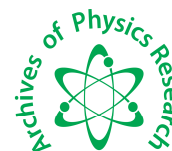




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### Growth, characterization and dielectric studies of yttrium heptamolybdate system by gel method

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#### ABSTRACT

Synthesis of yttrium heptamolybdate system has been achieved by room temperature solution growth method known as gel encapsulation technique. The system used is  $Y(NO_3)_3 - (NH_4)_6Mo_7O_{24} - NH_4NO_3 - HNO_3 - Na_2SiO_3$ . Various experiments were performed in order to find the optimum conditions conducive for the growth of yttrium heptamolybdate. The maximum size of the material synthesized in the form of crystals was  $1mm^3$ . X-ray diffraction analysis (XRD) studies reveal the crystalline nature of the grown material whereas the morphology was established by scanning electron microscopy (SEM). Energy dispersive X-ray analysis (EDAX) establishes stoichiometry of the grown crystal as  $Y_2Mo_7O_{24} \cdot xH_2O$ . Fourier transform infrared spectroscopy (FTIR) studies signify the presence of heptamolybdate ion and water of crystallization. The dielectric constant measurements were found to be strongly dependent on frequency and temperature. The dielectric constant behavior reveals that the yttrium heptamolybdate could be ferroelectric.

**Keywords:** Composite materials, Crystal growth, X-ray diffraction, Scanning electron microscopy (SEM), Dielectric properties.

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#### INTRODUCTION

Molybdates of rare earth in general, exhibit fluorescent, laser, piezoelectric, piezoacoustic, ferroelectric, ferroelastic and magnetoelectric properties [1-3]. These materials, therefore find use in optical equipment as well as for electronic and acoustic studies [4, 5]. Rare earth molybdates with general formula  $R_2Mo_7O_{24}$  belongs to the family of molybdates. Single crystals of rare earth molybdates of the type  $Ln_2(MoO_4)_7$  were grown by Brixner [6] by Czochralski technique at elevated temperature. However, due to thermal stress and other factors crystals were found to be defective. So, it is worthwhile to grow some new rare earth molybdates by an inexpensive, portable, devoid of heavy machinery, room temperature solution technique called silica gel technique. A large variety of crystals have been grown by silica gel method with relatively minimal thermal stress as compared to high temperature growth technique [7 - 12]. Some pure rare earth like neodymium, lanthanum, gadolinium [13 - 15] mixed rare earth didymium [16] and Gd - Ba [17] have been grown by this method i.e., gel encapsulation technique. However, there is no such report on the growth and characterization of yttrium heptamolybdate.

In this paper, therefore, we report detailed crystallization mechanism for growth of yttrium heptamolybdate in silica gel along with structural, morphological and dielectric characterization. To the best of author's knowledge no such report exists in the literature.

## MATERIALS AND METHODS

## 2.1 Materials Preparation

Crystal growth of yttrium heptamolybdate has been achieved by using single gel single tube [SGST] technique. The crystallizer used for the growth consists of borosilicate glass tube having dimensions 20 cm in length and 2.5 cm in diameter as shown schematically in Fig. 1.

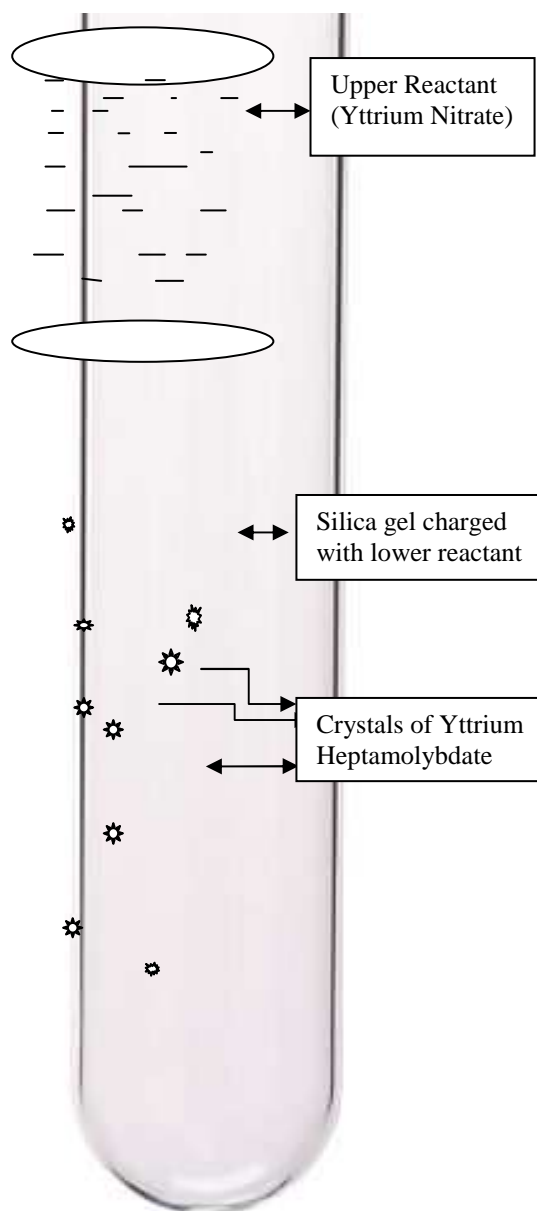
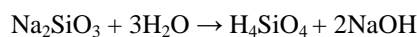
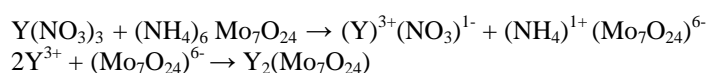


Fig. 1 Schematic diagram of crystallizer

The high quality pure grade chemicals such as yttrium nitrate (99% AR), ammonium nitrate (99.5% AR) and sodium metasilicate (97% LR), ammonium molybdate (99% AR) from s d fine - chem ltd are used as the starting material for the growth of yttrium heptamolybdate. The system used is  $Y(NO_3)_3 - (NH_4)_6Mo_7O_{24} - NH_4NO_3 - HNO_3 - Na_2SiO_3$ . Here, the gel used is the silica gel which is prepared by dissolving 284.20 g of sodium metasilicate ( $Na_2SiO_3 \cdot 9H_2O$ ) in 1000 c.c of distilled water in order to have a gel of 1 molar concentration. The sodium metasilicate solution was left undisturbed for three days and a clear solution was obtained on decantation. Moreover, silica hydrogel is one of the most commonly and preferred gel used for growth experiments. Further, unlike other gels, silica gel minimizes the effects due to precipitate – precipitate interaction and crystal impact on the wall of the container. The gelling reaction is based on the hydrolytic process given by the following chemical reaction which must be acidified to produce gel.



After the preparation of first solution i.e., silica hydrogel, second solution i.e., lower reactant was prepared by dissolving 10 g of ammonium molybdate  $[(\text{NH}_4)_6 \text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$  and ammonium nitrate each in 65 c.c of distilled water. The solution was slightly heated while mixing using magnetic stirrer and then allowed to cool. On cooling 30 c.c of concentrated  $\text{HNO}_3$  was added to it drop by drop till a white precipitate was formed. Further, 30 c.c of distilled water was added in order to have lower reactant of volume 125 c.c and molar concentration 0.06 M. The lower reactant so prepared was kept undisturbed for 12 h and then decanted in order to have clear solution. The lower reactant was then mixed together with silica gel in a crystallizer by using magnetic stirrer. The combined solution of different pH values (2, 3, 4, 4.5, 4.6, 4.7, 4.8, 4.9, 5, 5.5 & 6) and different gel ageing (24, 48, 72, 96, 120 & 144 h) were allowed to set for desired time. Since in the present work, our aim was to grow yttrium heptamolybdates crystals, therefore upper reactant of yttrium nitrate  $[\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$  of 1 molar concentration was prepared by dissolving 383.01 g of yttrium nitrate in 1000 c.c of distilled water. The upper reactant so prepared of desired molarity is poured drop wise along the sides of the tube, ensuring that this process does not break the gel. As the upper reactant diffuses into the gel impregnated with lower reactant, a reaction takes place between the upper reactant and lower reactant. The mechanism of reaction leading to the formation of yttrium heptamolybdates is as follows:



## 2.2 Characterization method

Optical microscope (Epignost of Carl Zeiss, Germany) was used to study the different morphologies exhibited by the grown crystals, whereas surface features of the crystals were studied by using scanning electron microscope (SEM, Model FEI Quanta 200). The powder X-ray diffraction pattern of the grown crystal was obtained by using PW1710 type diffractometer (40 kv, 30 mA, Cu Anode). Energy dispersive X-ray analysis (EDAX) was recorded using dispersive spectrometer attached to scanning electron microscope for carrying out elemental analysis of the grown crystals. Fourier transform elemental analysis was recorded in the wave number range of  $400 - 5000 \text{ cm}^{-1}$  on Bruker make FTIR spectrometer.

## 2.3 Dielectric method

Yttrium heptamolybdate grown from this method were either spherulite or in the form of powder so it was essential for the dielectric measurements that the materials should be grounded and made in the form of circular pallets. The powdered material was mixed with 1-2% of poly vinyl alcohol as binder and then compressed under high pressure of  $150 \text{ kg/cm}^2$  (or  $2200 \text{ lb/in}^2$  or 9 torr or  $1.2 \times 10^3 \text{ Pa}$ ) using KBr hydraulic press and a dye to make a circular pallet. The circular pallets of dimensions 13 mm diameter and thickness 1.625 mm were heated up to  $200^\circ\text{C}$ . A coating of silver paste was done on both the sides of the pallet and these were then mounted in a sample holder which was then placed in a furnace. The dielectric measurements were carried out in the frequency range 5 KHz to 1 MHz and in temperature range of  $25-500^\circ\text{C}$  with the help of fully automated impedance analyzer (LF 4192A model) interfaced with USB GPIB converter 82357 B (Agilent) and further automated by using a computer for data recording, storage and analysis.

## RESULTS AND DISCUSSION

### 3.1 Synthesis of yttrium heptamolybdates crystals

To establish optimum conditions for the synthesis of yttrium heptamolybdate (hereafter referred as YHM) for scientific investigations various experiments were performed under varying conditions of different growth parameters viz., gel concentration, gel pH, concentration of upper and lower reactant, gel ageing and temperature of the surroundings. The details of these growth parameters are given in the following sections.

**Effect of gel pH:** The pH of the gel varies from 2 to 6 (2, 3, 4, 4.5, 4.6, 4.7, 4.8, 4.9, 5, 5.5 & 6) and its effect was studied keeping the concentration of upper and lower reactant as 0.5 M and 0.6 M respectively. It was observed that gel does not set at  $\text{pH} \leq 3$ . At pH value greater than 3, the gel sets loose and does not support the upper reactant. However, pH value in the range of 4.5 to 4.8 is conducive for the growth of this material. As pH increases to 4.9 and 5, apart from precipitation, formation of Liesegang ring takes place as shown in Fig.2. With the further increase of pH value upto 5.5 and 6 quick reaction takes place and solution turns milky.

**Effect of gel ageing:** To study the effect of gel ageing, gel charged with lower reactant was kept for different ageing time i.e., 24, 48, 72, 96, 120 & 144 h keeping other parameters same. It was observed that nucleation density is

maximum for 72 h whereas it is minimum for 144 h. However, crystallization was observed for all gel ageing. The material grown assumes spherulitic morphology.

**Effect of lower reactant:** To study the effect of variation of lower reactant concentration, different concentration of lower reactant i.e., 0.3, 0.6 and 0.9 M was taken. It was observed that nucleation density was maximum at 0.9 M whereas minimum for 0.3 M concentration. In other words, it was observed that nucleation density increases with increase in molar concentration of lower reactant. But the morphology the crystals remain same i.e., spherulites.

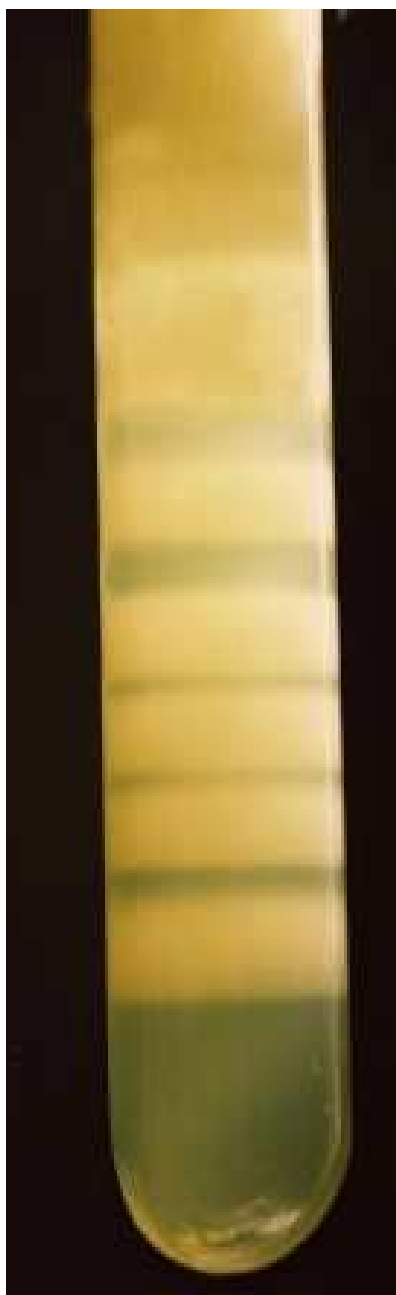


Figure 2 Liesegang ring formation of yttrium heptamolybdate (YHM) at gel + LR pH 5. Other growth conditions are gel + LR age 72hrs, gel conc. 0.5M, LR conc. 0.6M, UR conc. 0.5M

**Effect of lower reactant:** To study the effect of variation of lower reactant concentration, different concentration of lower reactant i.e., 0.3, 0.6 and 0.9 M was taken. It was observed that nucleation density was maximum at 0.9 M whereas minimum for 0.3 M concentration. In other words, it was observed that nucleation density increases with increase in molar concentration of lower reactant. But the morphology the crystals remain same i.e., spherulites.

**Effect of upper reactant:** The effect upper reactant concentration was studied by taking different concentration of upper reactant i.e., 0.2, 0.3, 0.5, 1 and 1.5 M keeping other parameters same. It was observed that reaction rate increases with the increase in the concentration of upper reactant. Nucleation density was maximum at 0.5 M.

**Effect of surrounding temperature:** Gel growth of YHM was found to be strongly temperature dependent. It was observed that gel might take 24 h to set in summer (30 – 40 °C) where as in winter (10 – 15 °C) it would take 14 days to set. Moreover, as the temperature increases, the free energy of formation of a critical nucleus increases but the degree of supersaturation decreases [18, 19]. This reflects that temperature of the surrounding plays an important role during the growth of the crystals. It was experimentally observed that temperature in the range 30 – 40 °C proved favorable for the growth of YHM system.

Thus, the best conditions for the growth of YHM by gel technique are: gel ageing 72 h, gel concentration 0.5 M, concentration of lower reactant 0.6 M, concentration of upper reactant 0.5 M, ph value 4.8 and temperature of the surroundings 30 – 40 °C. Under these conditions, good quality YHM materials with spherulitic morphology were obtained. Table 1 gives detailed information about various growth experiments conducted on YHM.

**Table 1 Detailed information about various growth experiments conducted under different conditions and results obtained on yttrium heptamolybdate (YHM) system.**

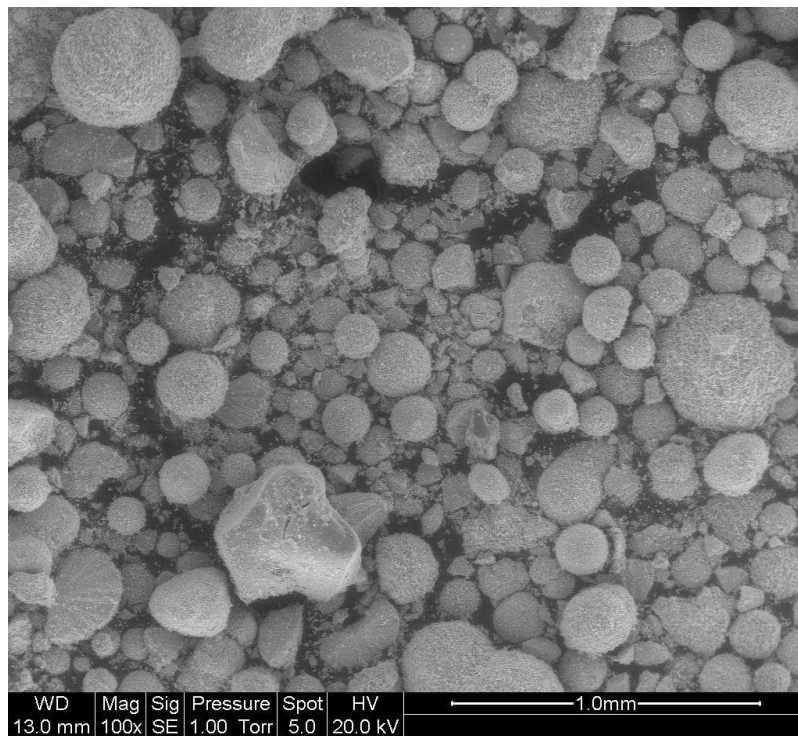
Experimental changing parameters	Constant parameters	Results
Variation of pH of Gel + LR 2, 3, 4, 4.5, 4.6, 4.7, <b>4.8</b> , 4.9, 5, 5.5, 6	UR Y(NO <sub>3</sub> ) <sub>3</sub> Conc .5M LR Conc .06M Gel + LR age 48hrs Gel conc .5M	Morphology spherulitic Liesegang rings at pH 4.9, 5 Maximum nucleation density at pH 4.8. pH values < 4.5 and > 5 not conducive for growth
Variation of gel + LR ageing 24, 48, <b>72</b> , 96, 120, 144 hrs	UR Y(NO <sub>3</sub> ) <sub>3</sub> Conc .5M LR Conc .06M Gel conc .5M Gel + LR pH 4.8	Morphology spherulitic at 48, 72, 120, 144hrs Optimum condition 72hrs Nucleation density decreases as gel + LR age increases
Variation of gel concentration .3, .5, .7 M	UR Y(NO <sub>3</sub> ) <sub>3</sub> Conc .5M LR Conc .06M Gel + LR age 72hrs Gel + LR pH 4.8	Morphology spherulitic at all concentrations, nucleation density max. at .5M
Variation of lower reactant (LR) concentration .03, .06, .09 M	UR Y(NO <sub>3</sub> ) <sub>3</sub> Conc .5M Gel + LR age 72hrs Gel + LR pH 4.8	Morphology spherulitic at all concentrations, nucleation density max. at .09M and min at .03M
Variation of upper reactant concentration .25, .5, 1, 2 M	Gel + LR conc .06 Gel + LR age 72hrs Gel + LR pH 4.8	Morphology spherulitic at all concentrations, nucleation density max. at .5M.
Note : pH value of gel was varied by mixing different volumes of LR and gel solution, keeping the total volume same (Gel + LR column 13 cm. Dimensions of crystallizer 2.5cm diameter x 20 cm length) UR: Upper reactant; LR: Lower Reactant; M: Molarity; Conc.: Concentration		

### 3.2 Optical and scanning electron microscopy

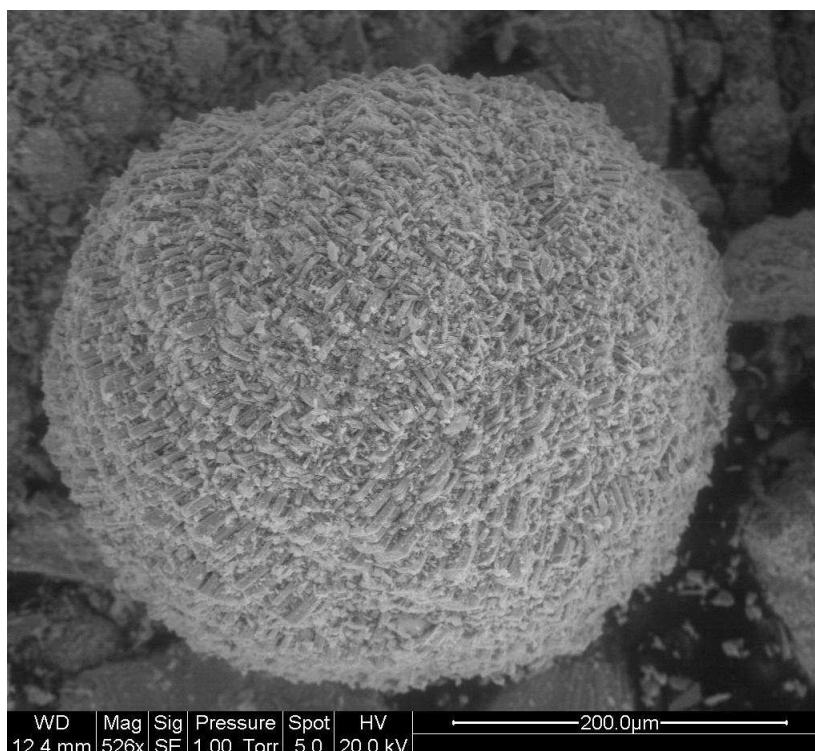
An optical and scanning electron microscopic (SEM) study was performed to see the surface morphologies of YHM system. Grown material exhibit mostly spherulitic morphology. These spherulites are infact agglomeration of number of tiny crystals. They consist of radially oriented micro-crystals arranged at non -crystallographic angles with in a spherical envelope. Klith and Padden [20] gave the first concept of spherulitic growth. They proposed that spherulitic growth be connected to diffusion fields that arise due to segregation of impurities into the melts. Random lamellar branching with preferred crystallographic mis-orientation is also observed to be responsible for spherulitic growth [21]. According to Boltov and Muravev [22], spherulites grow from a single crystal nucleus, drawn out in a direction perpendicular to c axis lying in the plane of the crystal. The spherical shape arises due to the surface tension forces acting on different faces. In gel diffusion method, synthesis takes place due to the chemical reaction between reagents at a controlled rate. However, if the value of supersaturation at any point in the gel becomes very high it results in the formation of spherulites.

In order to study the surface features of the grown crystals, scanning electron microscopic study was performed. Fig. 3(a) is an electron micrograph showing formation of number of spherulites. When these spherulites are seen at higher magnification [Fig.3(b & c)], these spherulites appear to be result from aggregation of tiny single crystallites spreaded and stacked two dimensionally layer wise themselves and form a spherical envelope.





**Fig.3 (a)** Electron micrograph showing number of spherulities



**Fig.3 (b)** Spherulite seen at higher magnification appear to be result from aggregation of tiny single crystallites

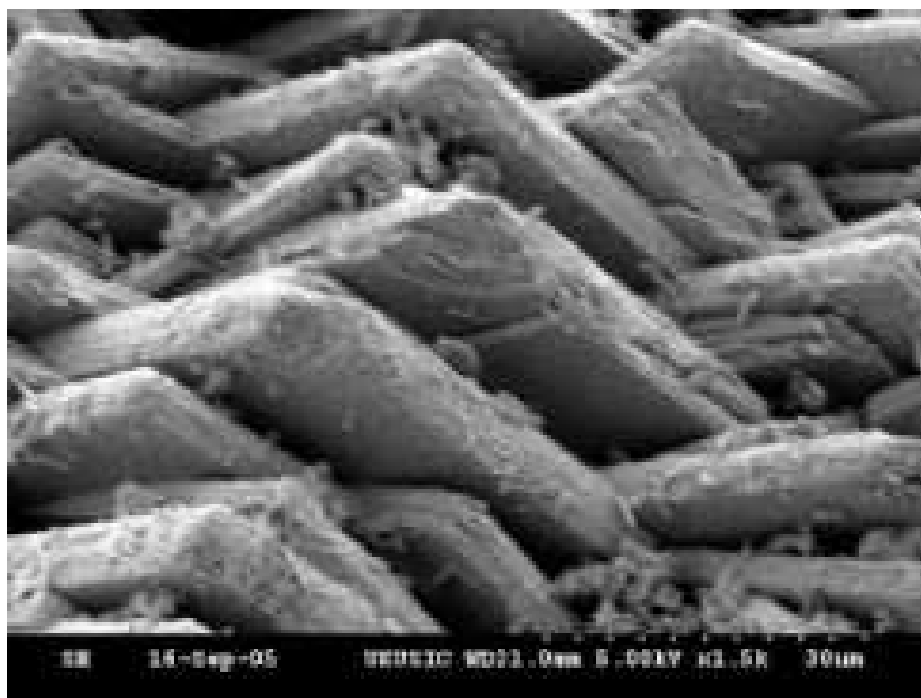


Fig.3(c) Spherulites seen at further higher magnification spread and stacked two dimensionally layer wise forming a spherical envelope

### 3.3 X-ray diffraction analysis

X-ray diffraction (XRD) methods are considered to be the preliminary analysis in the characterization of the materials. The powder X-ray diffraction pattern of YHM is shown in Fig. 4. The crystalline nature of the grown material is quite clear from the diffraction pattern because of the occurrence of the sharp peaks at specific  $2\theta$  Bragg angle. From the powder XRD data, it is clear that YHM belongs to monoclinic crystal system. The lattice parameters obtained are:  $a = 11.215 \text{ \AA}$ ,  $b = 12.011 \text{ \AA}$ ,  $c = 10.447 \text{ \AA}$  and  $\alpha = 90^\circ$ ,  $\beta = 115.363^\circ$ ,  $\gamma = 90^\circ$ , with cell volume  $1271.50 \text{ \AA}^3$ . The details of the XRD plot depicting  $d$  spacing and corresponding  $[hkl]$  values is given in the Table 2.

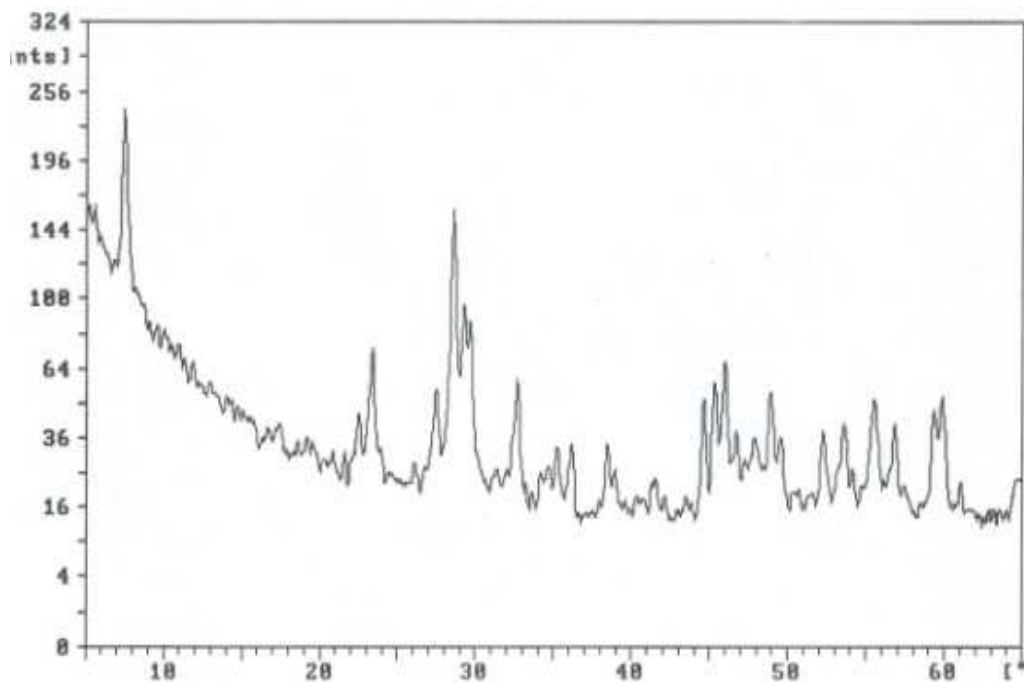


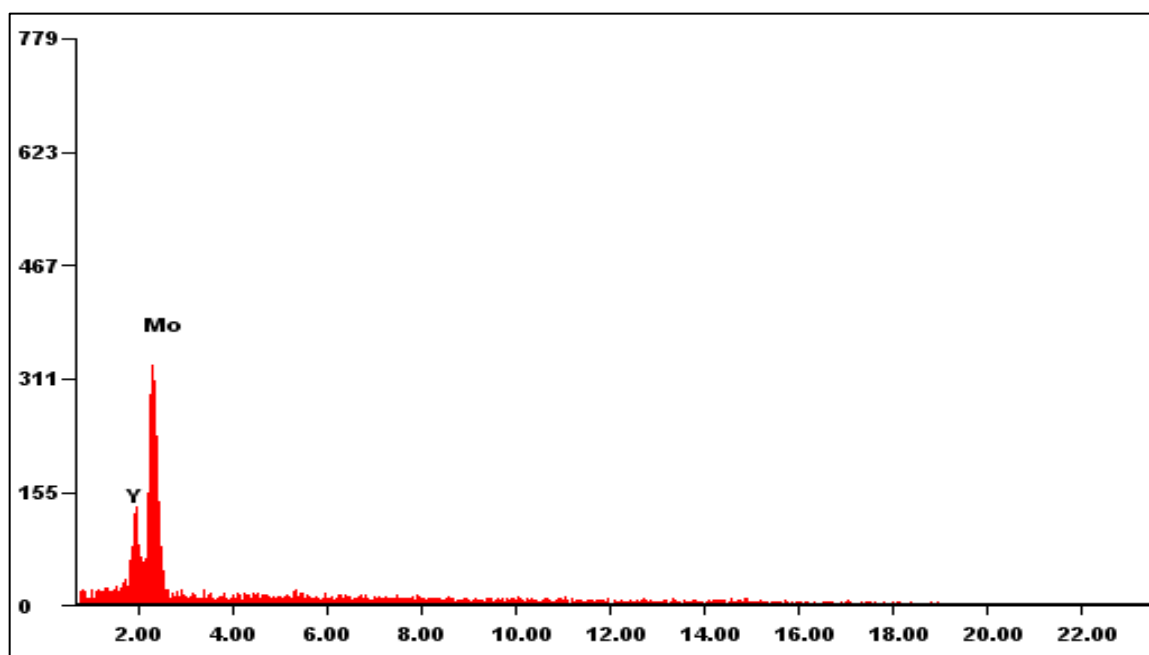
Figure 4 Powder X-ray diffraction pattern of yttrium heptamolybdate (YHM) showing well resolved peaks at particular Bragg's angle

Table 2 Compiled data of various hkl planes corresponding to different Bragg angle and interplaner spacing in case of yttrium heptamolybdate (YHM) system

2-Theta	d spacing	h k l
8.55	10.339	0 1 0
9.68	9.133	1 0 1
21.30	4.168	1 2 1
26.76	3.329	1 0 2
27.38	3.255	3 1 0
29.05	3.072	0 2 2
32.82	2.727	3 2 1
34.29	2.613	2 2 2
36.04	2.490	4 2 -1
38.72	2.324	4 0 -1
46.33	1.958	5 2 0
49.45	1.842	3 2 -4
55.51	1.654	-4 3 0

### 3.4 Energy dispersive X-ray analysis

Qualitative and quantitative analysis was performed by energy dispersive X - ray analysis (EDAX) in order to understand the elemental composition of the grown crystals. Fig. 5 shows the EDAX spectrum of the grown material. From the spectrum, it is clear that peaks corresponding to all major elements i.e., Y, Mo is present in the grown system. Table 3 gives experimental and theoretical calculated atomic and weight percentage of the elements present in the grown system. The experimental and theoretical values are in good agreement with each other. Thus, from qualitative and quantitative analysis it is clear that these crystals belong to heptamolybdate series with composition  $Y_2Mo_7O_{24}$  (yttrium heptamolybdate).



Vertical counts 300  
LSecs = 100

Energy Range in KeV.

Figure 5 Energy dispersive X - ray analysis (EDAX) showing the presence of various major elements in the yttrium heptamolybdate system

Table 3 Experimental and theoretical calculated values of major elements present in yttrium heptamolybdate (YHM) system using energy dispersive X-ray analysis (EDAX)

Element present	Atomic percentage (%)		Weight percentage (%)	
	Experimental	Calculated	Experimental.	Calculated
Yttrium	20.84	22.22	19.61	20.93
Molybdate	79.16	77.77	79.16	79.06



### 3.5 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) has been carried out to study the presence of various functional groups present in the grown system. Fig. 6 shows FTIR spectra recorded in the wave number range of 500 – 4000  $\text{cm}^{-1}$ . It is observed that there is broad peak at 3400  $\text{cm}^{-1}$  which is due to water and strong stretching modes of OH group ( $\nu_1$  water symmetry structure). The peaks at 1628 – 1631  $\text{cm}^{-1}$  can be attributed to water ( $\nu_2$  water bending). Also peak at 400  $\text{cm}^{-1}$  indicate vibration of oxygen ion. The multiple peaks between 858 and 932  $\text{cm}^{-1}$  is due to symmetric or antisymmetric stretching vibrations of the heptamolybdate ion ( $\text{Mo}_7\text{O}_{24}$ ) [23 – 25] and those occurring at various intervals with in the range 400- 800  $\text{cm}^{-1}$  are attributed to the presence of metal oxygen (Mo – O – Mo) bonds. Since the grown material do contain water of crystallization as revealed by FTIR hence the propose formula as suggested by EDAX and FTIR is  $\text{Y}_2\text{Mo}_7\text{O}_{24} \cdot x\text{H}_2\text{O}$ .

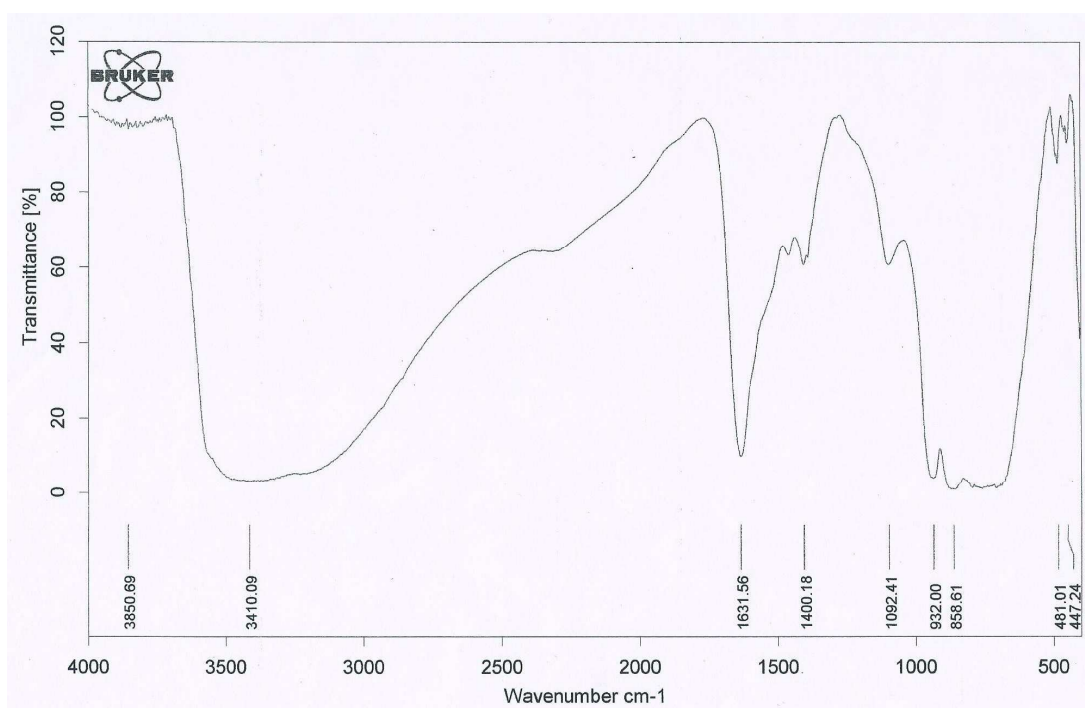


Figure 6 Fourier transform infra red spectrum depicting the presence of major functional groups in the grown material

### 3.6 Dielectric properties

The variation of dielectric constant ( $\epsilon'$ ) as a function of temperature at different frequencies (5 kHz - 1 MHz) for YHM system is shown in Fig.7. From the graph, following points are noteworthy.

- The dielectric curve shows two anomalies, one at 358  $^{\circ}\text{C}$  and other at 394  $^{\circ}\text{C}$ . The value of  $\epsilon'$  increases with increase in temperature, attaining maximum value firstly at 358  $^{\circ}\text{C}$  and then at 394  $^{\circ}\text{C}$ , thereby suggesting two phase transitions in the system. Such type of behavior was observed for other materials which exhibit two phase transitions [26, 27].
- The maximum value of  $\epsilon'$  obtained at 5 kHz was 131 for first transition (358  $^{\circ}\text{C}$ ), whereas for second transition (394  $^{\circ}\text{C}$ ) the maximum value was 247. In this case, no drift in transition temperature was observed.
- At frequency 1MHz there is only one peak with dielectric constant value of 31.62.
- It is important to point out that at lower frequencies like 5 kHz and 10 kHz, the second transition is more prominent as compared to first transition, however, with increase of frequency the prominence of second transition decreases and ultimately dying down for the frequency if 1 MHz, thereby suggesting that the onset of ferroelectric transition occurs at 358  $^{\circ}\text{C}$ . This may be due to the suppression of the space charge polarization at high temperature and at high frequency. Table 4 gives dielectric constant values for two different transition peaks.

Therefore, from the above observations we can suggest that yttrium heptamolybdate (YHM) system synthesized by room temperature solution growth technique have two transition peaks and is suggested to be a ferroelectric material.

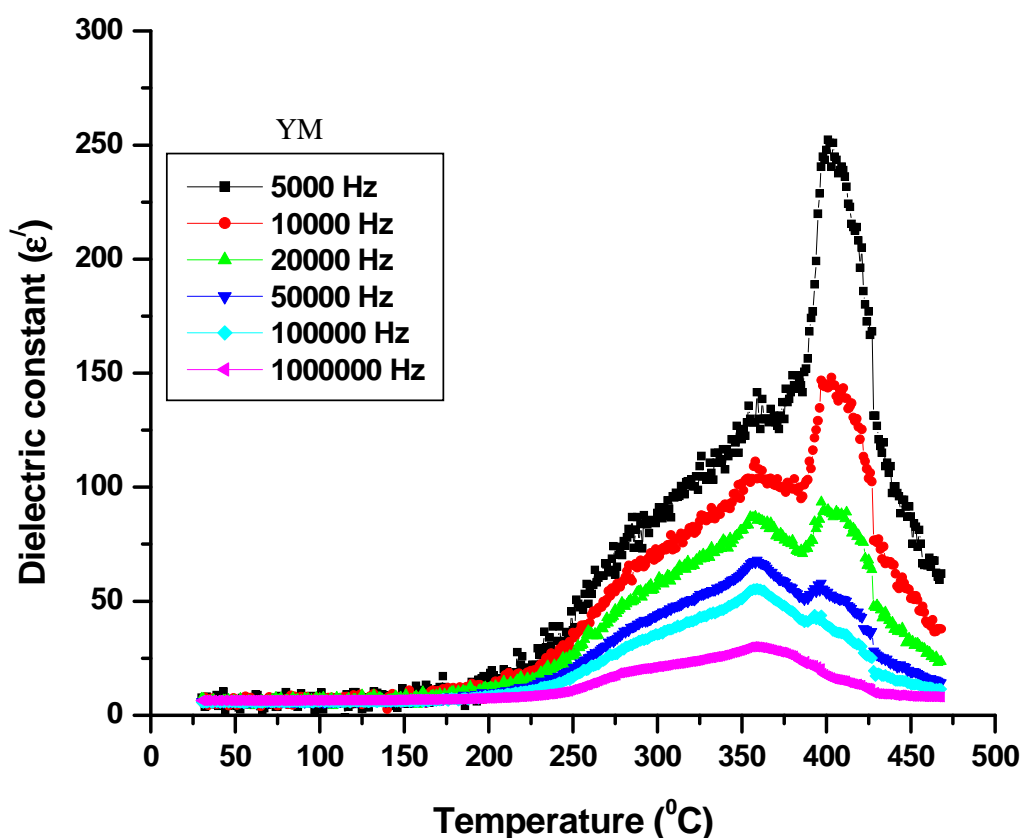


Figure 7 Variation of dielectric constant at different temperatures with respect to different frequency ranges

Table 4 Peak values of dielectric constant for different frequencies

Frequency	Dielectric Constant ( $\epsilon'$ ) value for first transition 358 °C	Dielectric Constant ( $\epsilon'$ ) value for second transition 394 °C
5 KHz	131	247
10 KHz	107	147
20KHz	89	89
50 KHz	69	58
100 KHz	57	46
1 MHz	32	--

## CONCLUSION

Based on the experiment and results, following broad conclusions can be withdrawn:

- Synthesis of yttrium heptamolybdate crystals were accomplished by single gel single tube technique.
- Optimum conditions for the growth of yttrium heptamolybdate crystal have been established by varying different parameters viz., temperature of surroundings, gel pH, gel ageing, concentration of gel, and concentration of upper and lower reactant.
- Optical and scanning electron microscopic studies reveal growth of yttrium heptamolybdate exhibiting various types of morphologies most of which include spherulites.
- Crystallinity of yttrium heptamolybdate crystals has been established by X- ray diffraction and lattice parameters obtained are:  $a = 11.215 \text{ \AA}$ ,  $b = 12.011 \text{ \AA}$ ,  $c = 10.447 \text{ \AA}$  and  $\alpha = 90^\circ$ ,  $\beta = 115.363^\circ$ ,  $\gamma = 90^\circ$ , with cell volume  $1271.50 \text{ \AA}^3$ .
- The qualitative and quantitative elemental analysis employing EDAX technique confirms the presence of major elements like yttrium and molybedum with formula suggested to be  $Y_2Mo_7O_{24}$ .
- FTIR results support the presence of water of hydration and other functional groups in YHM crystal.
- Dielectric constant measurements reveal two transitions and suggest that yttrium heptamolybdate could be ferroelectric material.

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