\}$ (0.1g, 8.74μmol, 20mL) and $AgNO_3$ (0.14g, 0.87mmol, 10mL H_2O) was refluxed for 18 hours at 100˚C in the absence of light. The resultant yellow colored precipitate was washed with deionised water and vacuum filtered. The dry precipitate was then calcined at 450˚C for 120 hours. (Yield: 57% based on Fe)

Temperature dependent synthesis: Heating the yellow colored precipitate obtained on refluxing aqueous solution of $\{Mo_{72}Fe_{30}\}$ cluster with $AgNO_3$ solution was carried for a range of temperatures. The reaction was carried at 400˚C, 450˚C, 480˚C and 540˚C. When the reaction was carried out at 400˚C, the desired compound was not obtained. Heating at 540˚C resulted in the formation of the compound but the fraction of unknown phase in the desired compound also increased. α-$AgFe(MoO_4)_2$ was obtained when the temperature ranged between 450˚C to 480˚C. The optimum temperature for the synthesis was found to be 450˚C.

Time dependent synthesis: The first reaction performed in the direction of the synthesis of α-$AgFe(MoO_4)_2$ from the yellow colored precipitate involved heating the compound for 120 hours. The duration of heating was then reduced to 60 hours, 24 hours and finally 12 hours. The final product obtained in all the cases was the same.

2.3. Known synthesis of α-$AgFe(MoO_4)_2$

The compound was synthesized according to the reported procedure in the literature.[2] The compound was synthesized by a solid state reaction between stoichiometric mixture of $AgNO_3$ (0.36g, 2.15mmol), Fe_2O_3 (0.17g, 1.09mmol) and MoO_3 (0.62g, 4.37mmol) which was annealed at 540˚C.

3. Characterization techniques

3.1 IR Spectroscopy

3.1.1. The IR spectra of yellow colored precipitate, obtained on refluxing aqueous solution of $\{Mo_{72}Fe_{30}\}$ compound with $AgNO_3$ (in the ratio of 1:100) for 18 hours, are shown below. The comparative IR plot show that, on refluxing, the $\{Mo_{72}Fe_{30}\}$ cluster disintegrates.

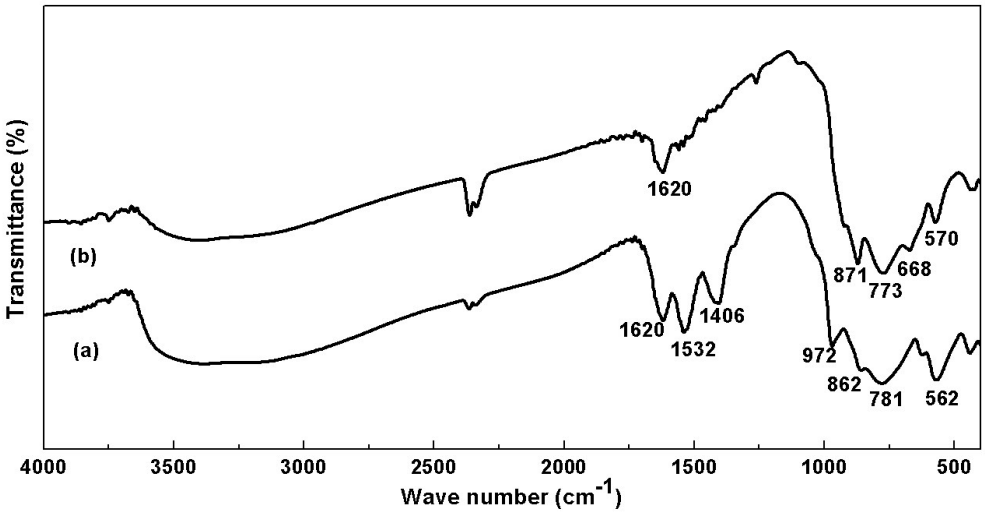


Fig. S1: IR spectra of (a) $\{Mo_{72}Fe_{30}\}$ cluster and (b) amorphous yellow precipitate obtained on refluxing $\{Mo_{72}Fe_{30}\}$ cluster with $AgNO_3$. The IR plot shows the disintegration of the cluster under reflux conditions.

Characteristic IR bands of (a): $\bar{\upsilon}$ = 1620 (m, $\delta(H_2O)$), 1532 (m, ν_{as} (COO)), 1406 (s-m, ν_s(COO)), 972 (m, ν(Mo=O)), 862 (m), 781(s), 623 (m), 568 (s). Characteristic IR bands of (b): $\bar{\upsilon}$ = 1620 (m, $\delta(H_2O)$), 871 (m, ν(Mo=O)), 773 (m), 668 (m), 570 (m).

3.1.2. Refluxing $\{Mo_{72}Fe_{30}\}$ cluster with $AgNO_3$ (in the molar ratio of 1:30), gives a colorless solution which when evaporated gives a yellow colored precipitate. The IR studies show that yellow colored precipitate on calcination at 450˚C does not yield α-$AgFe(MoO_4)_2$.

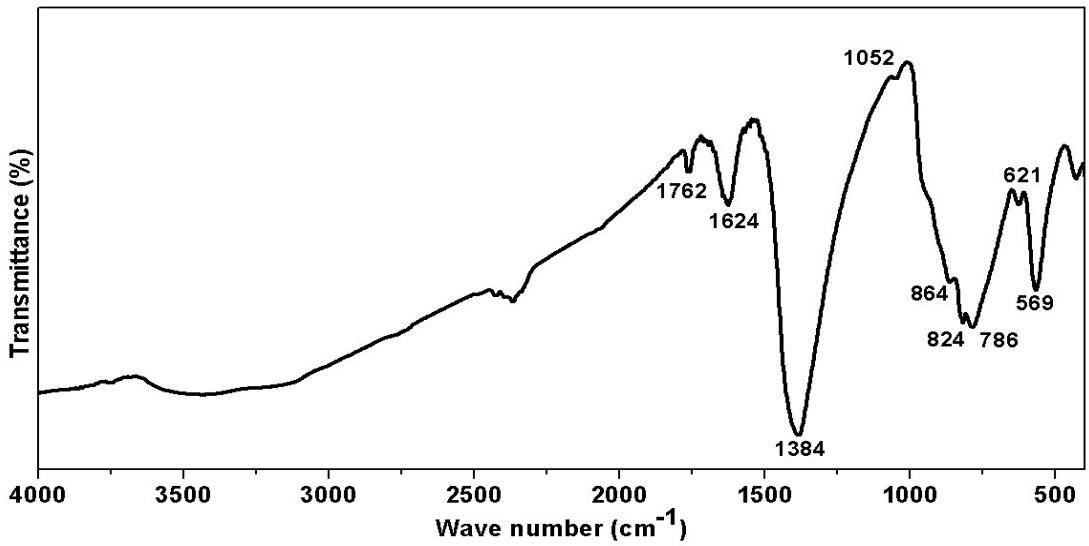


Fig. S2: IR spectrum of amorphous yellow precipitate obtained on refluxing $\{Mo_{72}Fe_{30}\}$ cluster with $AgNO_3$ (in the molar ratio of 1:30), calcined at 450˚C.

Characteristic IR bands: $\bar{\upsilon}$ = 1624 (m, $\delta(H_2O)$), 1384 (s-m, $\nu_s(COO)$), 864 (m, $\nu(Mo{=}O)$), 824 (m), 786 (m), 621 (m), 569 (m).

3.1.3. Refluxing $\{Mo_{72}Fe_{30}\}$ cluster with $AgNO_3$ (in the molar ratio of 1:60), gives a colorless solution which when evaporated gives a yellow colored precipitate. The IR studies show that yellow colored precipitate on calcination at 450˚C does not yield α-$AgFe(MoO_4)_2$.

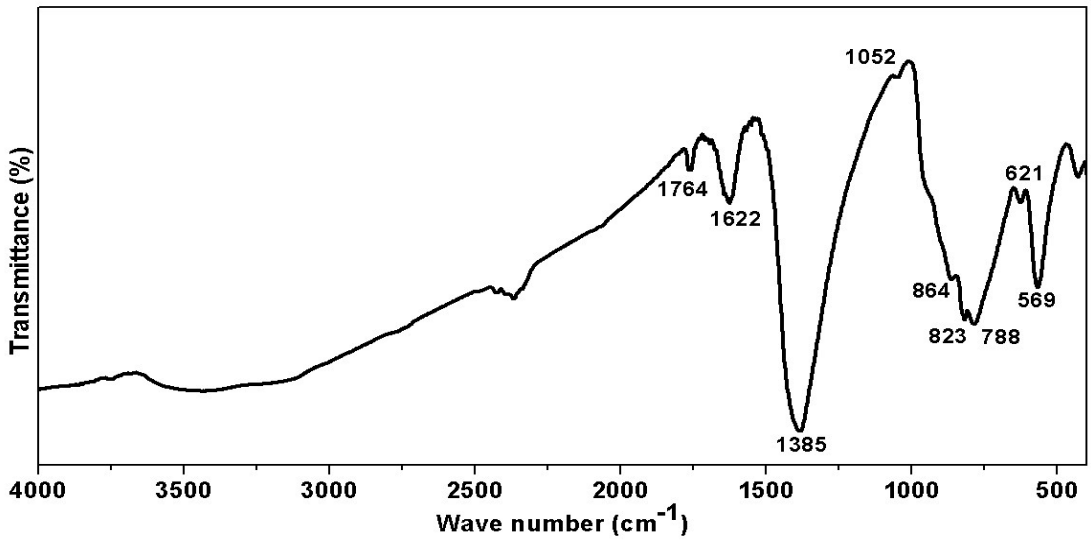


Fig. S3: IR spectrum of amorphous yellow precipitate obtained on refluxing $\{Mo_{72}Fe_{30}\}$cluster with $AgNO_3$ (in the molar ratio of 1:60), calcined at 450˚C.

Characteristic IR bands: $\bar{\upsilon}$ = 1622 (m, $\delta(H_2O)$), 1385 (s-m, $\nu_s(COO)$), 864 (m, $\nu(Mo{=}O)$), 823 (m), 788 (m), 621 (m), 569 (m).

3.2. Powder XRD studies

3.2.1. While optimizing the synthetic route for formation of α-$AgFe(MoO_4)_2$ from $\{Mo_{72}Fe_{30}\}$ cluster, the reaction was carried out at different temperatures. The comparative PXRD patterns for the temperature dependent synthesis are given below. The temperature was varied between 400-550˚C.

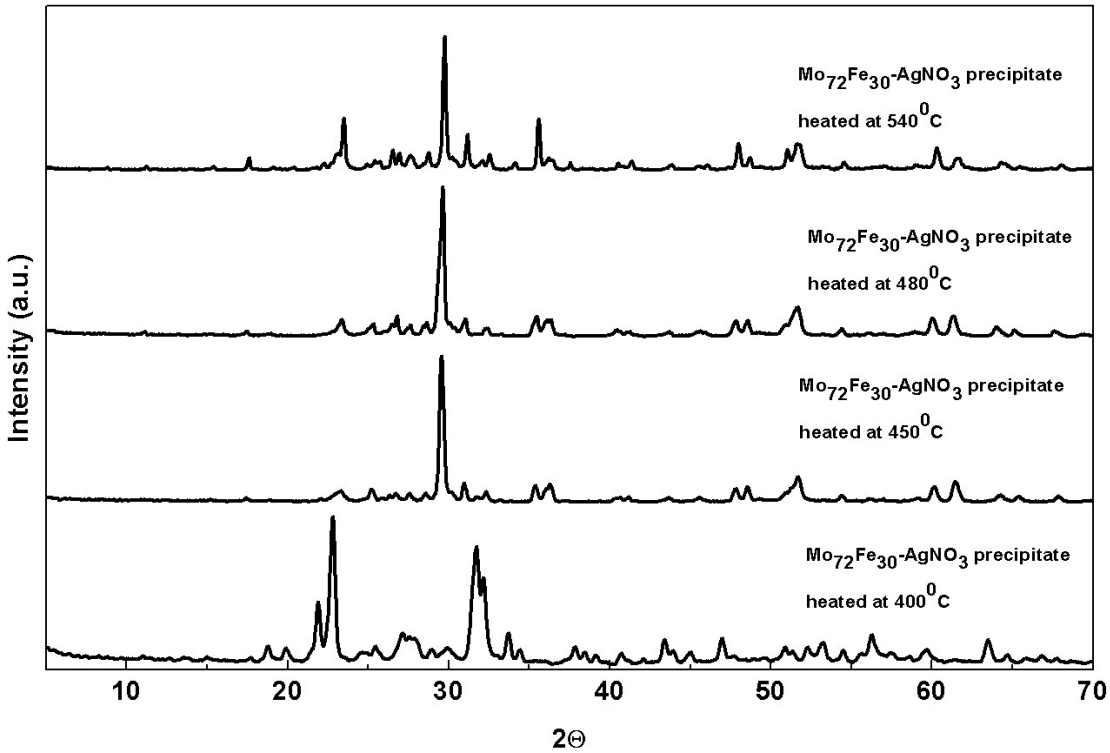


Fig. S4: Temperature dependent powder XRD plots during the synthesis of α-$AgFe(MoO_4)_2$.

3.2.2. The synthesis of α-$AgFe(MoO_4)_2$ from $\{Mo_{72}Fe_{30}\}$ cluster is also time dependent. As the time of calcination is increased from 12 hours to 120 hours, the amount of the unidentified phase formed along with α-$AgFe(MoO_4)_2$ also decreases. A comparative time dependent powder XRD plots are given below.

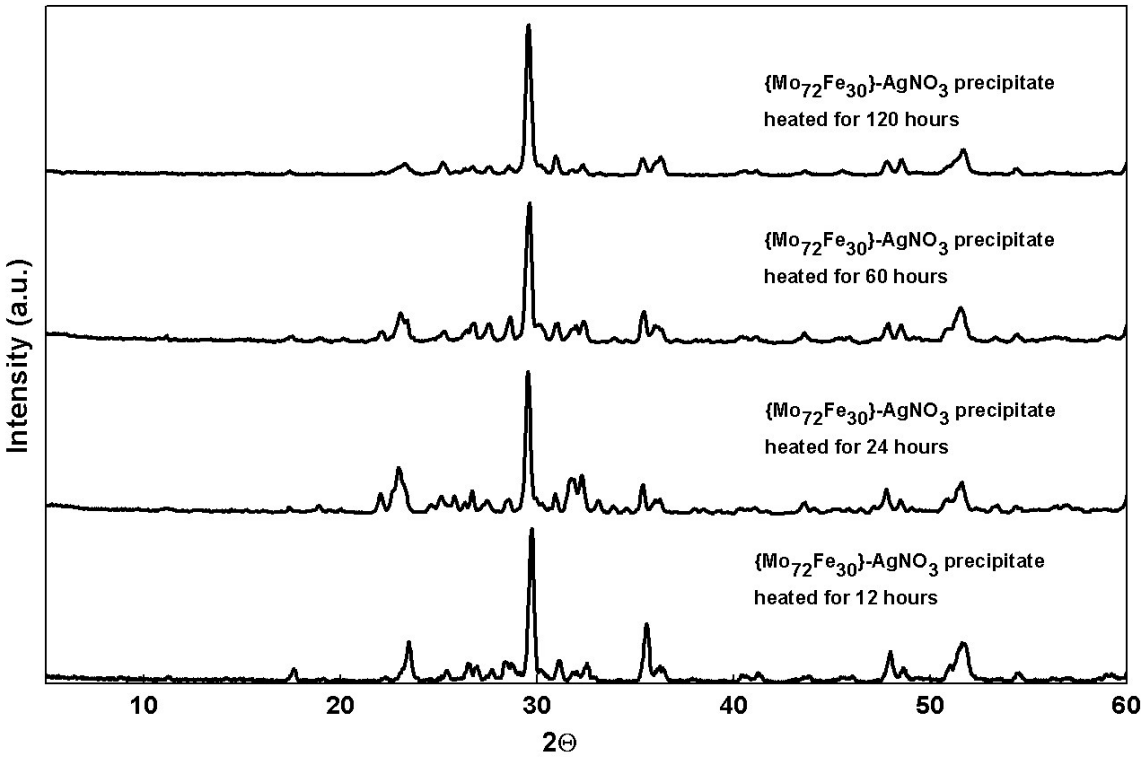


Fig. S5: Time dependent powder XRD plots during the synthesis of α-$AgFe(MoO_4)_2$.

3.2.3. When $\{Mo_{72}Fe_{30}\}$ cluster is refluxed with $AgNO_3$ (in the molar ratio 1:30 and 1:60), a colorless solution is obtained which when evaporated gives a yellow colored precipitate. PXRD studies show that yellow colored precipitate on calcination at 450˚C does not yield α-$AgFe(MoO_4)_2$.

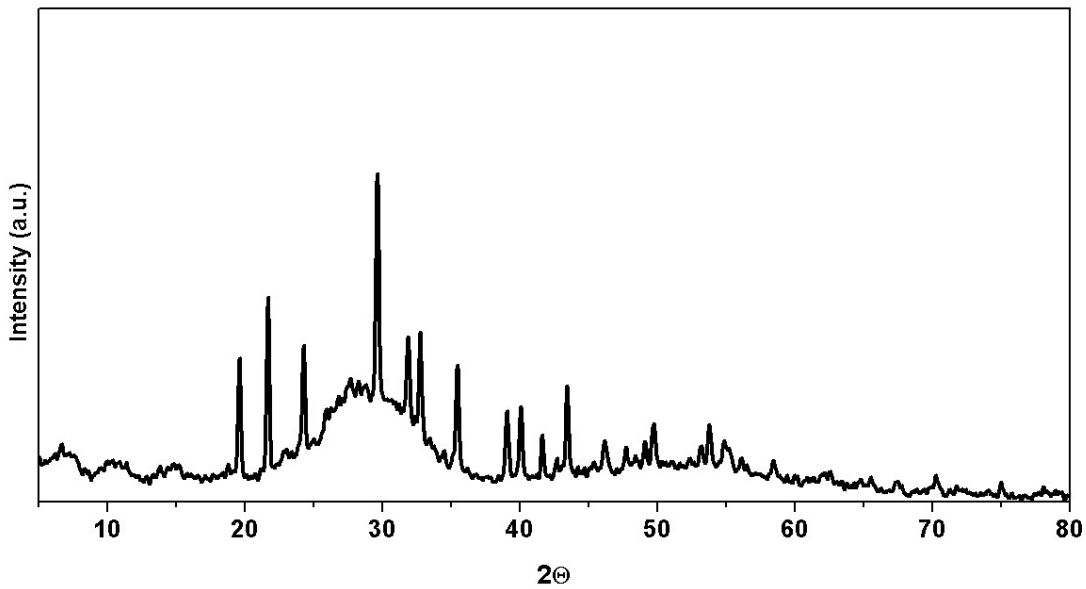


Fig. S6: PXRD plot for the yellow precipitate, obtained on refluxing $\{Mo_{72}Fe_{30}\}$cluster with $AgNO_3$ (in the molar ratio of 1:30), calcined at 450˚C.

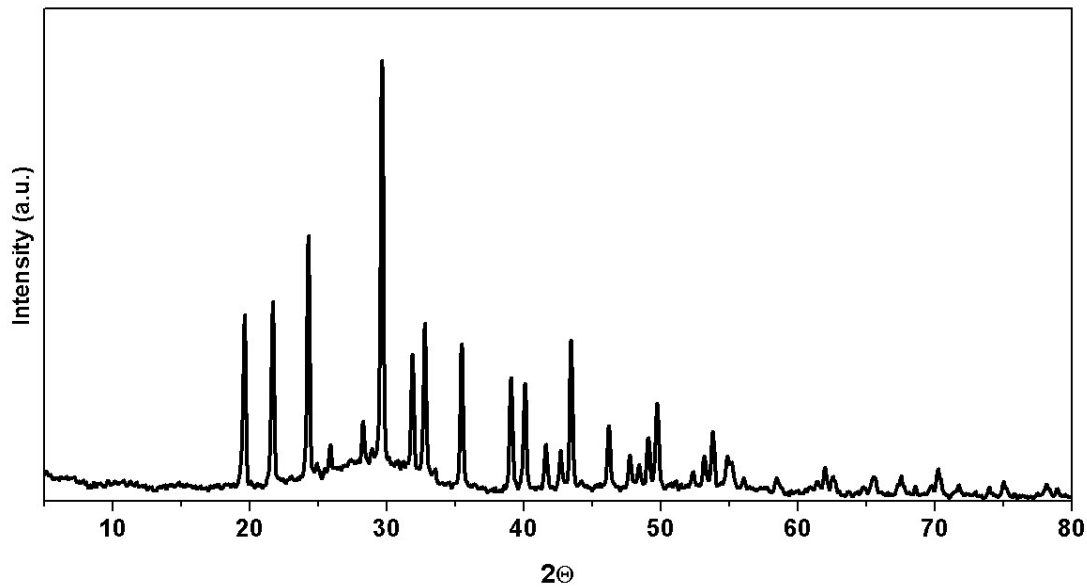


Fig. S7: PXRD plot for the yellow precipitate, obtained on refluxing $\{Mo_{72}Fe_{30}\}$cluster with $AgNO_3$ (in the molar ratio of 1:60), calcined at 450˚C.

3.2.4. Refluxing $\{Mo_{72}Fe_{30}\}$ cluster with $AgNO_3$ (in the molar ratio 1:100) results in a yellow colored amorphous precipitate and a pale yellow filtrate. When the filtrate is evaporated an amorphous precipitate is obtained. Calcination of these at 450˚C does not generate the desired α-$AgFe(MoO_4)_2$ as confirmed by powder XRD studies.

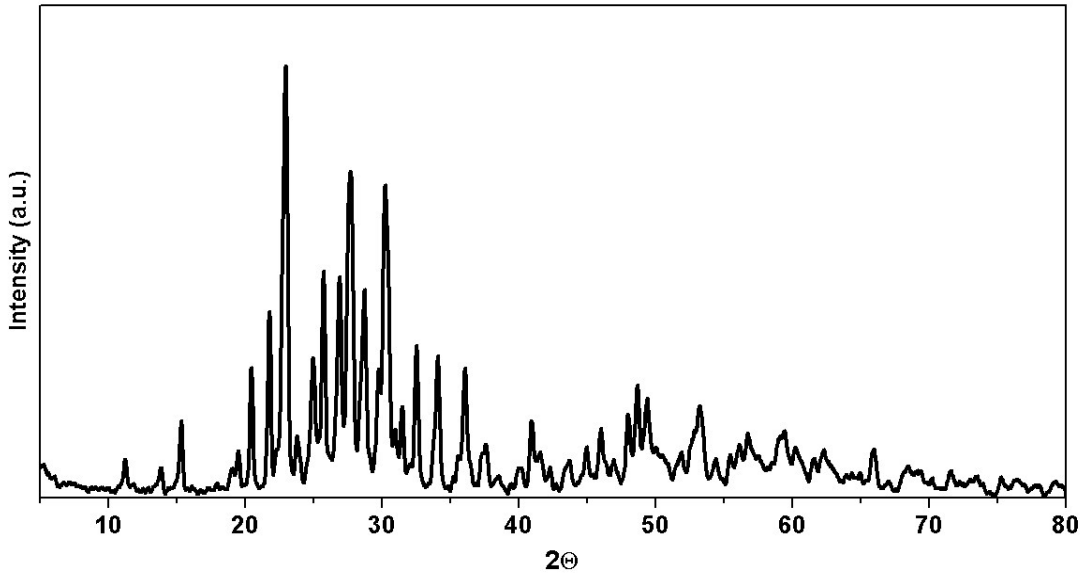
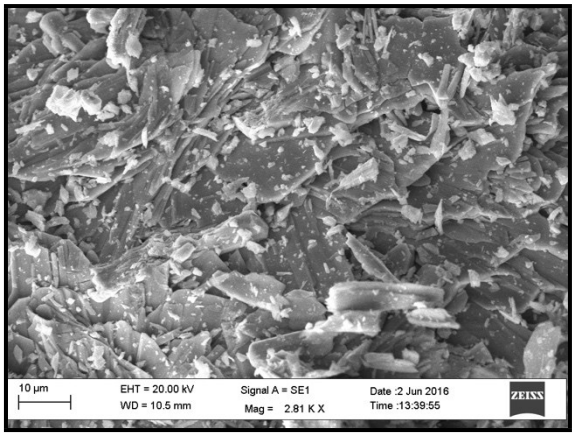
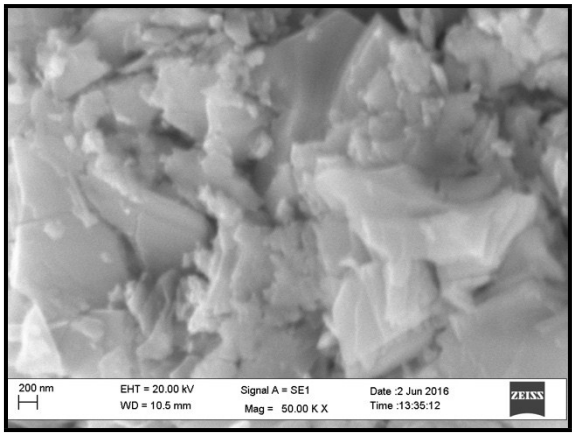


Fig. S8: PXRD plot for the yellow precipitate, obtained on refluxing $\{Mo_{72}Fe_{30}\}$cluster with $AgNO_3$ (in the molar ratio of 1:100), calcined at 450˚C.

3.3. FESEM and TEM studies

3.3.1. The FESEM pictures show the aggregates of nanoparticles.





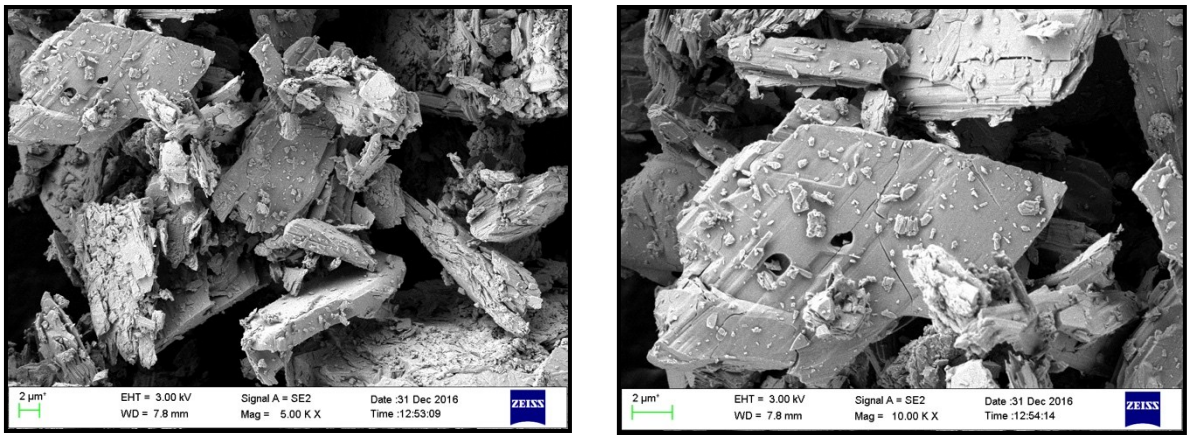


Fig. S09: SEM pictures of α-$AgFe(MoO_4)_2$ synthesized from $\{Mo_{72}Fe_{30}\}$ cluster.

3.3.2. The TEM pictures show the formation of bulk α-$AgFe(MoO_4)_2$ material coated with the unknown phase.

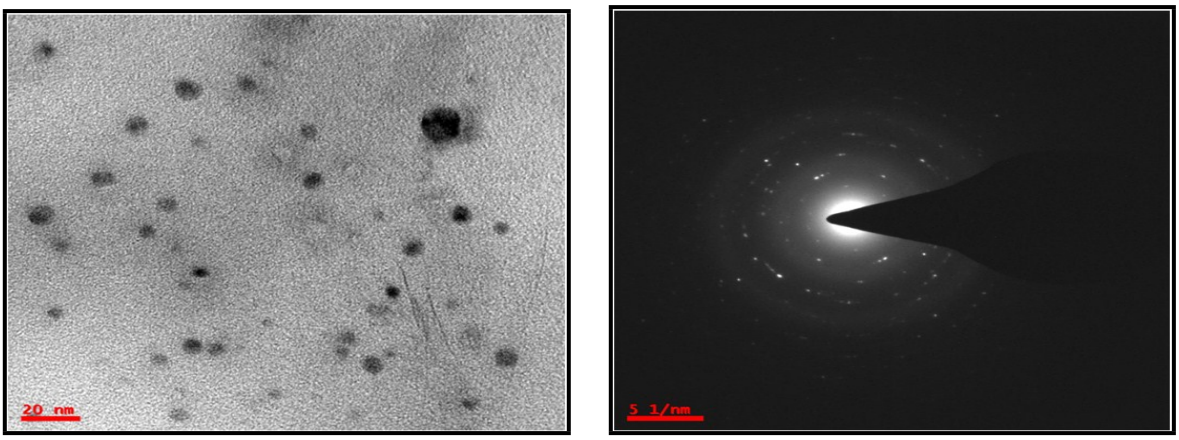


Fig. S10: TEM pictures of α-$AgFe(MoO_4)_2$ synthesized from $\{Mo_{72}Fe_{30}\}$ cluster.

3.3.3. The FESEM-EDX data confirm the formation of an unknown phase along with the bulk material α-$AgFe(MoO_4)_2$. Two separate areas have been identified on the surface of the sample where one area shows the presence of Fe and the other shows the absence of Fe. The absence of Fe indicates that the unknown phase is composed of Mo, Ag and O.

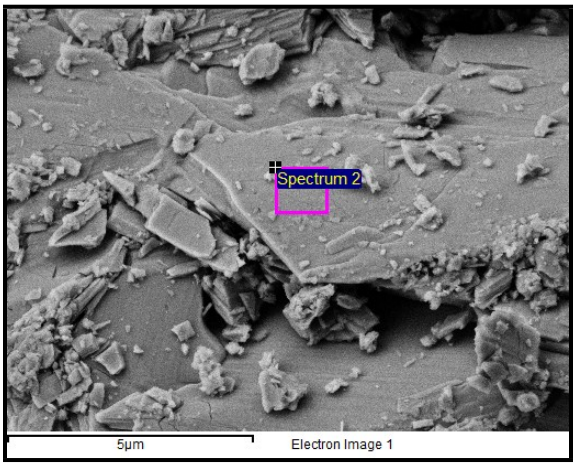


Fig S.11: FESEM image for EDX analysis.

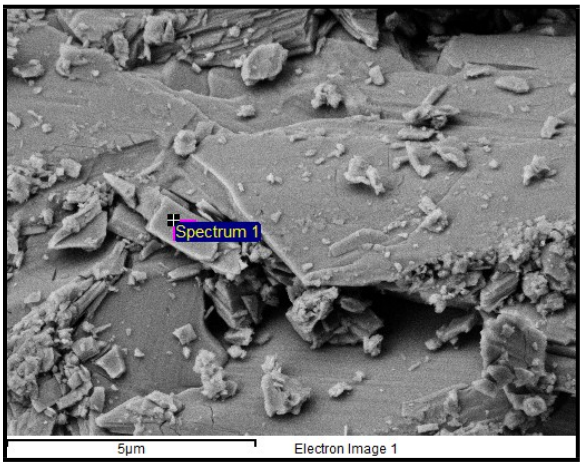


Fig S.12: FESEM image for EDX analysis.

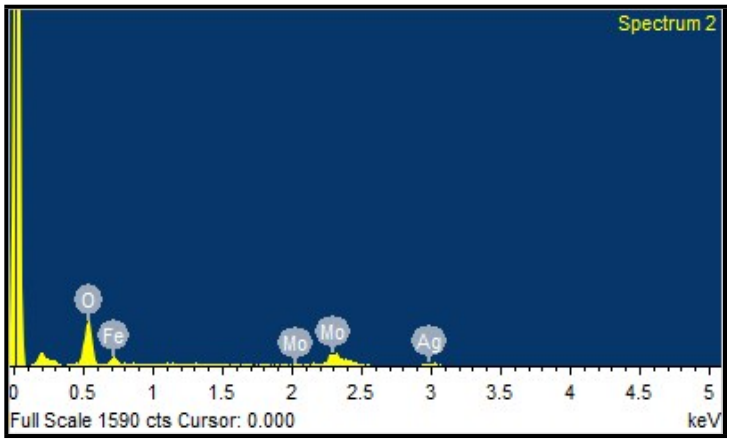


Fig. S13: FESEM-EDX plot showing the presence of Fe.

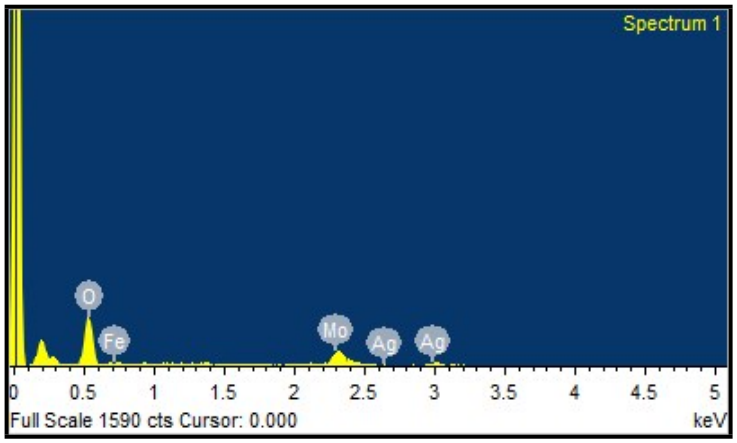


Fig. S14: FESEM-EDX plot showing the presence of Fe.

Table S1: FESEM-EDX data showing presence of Fe in the area under study

Element	Weight %	Atomic %
Oxygen (O)	22.31	60.92
Iron (Fe)	14.28	11.17
Molybdenum (Mo)	44.24	20.14
Silver (Ag)	19.17	7.76

Table S2: FESEM-EDX data showing absence of Fe in the area under study

Element	Weight %	Atomic %
Oxygen (O)	24.87	67.42
Iron (Fe)	-0.23	-0.18
Molybdenum (Mo)	49.18	22.23
Silver (Ag)	26.18	10.53

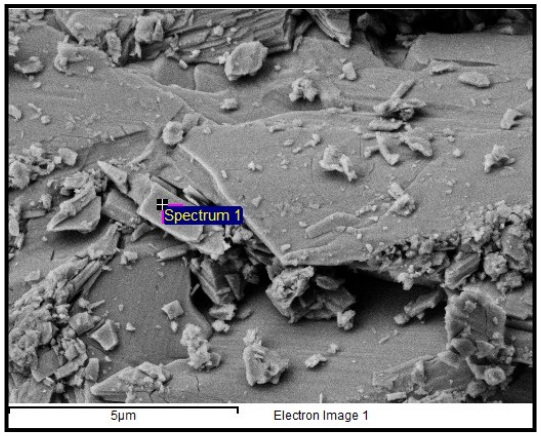


Fig. S15: FESEM image for quantitative analysis.

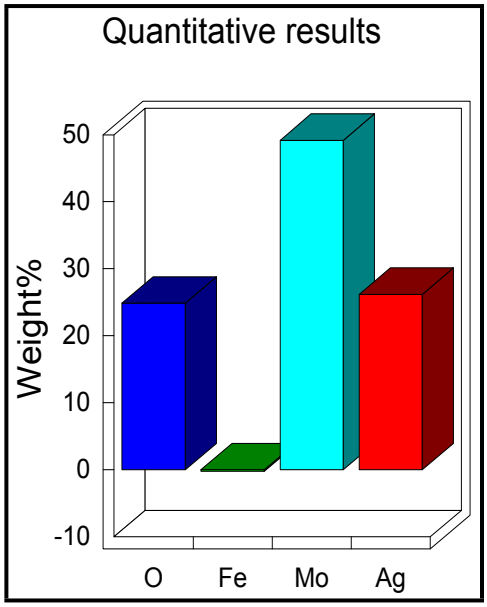


Fig. S16: Quantitative analysis for the α-$AgFe(MoO_4)_2$ sample showing absence of Fe.

3.4. FESEM Mapping

The FESEM mapping shows the presence of Mo, Fe, Ag and O on the surface of α-$AgFe(MoO_4)_2$.

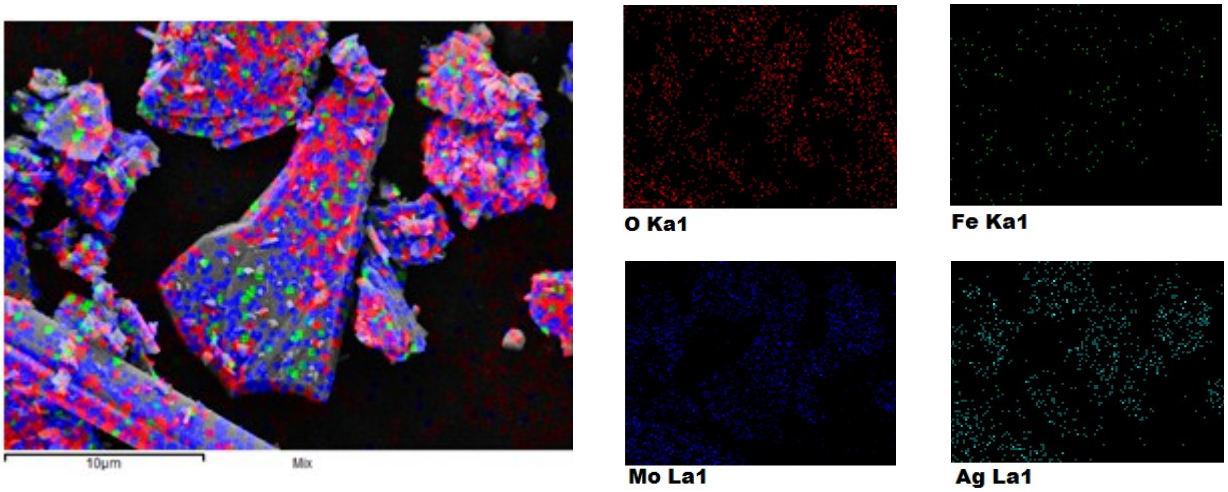


Fig. S17: FESEM mapping of α-$AgFe(MoO_4)_2$ from $\{Mo_{72}Fe_{30}\}$ showing presence of Fe.

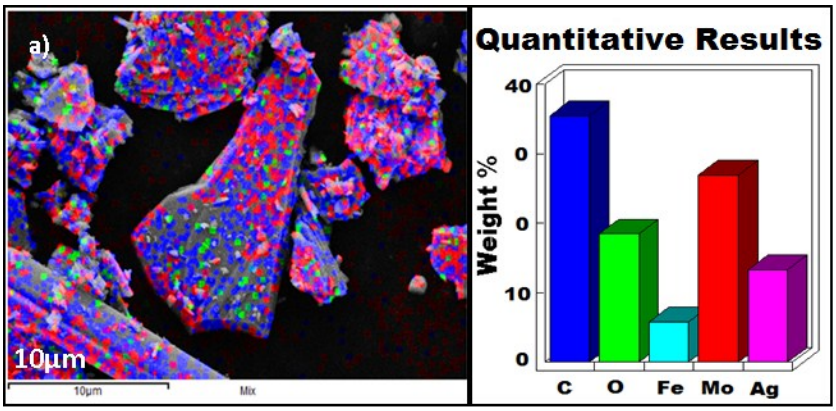


Fig. S18: (a) The EDX mapping image of α-$AgFe(MoO_4)_2$ obtained from 1; (b) the corresponding elemental distribution.

References

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