

Immobilization of "Mo⁶⁺" in Monazite Lattice: Synthesis and Characterization of New Phosphomolybdates, $La_{1-x}Ca_xP_{1-y}Mo_yO_4$, Where x = y = 0.1-0.9

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In the process of high-level nuclear waste (HLW) disposal, monazite, LaPO₄ is considered as one of the potential phosphate ceramics to immobilize lanthanides and actinides. HLW along with hazardous long-lived nuclides contains elements such as Zr, Mo, etc. in higher wt%. In the current investigation, an attempt was made to introduce "Mo" into the monazite lattice. The phosphomolybdates of the formula $La_{1-x}Ca_xP_{1-y}Mo_yO_4$, x, y = 0.1-0.9 were synthesized by a solution route and characterized by powder X-ray diffraction, FT-IR, TGA/DTA, and scanning electron microscopic techniques. The phases with compositions La_{0.9}Ca_{0.1}P_{0.9}Mo_{0.1}O₄, La_{0.8}Ca_{0.2}P_{0.8}Mo_{0.2}O₄, and La_{0.7}Ca_{0.3}P_{0.7}Mo_{0.3}O₄ were found to be crystallized in monazite structure. The composition La_{0.1}Ca_{0.9}P_{0.1}Mo_{0.9}O₄ with X = Y = 0.9 crystallized in the scheelite structure. The compositions indicate the immobilization of $\sim 4.1, 8.5, 12.9, and 42.5$ at. wt% of "Mo." With x, y = 0.6, 0.5, 0.4, 0.3, and 0.2, alongwith the monazite phase, formation of a secondary phase LaP₃O₉ was observed.

I. Introduction

IGH-LEVEL nuclear waste (HLW) contains a mixture of ra-H dioactive metal ions of different sizes and charges.¹ Borosilicate glass, iron phosphate glass, glass-ceramics, synroc, and phosphate-based ceramics have been studied as host lattices for the immobilization of such radioactive waste elements.²⁻⁶ For long-term storage, the waste immobilized lattice (wasteform) should possess phase stability and high leach resistance. Generally, phosphate ceramics are considered as highly stable and low-soluble minerals. Phosphate-based ceramics such as apatites,⁷ britholites,⁸ monazites,⁹ sodium zirconium phosphate (NZP),¹⁰ and zirconium phosphates¹¹ are considered as potential single phasic crystalline host lattices for the immobilization of radioactive elements. Based on their structural flexibility, ions of different sizes and charges are accommodated into their crystal lattice. Molybdenum is one of the major waste elements present in HLW and its immobilization in an inert matrix is essential from the nuclear waste disposal point of view.¹² At present, "Mo" and other nuclides are solidified by incorporation in borosilicate glass.¹³ It is suggested that incorporation of "Mo" into monophasic phosphate ceramics may result in low leach rate of molybdenum as compared with other matrices.¹

Molybdenum is a multivalent element; it exists in compounds with +4 or +6 oxidation states. If the wasteforms are fabricated in air, "Mo" will occur in hexavalent form and in an inert atmosphere it could exist in tetravalent form. The high-level radioactive waste composition contains ~13 wt% of MoO₃ in which molybdenum is in "+6" oxidation state.¹⁴ NZP structure compounds containing "Mo⁴⁺" with octahedral coordination are reported. Examples include: NaMo₂(PO₄)₃, AMo₂P₃O₁₂ (A = K, Rb, Ti), and AMo₂(PO₄)₃ (A = Ba, Sr, Ca).^{15–17} Similarly, "Mo⁴⁺" substitution in pyrochlore structure is also studied.¹⁸ Even though these phases can accommodate higher percentage of molybdenum, they are not stable under an ambient condition in air over a period of time.

Petkov *et al.*¹³ reported the incorporation of Mo^{6+} in NZP lattice. Stewart and Vance explored various systems of multiphasic ceramic wasteforms such as NZP–powellite, pyrochlore–sodium titanium phosphate (NTP)–perovskite, and NTP–perovskite–powellite as potential hosts for the incorporation of "Mo⁴⁺" and "Mo⁶⁺."¹⁸ Chourasia *et al.*¹⁹ have studied the structural details of the "Mo⁶⁺"-inserted NZP phase of the formula Na_{0.9}Zr₂Mo_{0.1}P_{2.9}O₁₂.

Monazite (LaPO₄) is a natural orthophosphate considered as one of the most water-resistant minerals. Monazite crystallizes in a monoclinic structure with the space group of $P2_1/n$. A threedimensional network of the structure is formed by interconnected REO₉ polyhedra and PO₄ tetrahedra. The crystal chemistry of monazite structure exhibits considerable flexibility to incorporate ions of different sizes and charges.^{20–22} Studies on the incorporation of lanthanides,²³ actinides,^{24–26} and a combi-nation of trivalent and divalent²⁷ ions have been reported. The phase stability of monazite compound under radiation damage²⁸ is found to be excellent. Terra *et al.*²³ have studied lanthanum– gadolinium monazite, $La_{1-x}Gd_xPO_4$ as wasteform for radioac-tive waste storage. Bregiroux *et al.*²⁴ have studied Pu³⁺ and Am³⁺ containing monazite phases. The incorporation of thorium and uranium in the monazite structure is reported by Mc-Carthy et al.²⁵ Double orthophosphates of tetravalent actinides such as Ce, Th, U, Np, and Pu crystallizing in monazite structure have been investigated by Kitaev et al.26 Monazite-based wasteforms are found to be highly leach resistant even at elevated temperatures. Nevertheless, studies on molybdenum (Mo⁶⁺) containing monazite wasteform have not been reported. Hence, in the current study the feasibility of substitution of P⁵⁺ by Mo⁶ in the monazite lattice is explored. The effect of an increase in "Mo" content on the monazite phase formation is investigated.

II. Experimental Procedure

(1) Materials

La₂O₃ (99.9%, SRL Pvt. Ltd., Mumbai, India), CaCO₃ (99+%, Sigma Aldrich, St. Louis, MO), SrCO₃ (99+%, Sigma Aldrich), NH₄H₂PO₄ (99%, S. D. Fine chemicals, Mumbai, India), and (NH₄)₆Mo₇·4H₂O (98.5%, Titan Biotech Ltd., Delhi, India).

(2) Synthesis

The compounds based on the general formula $La_{1-x}Ca_xP_{1-y}$ Mo_yO₄, where x = y = 0.0-1.0 were synthesized. Lanthanum oxide was preheated at 1000°C for 12 h before use. Stoichiometric amounts of lanthanum oxide and calcium carbonate were dissolved in 1:1 nitric acid separately (solution I and solution II, respectively). Similarly, stoichiometric amounts of ammonium molybdate and ammonium dihydrogen phosphate were dis-

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solved in distilled water separately (solution III and solution IV, respectively). The solutions were mixed in the following order under constant stirring. First, solution I was mixed with solution II. To the homogenized mixture, solution III was added. Finally, to the above mixture, solution IV was added drop wise. The mixture was continuously stirred to maintain the homogeneity. The pH of the mixed solution (<1.0) was slightly increased and maintained at 2.5–3.0 using ammonia solution. The precipitate formed was filtered and dried at 150°C for 24 h. The dried precursor was ground well using a mortar and pestle and the powder was heat treated in air at 600°C for 5 h. The cooled product was ground well and heated at 800°C for 24 h. Strontium analogues of the formula La_{1-x}Sr_xP_{1-y}Mo_yO₄ where x, y = 0.0-1.0 were synthesized by a similar procedure.

(3) Characterization

The synthesized products were characterized using powder X-ray diffraction (XRD) method (CuKa, PNAnalytical, Almelo, the Netherlands) at room temperature. The lattice parameters were obtained by LSQ fitting of high-angle reflections. The infrared spectra (FT-IR spectrometer-ThermoNicolate Company Avatar 330, Madison, WI) were recorded using the KBr disk technique. The chemical analysis of selected compositions, viz., La_{0.9}Ca_{0.1}P_{0.9}Mo_{0.1}O₄, La_{0.8}Ca_{0.2}P_{0.8}Mo_{0.2}O₄, La_{0.7}Ca_{0.3} $P_{0.7}Mo_{0.3}O_4$, and $La_{0.1}Ca_{0.9}P_{0.1}Mo_{0.9}O_4$ obtained after the heat treatment at 600°C was performed by electron probe microanalysis (EPMA) using a Jeol 8600M Electron Probe Microanalyzer (JEOL Surface Analysis Instruments, Tokyo, Japan). The powder samples were pressed into pellets and the pellets were analyzed with a beam of 10 µm. For each sample, four points were analyzed. Thermogravimetric analysis was performed in air using TA Instruments Model SDT Q600 (TA Instruments, New Castle, DE) in the temperature range of RT-1200°C. The heating rate was 20°C/min. Scanning electron microscopic (SEM) analysis of the selected samples was carried out using a Cambridge S360 SEM (Class One Equipment, Decatur, GA).

III. Results and Discussion

(1) Phase Formation, Structural Analysis, and Thermal Stability

(A) Powder XRD : In order to understand the extent of accommodation of "Mo⁶⁺" into the tetrahedral site of monazite lattice, compositions of the general formula $La_{1-x}Ca_x$ $P_{1-y}Mo_yO_4$, where x = y = 0.1-0.9 have been synthesized. Because of the replacement of trivalent "La" by divalent "Ca" for charge compensation, it is expected that with lower "Mo" content the composition may prefer to crystallize in monazite structure while the higher "Mo" concentration may lead to the crystallization in scheelite structure. The radii of the ions under consideration in schedules in define and the radio of the ball of the radio of the and the pure phase formation were studied by characterizing all the products of the composition $La_{1-x}Ca_xP_{1-y}Mo_yO_4$ obtained by heating the precursor at 600°-800°C. Powder XRD of the products obtained by heating the precursors at 600°C designates the effect of the concentration of "Mo" in the formation of single-phase "Mo"-incorporated monazite. The details of the crystallization of the compositions into monazite and scheelite structure are given in Table I. However, heating the precursors of the compositions at 800°C yields the monazite phase, LaPO₄ as the major product. This could probably be due to the loss of molybdenum that occurs on heating the precursors above 600°C. A similar observation has been reported by Petkov and Sukhanov¹² in their study on the immobilization of molybdenum into NZP ceramics.

The powder XRD patterns of the nine compositions prepared at 600° C are compiled in Figs. 1 and 2. The patterns of the end products LaPO₄ and CaMoO₄ are provided for comparison.

Table I. Crystallization of $La_{1-x}Ca_xP_{1-y}Mo_yO_4$ Compositions, Where x = y = 0-1.0

$La_{1-x}Ca_xP_{1-y}Mo_yO_4$	At.% of Mo	Crystallization of the phase after 600°C calcination
x = 0	0	Monazite
x = 0.1	4.06	Monazite
x = 0.2	8.45	Monazite
x = 0.3	12.87	Monazite
x = 0.4	17.42	Monazite+LaP ₃ O ₉
x = 0.5	22.11	Monazite+LaP ₃ O ₉
x = 0.6	26.95	Monazite+LaP ₃ O ₉
x = 0.7	31.95	Monazite+LaP ₃ O ₉
x = 0.8	37.12	Monazite+LaP ₃ O ₉
x = 0.9	42.45	Scheelite
x = 1	47.97	Scheelite

The sharpness of the peaks increases with the increasing "Mo" content. Analysis of the XRD data indicates that the compositions La_{0.9}Ca_{0.1}P_{0.9}Mo_{0.1}O₄, La_{0.8}Ca_{0.2}P_{0.8}Mo_{0.2}O₄, and La_{0.7} Ca_{0.3}P_{0.7}Mo_{0.3}O₄ crystallize in monoclinic structure and are isostructural with monazite. The diffraction patterns are indexed based on the reported data of LaPO₄ [JCPDS file 32-0493]. With a further increase in "Mo" content (y), formation of monazite phase along with a secondary phase LaP₃O₉ is observed in the powder XRD patterns of the compositions La_{0.6}Ca_{0.4}P_{0.6} $Mo_{0.4}O_4$, $La_{0.5}Ca_{0.5}P_{0.5}Mo_{0.5}O_4$, $La_{0.4}Ca_{0.6}P_{0.4}Mo_{0.6}O_4$, $La_{0.3}$ Ca_{0.7}P_{0.3}Mo_{0.7}O₄, and La_{0.2}Ca_{0.8}P_{0.2}Mo_{0.8}O₄. Such an observation of the formation of LaP₃O₉ is reported by Damien et al.³ Powder XRD analysis shows the composition $La_{0,1}Ca_{0,9}P_{0,1}$ $Mo_{0.9}O_4$ crystallizes in the scheelite structure. The pattern is indexed based on the reported data of CaMoO₄ (JCPDS file 85-1267). Thus, it is concluded that up to a maximum of 12.9 at. wt% of "Mo" could be accommodated in its +6 oxidation state in the monazite lattice without any structural changes. In the case of the scheelite phase of the composition $La_{0,1}Ca_{0,9}P_{0,1}$



Fig. 1. Powder X-ray diffraction patterns of $La_{1-x}Ca_xP_{1-y}Mo_yO_4$, where x = y = 0, 0.1, 0.2, 0.3, and 0.5.



Fig. 2. Powder X-ray diffraction patterns of $La_{1-x}Ca_xP_{1-y}Mo_yO_4$, where x = y = 0.6, 0.7, 0.8, 0.9, and 1.0.

 $Mo_{0.9}O_4$, the molybdenum content is 42.4 at. wt% and lanthanum content is 6.8 at. wt%.

The results of the chemical analysis of the compositions $La_{0.9}Ca_{0.1}P_{0.9}Mo_{0.1}O_4$, $La_{0.8}Ca_{0.2}P_{0.8}Mo_{0.2}O_4$, $La_{0.7}Ca_{0.3}P_{0.7}Mo_{0.3}O_4$, and $La_{0.1}Ca_{0.9}P_{0.1}Mo_{0.9}O_4$ by "EMPA" in terms of the wt% of oxides are given in Table II. The relatively low standard deviations show that the samples are homogeneous. The experimentally determined values of at. wt% of the elements are found to be in good agreement with the calculated values of the nominal compositions.

The powder XRD patterns of the phases crystallizing in the monazite structure display broader peaks. The appearance of very sharp peaks is observed in the case the composition crystallizes in scheelite structure. It is also observed that the peaks representing the formation of the secondary phase LaP₃O₉ are sharper. This observation implies that most probably the substitution of Mo⁶⁺ for P⁵⁺ in monazite structure distorts the lattice while retaining the structure up to x, y = 0.1-0.3. At the same time, an increase in "Mo" content leads to monazite phase formation to a limited level and ejects LaP₃O₉ as a secondary phase. This could be due to the incompatibility in accommodating the increased concentration of "Mo⁶⁺" ion. Whereas, the high cry-

stallinity of the scheelite structured phase $La_{0.1}Ca_{0.9}P_{0.1}Mo_{0.9}O_4$ indicates an ordered arrangement of the ions in the lattice.

The lattice parameters of the monoclinic unit cells of the compositions La_{0.8}Ca_{0.2}P_{0.8}Mo_{0.2}O₄ and La_{0.7}Ca_{0.3}P_{0.7}Mo_{0.3}O₄ have been evaluated. Similarly, the dimensions of the tetragonal unit cell of $La_{0.1}Ca_{0.9}P_{0.1}Mo_{0.9}O_4$ have been calculated. The lattice parameters are given in Table III. The values of the parent phases LaPO₄ and CaMoO₄ are given for comparison. With "Mo" substitution at "P" site and "Ca" substitution at "La" site, an increase in "a" lattice parameter and a decrease in "b" and "c" parameters are observed. An increase in " β " value is observed in both the compositions. Such changes in the unit cell dimensions could be correlated to the size of the ions occupying the "La" site and "P" site in the monazite structure. Substitution of P^{5+} (r = 0.17Å) by Mo⁶⁺ (0.41 Å) in LaPO₄ enlarges the size of a fraction of interconnecting tetrahedra made of MoO_4 . The substitution of La^{3+} $(r_c = 1.21 \text{ Å})$ by Ca²⁺ $(r_c = 1.18 \text{ Å})$ replaces a fraction of LaO₉ polyhedra by slightly smaller CaO₉ polyhedra. Thus, the combined effect of the substitution of "La³⁺" by slightly smaller "Ca²⁺" and "P⁵⁺" by larger "Mo⁶⁺" results in the corresponding change in the unit cell parameters and unit cell volume. An overall increase in the unit cell volume has been observed. Comparison of the lattice parameters of La_{0.1}Ca_{0.9}P_{0.1}Mo_{0.9}O₄ with that of the parent phase CaMoO₄ indicates the feeble influence of the introduction of "La" and "P" (x = 0.1) on the scheelite lattice. The change in "a" lattice parameter is found to be negligible. A slight increase in the "c" lattice parameter is observed. However, the crystal chemical substitution of "Mo⁶⁺" by "P⁵⁺" is confirmed by FT-IR spectroscopy and elemental analysis (Table II).

In order to study the effect of replacement of "Ca²⁺" by bigger "Sr²⁺," compositions of the general formula La_{1-x}Sr_xP_{1-y}Mo_yO₄ have been synthesized under similar experimental conditions. Structural analysis by powder XRD indicates that only the composition of the formula La_{0.9}Sr_{0.1}P_{0.9}Mo_{0.1}O₄ crystallizes in the pure monazite structure. From x = y = 0.2 onward appearance of LaP₃O₉ along with the monazite phase has been observed up to x = y = 0.4. With a further increase in "Sr²⁺" and "Mo⁶⁺" content, LaP₃O₉ is found to be the major phase. Compared with its calcium analogue crystallization in scheelite structure is not observed in the case of the composition La_{0.1}Sr_{0.9}P_{0.1}Mo_{0.9}O₄. Powder XRD patterns of selected compositions of the formula La_{1-x}Sr_xP_{1-y}Mo_yO₄ are shown in Fig. 3

(B) Infrared Spectroscopic Analysis: The replacement of "PO₄" moiety by "MoO₄" tetrahedron in monazite structure is also confirmed by the presence of their characteristic IR bands associated with stretching and bending vibrational modes. The infrared spectra of the selected compositions based on XRD such as $La_{0.9}Ca_{0.1}P_{0.9}Mo_{0.1}O_4$, $La_{0.8}Ca_{0.2}P_{0.8}Mo_{0.2}O_4$ $La_{0.7}$ Ca_{0.3}P_{0.7}Mo_{0.3}O₄, and La_{0.1}Ca_{0.9}P_{0.1}Mo_{0.9}O₄ are compiled in Fig. 4. The IR spectra of pure $LaPO_4$ and $CaMoO_4$ are also given for comparison. The transition of the structure of the composition from monazite to scheelite with the increasing content of "Mo" is visible. The characteristic bands appearing in the spectra of these compositions confirm the simultaneous presence of the phosphate and molybdate tetrahedral groups. It is noted that the bands appear at ~ 615 , 578, 562, and 540 cm⁻¹ in the v₄ region, and the v₃ bands found in the range of 990–1100 cm⁻¹ are attributed to the asymmetric bending and

Table II. Electron Microprobe Analysis (wt%, oxides) Results of the Selected Compositions

Composition	Wt. % of oxides						
	La ₂ O ₃	CaO	SrO	P_2O_5	MoO	Total	
$La_{0.9}Ca_{0.1}P_{0.9}Mo_{0.1}O_4$	85.16 (1.04)	0.98 (0.20)		8.64 (0.54)	5.23 (0.76)	100.01	
$La_{0.8}Ca_{0.2}P_{0.8}Mo_{0.2}O_{4}$	81.85 (0.44)	1.72 (0.04)	_	7.99 (0.84)	9.22 (0.67)	100.78	
$La_{0.7}Ca_{0.3}P_{0.7}Mo_{0.3}O_{4}$	76.21 (1.24)	3.00 (0.42)	_	7.33 (0.82)	13.81 (1.27)	100.35	
$La_{0,1}Ca_{0,9}P_{0,1}Mo_{0,9}O_{4}$	19.70 (1.92)	16.93 (1.78)		1.85 (0.66)	64.20 (1.71)	102.68	
$La_{0.9}Sr_{0.1}P_{0.9}Mo_{0.1}O_4$	83.32 (0.47)		3.95 (0.51)	8.49 (0.76)	4.81 (0.47)	100.57	

The number in the parentheses is the standard deviation compositions.

Table III. Lattice Parameter Variation of La_{1-x}Ca_xP_{1-y}Mo_yO₄

$La_{1-x}Ca_xP_{1-y}Mo_yO_4$	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (deg.)	Cell volume (Å ³)
LaPO ₄ (present work)	6.83 (2)	7.074 (5)	6.50 (2)	103.3 (7)	306.30
$La_{0.8}Ca_{0.2}P_{0.8}Mo_{0.2}O_{4}$	6.92 (1)	7.047 (2)	6.50 (1)	103.7 (3)	308.10
$La_{0.7}Ca_{0.3}P_{0.7}Mo_{0.3}O_4$	7.12 (2)	7.026 (3)	6.49 (1)	104.0 (1)	314.60
$La_{0,1}Ca_{0,9}P_{0,1}Mo_{0,9}O_4$	5.217 (2)		11.434 (4)	_ `	311.20
CaMoO ₄ (present work)	5.214 (2)		11.425 (4)		310.60

stretching vibrational modes of PO₄ group of monazite, respectively.³¹ The symmetric stretching vibrational mode of the P–O bond appears at around 950 cm⁻¹. The amplitude of P–O vibrational modes decreases with the increasing molybdenum content. In the spectra of these selected phases, the bands appearing in the region of ~800–892 cm⁻¹ are ascribed to the asymmetric stretching vibrational modes of "MoO₄" tetrahedral.^{13,32} The IR spectrum of the phase La_{0.1}Ca_{0.9}P_{0.1}Mo_{0.9}O₄ resembles that of scheelite (CaMoO₄).

Thus, the structural and spectroscopic data suggest that the integrity of the monazite structure is retained in the range of x, y = 0.1-0.3. The monazite lattice allows the substitution of "P⁵⁺" by "Mo⁶⁺" up to the maximum of 12.9 at. wt% of "Mo"(Table I).

(C) Thermal Analysis: The thermal stability of the phases $La_{0.9}Ca_{0.1}P_{0.9}Mo_{0.1}O_4$, $La_{0.8}Ca_{0.2}P_{0.8}Mo_{0.2}O_4$, $La_{0.7}Ca_{0.3}P_{0.7}Mo_{0.3}O_4$, and $La_{0.1}Ca_{0.9}P_{0.1}Mo_{0.9}O_4$ has been studied in the temperature range of RT-1200°C in air. The compositions with higher "Mo" content show lesser thermal stability than the compositions with lower "Mo" content. The phase $La_{0.7}Ca_{0.3}P_{0.7}Mo_{0.3}O_4$ crystallizing in monazite structure shows ~9% mass loss in the temperature range of 740°-930°C. This may be attributed to the loss of molybdenum occurring above 700°C. This observation corroborates the formation of LaPO₄ as the major product on heating the precursor at 800°C for 24 h as evidenced from the powder XRD analysis. Similarly, the composition $La_{0.1}Ca_{0.9}P_{0.1}Mo_{0.9}O_4$ crystallizing in the scheelite structure registers ~15% mass loss in the temperature range of



Fig. 3. Powder X-ray diffraction patterns of selected compositions of the formula $La_{1-x}Sr_xP_{1-v}Mo_vO_4$.

700°–900°C. No such striking mass loss is noticed in the case of the phases with "Mo" content of y = 0.1 and 0.2. The phases of the compositions La_{0.7}Ca_{0.3}P_{0.7}Mo_{0.3}O₄ (12.8 at. wt% Mo) and La_{0.1}Ca_{0.9}P_{0.1}Mo_{0.9}O₄ (42.4 at. wt% Mo) are thermally stable up to the maximum temperature range of 700°–750°C. However, annealing the compounds at 1200°C leads to the formation of LaPO₄ as the major phase in the case of La_{0.9} Ca_{0.1}P_{0.9}Mo_{0.1}O₄, La_{0.8}Ca_{0.2}P_{0.8}Mo_{0.2}O₄, and La_{0.7}Ca_{0.3}P_{0.7} Mo_{0.3}O₄. Whereas, powder XRD analysis of the residue obtained by annealing the phase La_{0.1}Ca_{0.9}P_{0.1}Mo_{0.9}O₄ shows LaPO₄ as a minor phase with trace amount of CaMoO₄ and possibly the formation of Mo₉O₂₆ as a major phase.

(5) Morphological Changes

(A) SEM Studies: The morphology and the elemental distribution of the four phases have been studied by SEM. The micrographs with x and y contents equal to 0.9, 0.3, 0.2, and 0.1 are shown in Fig. 5. The change in the particle morphology with the increasing "Mo" content is visible. With lesser "Mo" content where x, y = 0.1 and 0.2, no defined particle shape is



Fig. 4. FT-IR spectra of (a) $LaPO_4$, (b) $La_{0.9}Ca_{0.1}P_{0.9}Mo_{0.1}O_4$, (c) $La_{0.8}Ca_{0.2}P_{0.8}Mo_{0.2}O_4$, (d) $La_{0.7}Ca_{0.3}P_{0.7}Mo_{0.3}O_4$, (e) $La_{0.1}Ca_{0.9}P_{0.1}$ $Mo_{0.9}O_4$, and (f)CaMoO₄.

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Fig. 5. Scanning electron micrographs of (a) $La_{0.9}Ca_{0.1}P_{0.9}Mo_{0.1}O_4$, (b) $La_{0.8}Ca_{0.2}P_{0.8}Mo_{0.2}O_4$, (c) $La_{0.7}Ca_{0.3}P_{0.7}Mo_{0.3}O_4$, and (d) $La_{0.1}Ca_{0.9}P_{0.1}Mo_{0.9}O_4$.

observed and the particles are agglomerated. With higher "Mo" content, the particles attain a defined shape. In the case of x, y = 0.3, the beginning of a gentle growth of rod-like morphology is demonstrated and the formation of complete rod-like particles is observed for the compound La_{0.1}Ca_{0.9}P_{0.1}Mo_{0.9}O₄. Thus, SEM analysis reveals a gradual change in the morphology of the powder samples. Such changes in the morphology of the powder samples indicate the influence of the replacement of " PO_4 " moiety of monazite lattice by " MoO_4 " tetrahedra and "LaO₉" polyhedra by "CaO₉" polyhedra. With the increasing "Mo" and "Ca" contents, the particles transform from nonuniform shape and attained a uniform rectangular rod shape with x and y = 0.9. It is envisaged that the contribution toward such morphological changes could mainly be due to the replacement of smaller PO₄ tetrahedra by bigger "MoO₄" tetrahedra in comparison with the simultaneous replacement of "La³⁺" by "Ca²⁺." The effect of the latter may be negligible due to the similar size of the two ions.

IV. Conclusions

Fixation of "Mo⁶⁺" into monazite crystal lattice is studied. The hexavalent molybdenum insertion in LaPO₄ lattice is charge compensated by divalent calcium ions. The analysis of the compositions of the general formula $La_{1-x}Ca_xP_{1-y}Mo_yO_4$ where x = y = 0.1–0.9 by powder XRD technique suggests that the integrity of the monazite structure is retained in the range of x and y equal to that of 0.1–0.3. The spectroscopic and microscopic evidences confirm the crystal chemical incorporation of Mo^{6+} in the monazite ceramic matrix. All the compositions are prepared at 600°C. Based on the formation of pure single phase, it is concluded that the maximum of 12.9 wt% of "Mo" could be accommodated in its +6 oxidation state in the monazite lattice (nominal composition La_{0.7}Ca_{0.3}P_{0.7}Mo_{0.3}O₄). Elemental analysis of the sample of this composition by EPMA shows 11.6 wt% of "Mo" with a standard deviation of 1.0%.

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