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# Influence of Ruthenium doping on Structural and Morphological Properties of $MoO_3$ Thin Films

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**ABSTRACT**
The present work examines the effect of Ru doping on $MoO_3$ thin films on steel substrate deposited by Sol-gel spin coat method. The annealing temperature was $600^0$C for pure $MoO_3$ and $800^0$C for Ru doped thin films. The doping concentration of Ru was varied from 10 to 50wt%. The influence of Ru doping on structural and morphological properties of $MoO_3$ thin films were studied. The XRD revealed that all films are highly crystalline in nature with monoclinic phase for molybdenum peaks. In the doped XRD pattern some new peaks were observed and are matched with ruthenium orthorhombic phase indicating an incorporation of dopant in pure molybdenum oxide. The same is confirmed with the compositional analysis by EDAX. The SEM images of the $MoO_3$ resemble a rod like surface with porous morphology. Incorporation of Ru ions in molybdenum oxide decreases the length of the rods and vanishes after 40wt%. Tetragonal grain size increases from 20wt% of Ru and becomes maximum at 50wt% of Ru doped thin films

**Key Words:** XRD, SEM, EDAX, Sol-gel Spin Coating

## I. INTRODUCTION

For the last several years, molybdenum oxide has attracted attentions because of their potential applications in gas sensing devices, optically switchable coatingsand catalysis etc[1-6]. It also exhibits electrochromism, photochromism after intercalating with an appropriate cation (such as Li+, Na+) making suitable for use in display devices,smart windows and electrochemical storage. Such a wide range applications is due to the non-stoichiometric nature of molybdenum oxide. The dependence of electrical property on oxygen concentration is such that $MoO_3$is optically transparent [7-11] and electrically insulating in nature.

In order to deposit $MoO_3$thin film, number of methods have been adopted, such as electro-deposition[12], thermal evaporation[13] pulsed laser deposition, hot wire chemical vapour deposition,magnetron sputtering method, Sol-gel and Spray Pyrolysis etc[14-19]. In the present work, we reported our investigations on structural and morphological properties of molybdenum oxide $MoO_3$and Ru doped $MoO_3$thin films deposited by Sol-gel spin coat method.

## II. EXPERIMENTAL

### 2.1 Synthesis

$MoO_3$solution was prepared by dissolving Ammonium Molybdate Tetrahydrate with appropriate proportionin double distilled water. Once the solution became transparent, then drops of isopropyl alcohol were added as a solvent and the mixed solution was stirred on magnetic stirrer at $50^0$C for 4 hours and aged for 24 hours to yield a clear and viscous solution which was ready for sol gel spin coat deposition. The doped solution was prepared by adding to the precedent solution Ruthenium Trichloride as a dopant source. The weight percentages of Ru were 10%, 20%, 30%, 40% and 50%.The solution became clear and homogeneous after stirring for 4 hours at $50^0$ to $70^0$C on magnetic stirrer and aged for 24 hours to obtain viscous solution.

### 1.2 Deposition

Before deposition, the steel substrates were polished with zero grade polish paper and washed with double distilled water in an ultrasonic bath for 15 minute. To deposit the film by spin coat method, few drops of gel are placed on the steel substrate, which is then rotated at high speed (3000rpm) in order to spread the fluid by centrifugal force. The film thickness can be adjusted by varying the rotation speed, the rotation time, and the viscosity of the gel. After deposition, films were annealed under furnace. The annealing temperature for pure molybdenum film was $600^0$C and Ru doped molybdenum films was $800^0$C.

## III. RESULTS AND DISCUSSION

### 3.1 Structural Analysis by XRD

The structural analysis was performed by using Bruker D8 Advanced instrument with source CuKα1 with $\lambda$ =1.5406A$^0$. The 2θ angle is varied from $20^0$ to $90^0$. Figure 1(a), (b), (c), (d), (e) and (f) shows the XRD patterns of the undoped and Ru doped $MoO_3$thin filmswhich were deposited on the steel substrates. All samples exhibited crystalline nature.

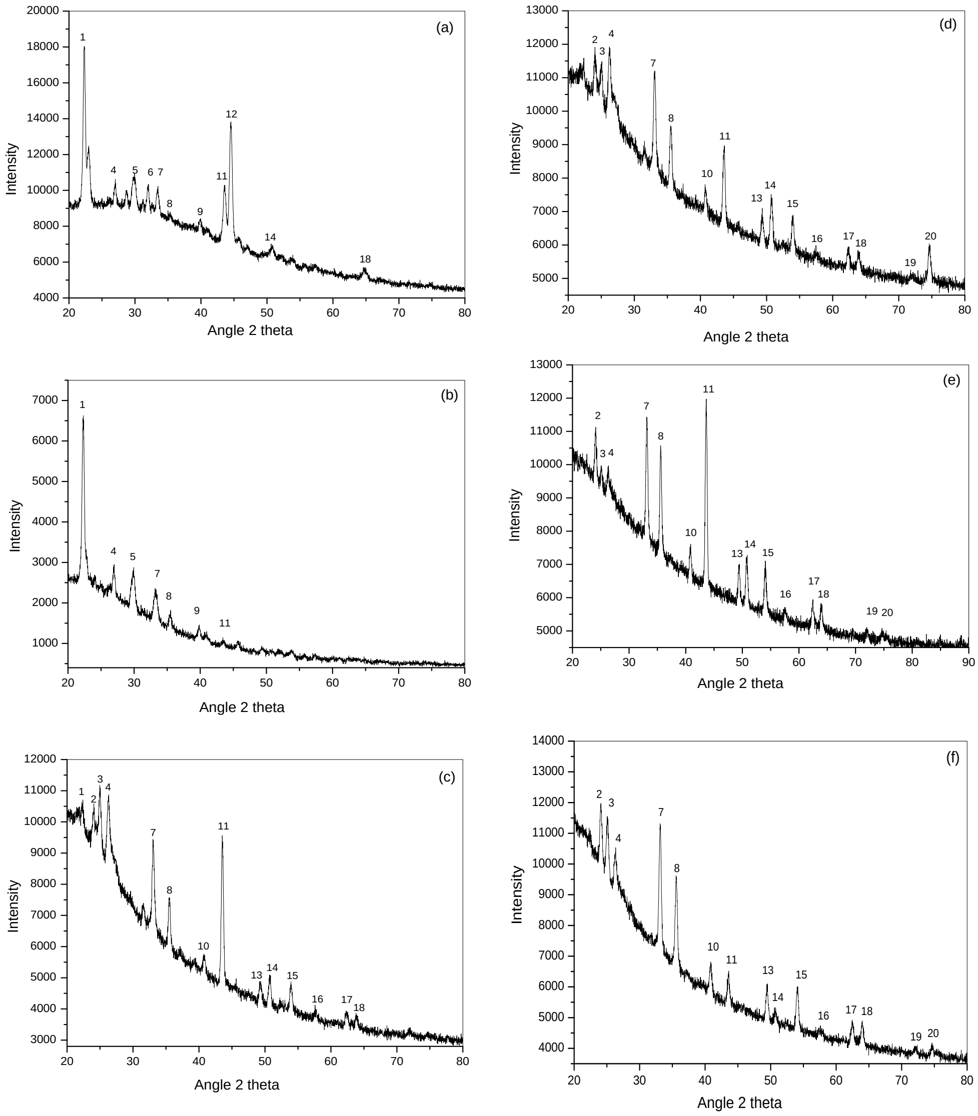


**Fig. 1** XRD patterns of Ru doped $MoO_3$ films (a) 0 % (b), 10%, (c) 20%, (d) 30%, (e) 40%, (f) 50%

The XRD patterns showed peaks for the planes [002], [311], [020], [111], [220] and [011] were matched with $MoO_3$ phase of molybdenum oxide with monoclinic structure. The peaks for plane [002] and [311] were observed in only pure molybdenum sample. Remaining peaks for the plane [111] and [020] were observed in all the samples whereas, the dominating peak with plane [011] was disappeared after 20wt% Ru doping. Some peaks with plane [011], [211], [220], [031] and [202] were also observed in the XRD patterns of doped thin films which were matched with $RuO_2$ phase with orthorhombicstructure.

| Peak | Ru doped $MoO_3$ (Doping Concentration) | | | | | | | | | | | | $MoO_3$ (JCPDS-89-1554) | | | $RuO_2$ (JCPDS-88-0323) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0% | 10% | 20% | 30% | 40% | 50% | 0% | 10% | 20% | 30% | 40% | 50% | | | | | | |
| | d | | | | | | Intensity | | | | | | d | Int | Plane | d | Int | Plane |
| 1 | 3.983 | 3.980 | 3.966 | - | - | - | 100 | 100 | 96 | - | - | - | 3.862 | 999 | [011] | - | - | - |
| 2 | - | - | 3.697 | 3.697 | 3.690 | 3.690 | 0 | - | 95 | 100 | 93 | 100 | - | - | - | - | - | - |
| 3 | - | - | 3.565 | 3.549 | 3.551 | 3.549 | 0 | - | 100 | 96 | 83 | 96 | 3.559 | 501 | [220] | - | - | - |
| 4 | 3.297 | 3.302 | 3.383 | 3.395 | 3.378 | 3.381 | 59 | 44 | 97 | 100 | 83 | 88 | 3.361 | 7 | [111] | - | - | - |
| 5 | 2.984 | 2.982 | - | - | - | - | 61 | 43 | - | - | - | - | 2.966 | 1 | [210] | - | - | - |
| 6 | 2.791 | - | - | - | - | - | 57 | - | - | - | - | - | 2.782 | 44 | [002] | - | - | - |
| 7 | 2.709 | 2.698 | 2.709 | 2.707 | 2.703 | 2.701 | 50 | 36 | 84 | 94 | 96 | 94 | 2.683 | 92 | [020] | - | - | - |
| 8 | 2.553 | 2.525 | 2.527 | 2.528 | 2.523 | 2.523 | 49 | 27 | 68 | 80 | 88 | 80 | 2.560 | 11 | [102] | 2.537 | 492 | [011] |
| 9 | 2.254 | 2.260 | - | - | - | - | 47 | 22 | - | - | - | - | 2.277 | 3 | [121] | - | - | - |
| 10 | | 2.208 | 2.208 | 2.248 | 2.206 | 2.207 | 0 | 18 | 52 | 66 | 64 | 57 | - | - | - | 2.208 | 63 | [111] |
| 11 | 2.077 | 2.080 | 2.078 | 2.074 | 2.072 | 2.074 | 57 | 17 | 86 | 75 | 100 | 54 | 2.059 | 1 | [212] | - | - | - |
| 12 | 2.032 | - | - | - | - | - | 77 | - | - | - | - | - | 2.044 | 1 | [311] | - | - | - |
| 13 | - | 1.849 | 1.846 | 1.845 | 1.824 | 1.840 | - | 14 | 44 | 60 | 59 | 51 | 1.852 | 15 | [122] | - | - | - |
| 14 | 1.801 | - | 1.800 | 1.799 | 1.794 | 1.800 | 39 | - | 46 | 63 | 61 | 45 | 1.837 | 2 | [302] | - | - | - |
| 15 | - | 1.703 | 1.698 | 1.696 | 1.695 | 1.694 | - | 13 | 44 | 58 | 59 | 50 | - | 41 | - | 1.68 | 272 | [211] |
| 16 | - | 1.605 | 1.599 | 1.602 | 1.601 | 1.599 | - | 11 | 37 | 50 | 48 | 40 | - | 32 | - | 1.576 | 123 | [220] |
| 17 | - | - | 1.489 | 1.486 | 1.486 | 1.486 | - | - | 35 | 50 | 50 | 41 | 1.483 | 24 | [420] | - | - | - |
| 18 | 1.436 | - | 1.458 | 1.456 | 1.455 | 1.454 | 32 | - | 35 | 49 | 49 | 41 | 1.433 | 12 | [313] | - | 52 | - |
| 19 | - | - | 1.310 | 1.314 | 1.309 | 1.305 | - | - | 30 | 44 | 43 | 34 | - | 1 | - | 1.333 | 68 | [031] |
| 20 | - | - | - | 1.271 | 1.270 | 1.271 | - | - | - | 51 | 42 | 35 | - | - | - | 1.273 | 29 | [202] |

**Table. 1** Detailed analysis of XRD patterns of pure and Ru doped $MoO_3$thin films

All peaks were matched with JCPDS card No. 89-1554, and 88-0323 for $MoO_3$and $RuO_2$ respectively. The detailed analysis of all XRD peaks and intensity variation for all the peaks is given in table.1. Lattice constants ‘a, ‘b’ and ‘c’ for $MoO_3$and $RuO_2$are calculated from the XRD data. It shows good agreement with the standard values (a=7.122Å, b=5.366Å, c=5.566Å) in JCPDS-89-1554 and (a=4.486Å, b=4.434Å, c=3.093Å) for $MoO_3$and $RuO_2$respectively. The effect of doping concentration on the values of lattice constants is shown in the graphical form in fig. 2 and 3.

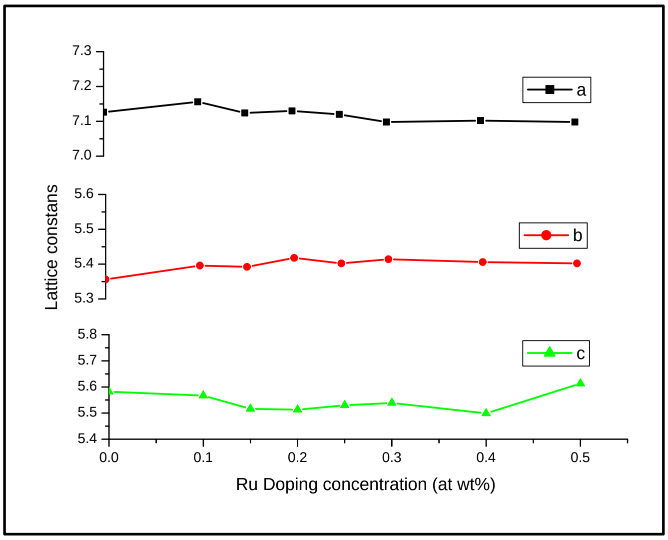


**Fig. 2** Variation in lattice constants of $MoO_3$with doping concentration

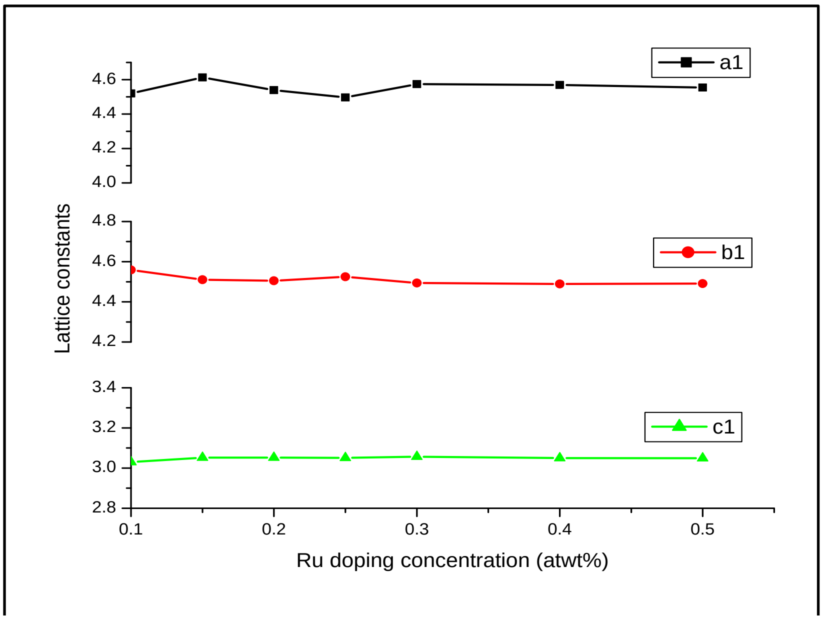


**Fig. 3**Variation in lattice constants of $RuO_2$ with doping concentration

### 3.2 Surface Morphology by SEM

Morphological studies have been carried out using a scanning electron microscope JEOL JSM-6360 instrument. The variation of grain size with doping concentration is calculated from the SEM images and is given in fig.4.

Figure 5(a), (b), (c), (d), (e) and (f) shows the SEM images of the undoped and Ru doped $MoO_3$films. SEM image of pure $MoO_3$resembles a granular surface with tetragonal and rod like structure. Incorporation of Ru modifies the surface morphology. With enhancement in doping concentration porosity of film surface increased and also grains with rod like structure become smaller in size and completely vanished after 30wt% Ru. In 10wt% doped film small clusters were formed and size of these clusters increased upto 30wt% Ru and at 50wt%, surface morphology completely changed to petals like granular structure with maximum grain size.

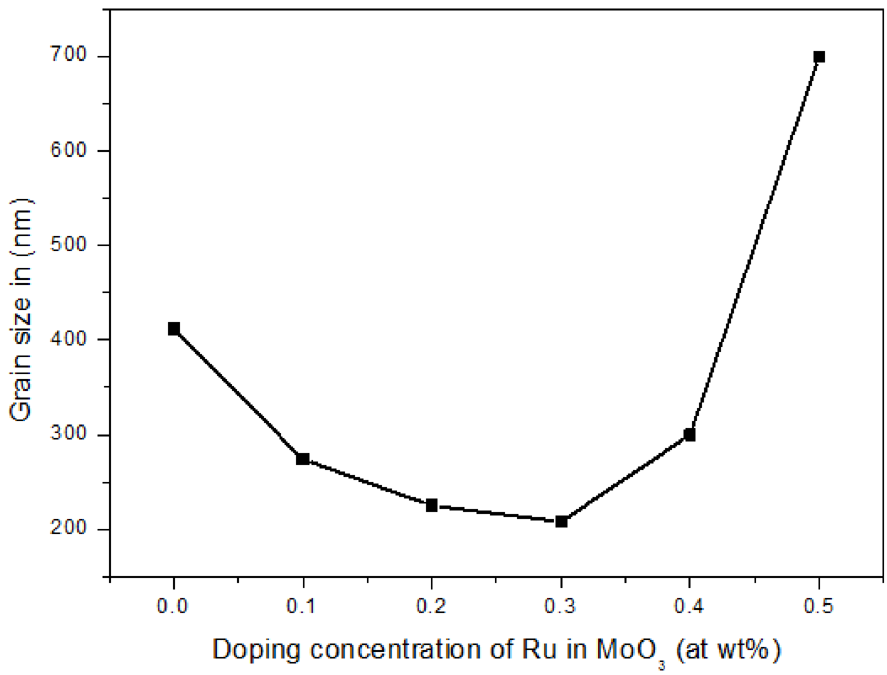


**Fig. 4** Variations in grain size with doping concentration

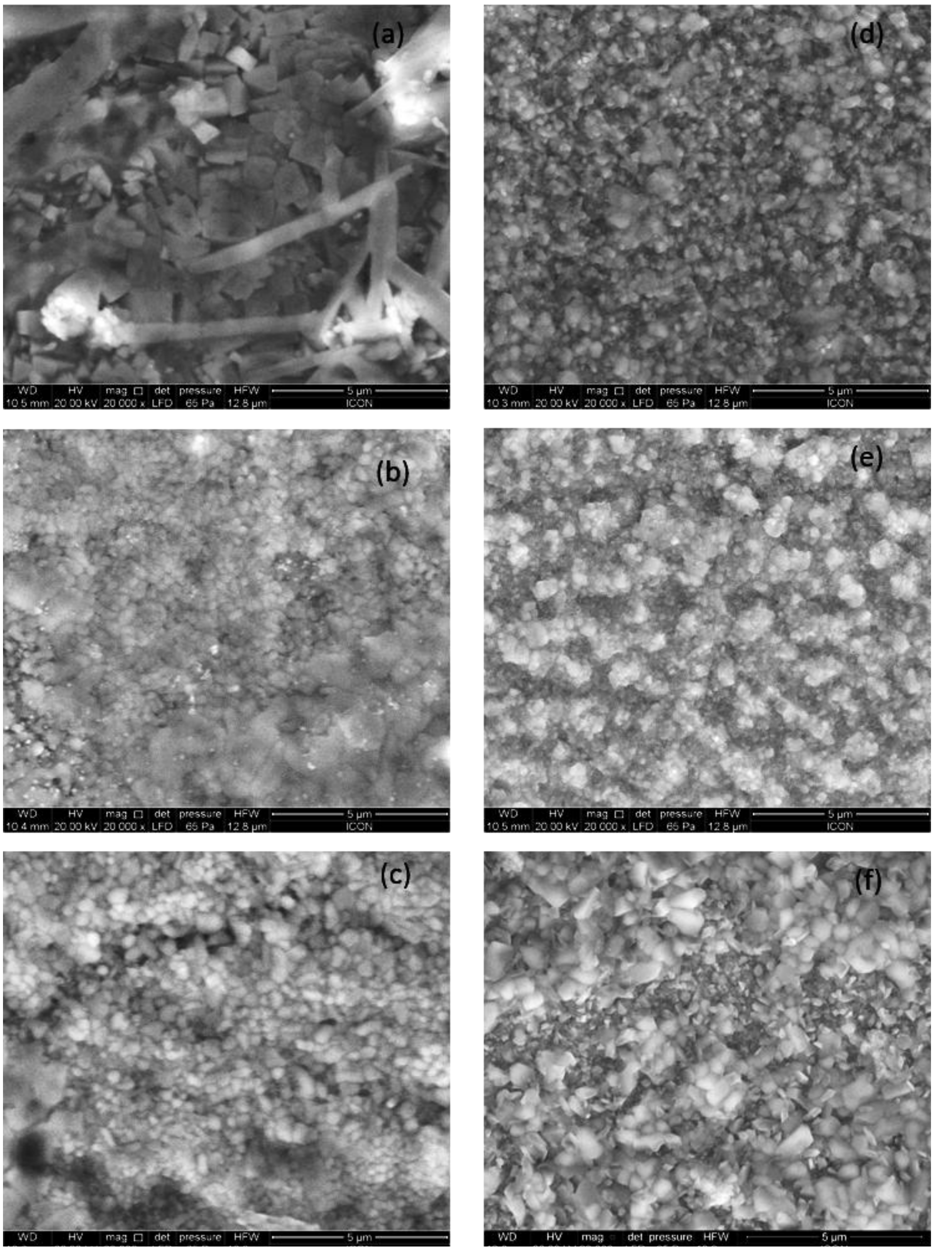


**Fig.5** SEM images of Ru doped MoO3 films(a)0%(b) 10%, (c) 20%, (d) 30%, (e) 40% and (f) 50%

**3.3 Compositional Analysis by EDAX**

EDAX analysis is carried out using Quanta 200 ESEM instrument. The EDAX spectrum of pure and Ru doped $MoO_3$thin film is shown in Figure 6(a), (b), (c), (d), (e) and (f). Table. 2 gives the ratio of Mo:Ru:O elemental composition. EDAX analysis showed that the amount of doped element in the sample increased depending on the increasing doping concentration in the solution. As a result Ru incorporation has a strong effect on structural and morphological properties of $MoO_3$thin films.

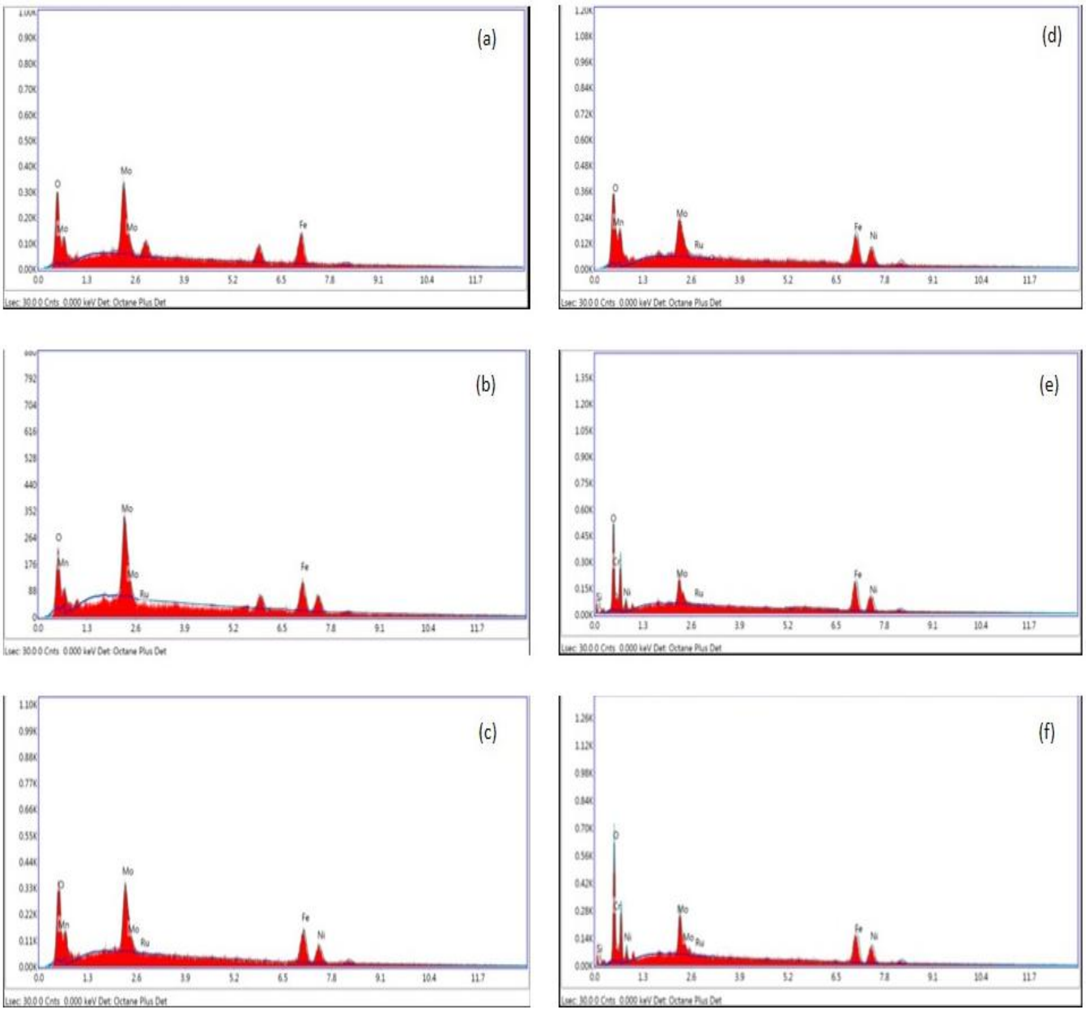


**Fig.6** EDAX patterns of Ru doped MoO3 films (a) 0%, (b)10%,(c)20%,(d) 30%,(e) 40% and (f) 50%

| **Doping Concentration (%)** | **Experimental Result (Weight %)** | | |
|---|---|---|---|
| | **Mo** | **Ru** | **O** |
| 0.00 | 53.38 | 0 | 46.61 |
| 10.00 | 44.34 | 1.05 | 54.60 |
| 20.00 | 41.13 | 1.21 | 57.54 |
| 30.00 | 32.48 | 2.05 | 65.45 |
| 40.00 | 31.82 | 2.42 | 65.74 |
| 50.00 | 31.08 | 2.69 | 66.22 |

**Table. 2** Composition analysis by EDAX

## IV. CONCLUSION

Ru doped $MoO_3$thin films were prepared with different values of Ru content by the sol-gel spin coating method. The diffraction patterns reveal a good crystalline behaviour for all the films with the monoclinic and orthorhombic phase for $MoO_3$ and $RuO_2$ diffraction peaks. SEM micrographs showed that incorporation of dopant changes the surface morphology of films by changing grain structure and grain size. Maximum porosity was observed for 30wt% of Ru. The EDAX analysis of thesamples were done with the Mo/Ruweight ratio and it is confirmed that, Ru is well incorporated in $MoO_3$.As a result Ru incorporation has a strong effect on structural and morphological properties of $MoO_3$thin films.

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