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Crystal size effect on the photoluminescence of calcium aluminate doped Mn$^{2+}$ nanocrystals

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Research into finding environmentally friendly, efficient and economic viable nanophosphors is still ongoing as the incorporation of radioactive substances into phosphors to improve their short time luminescence poses serious environmental concern. The present paper investigates the effect of particle size on the morphology and photoluminescence of environmentally friendly CaAl$_2$O$_4$: Mn$^{2+}$ nanocrystals. The phosphor was prepared by the high temperature reaction technique. X-ray diffraction analysis revealed monoclinic structure. Average crystal size of the unpassivated nanomaterial (CAU) was found to be higher (41.49 nm) than that of the passivated (CAP) one (34.81 nm). Photoluminescence investigation at 345 nm excitation showed emission wavelengths that match Mn$^{2+}$ emission. Both the emission color and intensity of the nanocrystals were observed to be crystal-size dependent with high luminescence intensity and deep blue emission peaks coming from CAP; while low luminescence intensity, prominent violet peaks and a weak blue emission peak were registered on CAU. Investigation of the samples responds to different excitation wavelengths revealed that both materials received corresponding colour emission and maximum intensity at 465 nm excitation.

Key words: Photoluminescence, morphology, passivation, fluorescence phosphor.

INTRODUCTION

Last two decades have witnessed a rapid advancement in various techniques for the fabrication of nanoparticles (Senapati et al., 2013). The interest in semiconductor nanoparticles is justified by the fact that their fundamental physical and chemical properties can be very different from those of bulk materials. The advantages of nanoparticles over their bulk counterparts include small particle size with large surface area, improved optical, electrical and mechanical properties. According to Kelviv (2013), nanoparticles have the advantage over bulk materials due to their surface plasmon response, enhanced Rayleigh scattering and surface enhanced Raman scattering in metal nanoparticle and their quantum size effect in semiconductors and supermagnetism in magnetic materials. The II-VI nanostructures with their distinct optical and electrical properties due to their two-dimensional confinement and anisotropic shape have become potential candidates for application in electronics, optoelectronics, lasers and environmental control (Sugaderan, 2013; Kenanakis et al., 2007; Mou et

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Nanostructures have been successfully synthesized by various methods like chemical or physical vapor deposition, thermal evaporation, magnetron sputtering, laser ablation, hydrothermal method, spray pyrolysis, catalyst-mediated organization, electrodeposition, homogeneous precipitation, solvothermal synthesis, sonochemical process and sol-gel process (Amita and Srivastava, 2011). Amongst these methods, monocalcium aluminate (CaAl₂O₄) has been successfully prepared by solution combustion method (Vijay et al., 2007; Nguyen et al., 2004; Ali, 2011; Dejene et al., 2010), hydrazine assisted self-combustion (Satapathy and Mishra, 2014), sol-gel and solid state method (Toumas et al., 2012; Jagjeet et al., 2002; Madhukumar et al., 2006; Bo et al., 2005; Rivas et al., 2004). But the use of urea in solid state synthesis has been negligible.

The role of urea (CH₄N₂O) in the development of blue-emitting monocalcium aluminate nanoparticles was to tailor the structural, morphological and luminescence properties of the nanomaterial. Urea finds several roles in the preparation of nanomaterials. For example, urea is used as a flux by many researchers to promote the formation of a good crystalline phase system (Haranath et al., 2010). Exothermic redox reaction occurs between fuel and oxidizers (nitrates) (Toniolo et al., 2005) which generate high temperature in the reaction.

In the present paper, we investigated the morphology, crystal structure and size, and photoluminescence emission behavior of CaAl₂O₄:Mn²⁺ nanocrystals prepared by slurry. Solid state diffusion is the most popular method for the preparation of nanophosphors even at commercial scale (Kartik et al., 2012). The monocalcium aluminate was doped to introduce new properties by changing the mass transport properties (Saied et al., 2012). Fluorescence phosphors like CaAl₂O₄, BaMgAl₁₂O₁₉, SrAl₂B₂O₇ finds application in light emitting devices, plasma display panels, medical lamps and fluorescent lamps (Haranath et al., 2010). Our success in this research is anchored on the reduction of crystallite size of the nanoparticles synthesized by the high temperature reaction using urea as passivating agent; knowing that reduced particle size and hence large surface area, enhances photoluminescence mechanism by providing reinforcement and catalytic effect. (Ali, 2011) asserts that when the diameter of a particle is reduced the band gap is blue-shifted due to the effect of quantum confinement.

**MATERIALS AND METHODS**

The requisite materials used for the successful execution of the research include the following. Calcium carbonate (CaCO₃), aluminum oxide (Al₂O₃), manganese carbonate (MnCO₃), calcium fluoride (CaF₂), ammonium chloride (NH₄Cl), pure urea (CH₄N₂O), distilled water and muffle furnace. All chemicals are of analytical grade and where used without further purification. Chemicals were purchased from Suzhou Yacoo Chemical Reagent Co. Ltd, China. In this present study, the nanomaterial was prepared according to the chemical formula Ca₀.₂Al₂O₄:Mn₀.004. All the precursors were of analytical grade and were used without further purification. In order to study the effect of urea on the nanoparticles, two samples were prepared. Sample CAU was prepared by slurring CaCO₃, Al₂O₃, CaF₂, and MnCO₃ in distilled water for 20 min and left to dry in air. The resulting powder was grounded into fine particles using pestle and mortar. Muffle furnace was used to maintain the crucibles containing the samples at 1300°C for 1 h in order to cause changes in the physical and chemical constitution of the nanomaterials and also to drive off carbon dioxide. Sample CAP was synthesized in a similar way though by slurrying the precursors in a solution of 2.0g urea in order to reduce the crystal size of the nanomaterial. Both samples, CAU and CAP were washed in 0.25l of water using 4.0g ammonium chloride to extract the impurities and left to dry in air.

Characterization of the nanocrystals was carried out using X-ray diffractometer PW3050/60 at the Sheda of Science and Technology Abuja, Nigeria. The nature and form of the material was studied using scanning electron microscope an oxford instrument at the Amadu Bello University Zaria, Nigeria. The photoluminescence property was examined using photoluminescence spectrometer model Perkin-Elmer LS-55 domiciled at National Centre for Nanostructured Materials (CSIR), Pretoria, South Africa.

The chemical reactions leading to the synthesis process are as presented in equations 1 to 3 while the flowchart showing summary of the synthesis is presented in Figure 1.
Crystal structure and size determination

The X-ray diffraction patterns of the synthesized CaAl$_2$O$_4$:$\text{Mn}^{2+}$ nanocrystals is shown in Figures 2a and b. Six prominent peaks were observed in the diffractograms around 2$\theta$ values of 33.63, 30.08, and 18.22° corresponding to (124), (201), (110) for CAU and 30.15, 25.53 and 18.29° corresponding to (220), (111), (110) for CAP (Table 1). All the planes can be indexed to CaAl$_2$O$_4$. Structural identification of the nanomaterials from the XRD revealed monoclinic structure of the Mn$^{2+}$ doped calcium aluminate nanophosphor. The high intensity of the peaks reveals the high crystallinity of the synthesized nanomaterials (Arunachalam, 2012). Average crystal size calculated from three prominent peaks show that the unpassivated sample, CAU, has the largest crystal size of 41.49 nm as a result of low strain and dislocation in the crystals; while the passivated sample, CAP, has 34.81 nm due to high dislocation and strain in the crystals. This is an indication that the presence of urea assists in the dissolution and combustion of the particles leading to increased crystal defect and strain. Urea has been applied in the preparation of nanomaterials using solution combustion synthesis (Qui et al., 2007; Krsmenovic et al., 2007). All these led to a homogeneous system with blended morphology and enhanced luminescence with reduced particle size. This of course is evident in the present paper.

Photoluminescence studies

The ability of the nanoparticles to absorb incident energy and convert it into visible radiation was confirmed by PL investigation. Photoluminescence emission spectrum at 345 nm excitation shows three distinct peaks centered at 406, 454 and 493 nm for CAP with the maximum intensity obtained at 454 nm (Figure 4). Four distinct peaks were

\[ \text{where } \beta \text{ is FWHM (in radian) and } \theta \text{ is diffraction angle (in radians).} \]

The amount of defect in the sample can be estimated from:

\[ \delta = \frac{1}{4\lambda} \]

where D is average particle size and \( \delta \) is dislocation density.
Table 1. The structural data of sample CAP and CAU.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>2θ(°)</th>
<th>FWHM (°)</th>
<th>Interplanar Spacing ‘d' (Å)</th>
<th>Plane (hkl)</th>
<th>Intensity</th>
<th>Average crystal size (nm)</th>
<th>Average dislocation density (lines/m)</th>
<th>Average crystal strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAP</td>
<td>30.15</td>
<td>0.3296</td>
<td>2.964</td>
<td>220</td>
<td>644.0</td>
<td>34.81</td>
<td>9.87 x 10^-4</td>
<td>2.82 x 10^-1</td>
</tr>
<tr>
<td></td>
<td>25.53</td>
<td>0.1978</td>
<td>3.500</td>
<td>111</td>
<td>542.2</td>
<td>2.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>18.29</td>
<td>0.1978</td>
<td>4.869</td>
<td>110</td>
<td>604.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAU</td>
<td>33.57</td>
<td>0.1978</td>
<td>2.673</td>
<td>124</td>
<td>574.5</td>
<td>30.08</td>
<td>8.73 x 10^-4</td>
<td>2.3 x 10^-4</td>
</tr>
<tr>
<td></td>
<td>30.08</td>
<td>0.3296</td>
<td>2.969</td>
<td>201</td>
<td>617.1</td>
<td>18.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>18.22</td>
<td>0.1319</td>
<td>4.884</td>
<td>110</td>
<td>583.7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3. The SEM micrograph analysis of sample (a) CAP (b) CAU nanocrystals.

Figure 4. Photoluminescence emission spectra of the samples at 345 nm excitation.

The peaks are in good agreement with the well-known Mn$^{2+}$ emission transitions (Jubu et al., 2015). The emission wavelengths indicate characteristic blue emission which is typical of Mn$^{2+}$. Similar blue emission wavelengths were also obtained by Lin et al. (2008). The luminescent intensity of the thermal treated products varied appreciably with the presence of urea as CAP has the highest luminescence intensity. The emission intensity of the nanomaterials vary with crystal size such that CAU with high crystal size has a low emission intensity. According to (Dhlamini, 2008) the emission colors of phosphors vary with crystallite size. This is evident on CAU with dominant violet (380-450) nm emission peaks, and a low blue (450-495) nm emission peak due to high particle size of 41.49 nm; and CAP with deep blue emission peaks as a result of reduced particle size of 34.81 nm (Jagjeet et al., 2002) obtained blue-green emission on the phosphor at 254 nm UV excitation. The blue emission originates from the electron-hole recombination of self-trapped exciton (Yit-Tsong, 2002). As can be seen on Figure 5, the samples showed unique responds to different excitation wavelengths. The CAP sample has low responses at 320 and 395 nm. The presence of urea seemingly enhanced the sensitizers of the CAP sample giving them better responses to a wide range of excitation wavelengths as a result of reduced brightness.
The hindered overlap reduces the energy transfer rate between exciton wave functions with the activator (Diane, 2002). The hindered overlap reduces the energy transfer rate from the exciton to the impurities and as a result the non-radiative decay rate is increased and therefore the photoluminescence efficiency is decreased. A sharp responds by sensitizers is also recorded at 465 nm excitation on CAU. The samples respond differently to excitation on CAU. The samples respond differently to different excitation wavelengths as a result of variation in their particle sizes. Equivalent responses are recorded at 330, 395 and 465 nm respectively. The significant effect of particle size on photoluminescence emission intensity of the samples is quenched at the highest excitation wavelength, 465 nm, which gave the sensitizers of both samples a similar highest responds.

**Conclusion**

The manipulation of morphology and particle size by urea, and the effect of crystal size on the photoluminescence of manganese doped calcium aluminate nanocrystalline material was successfully carried out. Study revealed that the presence of urea reduced the average crystallite size of CAU from 41.49 to 34.81 nm for CAP, with the prepared CaAl$_2$O$_4$:Mn$^{2+}$ samples being monoclinic in structure. The SEM micrograph of CAU revealed spherical particles connected by nanorods, while the SEM image of CAP unveiled the foamy nature of the nanocrystals. The emission color and intensity of the nanocrystals were observed to be crystal-size dependent with high luminescence intensity and deep blue emission peaks recorded on CAP; while low luminescence intensity, prominent violet peaks and a weak blue emission peak were registered on CAU. Particle size was observed to have no effect on photoluminescence emission intensity at 465 nm excitation wavelength.

**Conflict of Interest**

The authors have not declared any conflict of interest.

**REFERENCES**


Madhukumar K, Rajendra KB, Ajith PKC, James J, Elias TS,


Hydrothermal synthesis and structural characterization of an organically-templated open-framework trimolybdates

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A new one-dimensional coordination polymer formulated as $[\text{C}_2\text{H}_{10}\text{N}_2][\text{Mo}_3\text{O}_{10}]$, 1, has been synthesized under hydrothermal conditions in the presence of ethylenediamine. The surface morphology of the as-synthesized product reveals colorless rod-like single crystals of 1. The compound crystallizes in monoclinic space group $P2_1/n$ with $a = 8.08$ Å, $b = 14.39$ Å, $c = 8.89$ Å; $\beta = 97.76^\circ$, $V = 1033.65(12)$ Å$^3$, $Z = 4$. The structure is a one-dimensional chain consisting of $[\text{Mo}_3\text{O}_{10}]^{2-}$ clusters of Mo (VI) octahedral interspersed by the amine molecules. In the infrared spectrum of the compound, the symmetric stretching vibrational mode of the $-\text{NH}_2$ group is observed at 3278 cm$^{-1}$, while the band at 1604 cm$^{-1}$ is assigned to scissoring mode of the $-\text{NH}_2$ group. The peaks in the spectral range 1913 - 2492 and 2962 cm$^{-1}$ are attributed to $-\text{CH}_2$ symmetric and asymmetric stretching vibrations respectively. The absorption bands at 1404 cm$^{-1}$ is due to scissoring, while the one at 1149 cm$^{-1}$ is attributable to twisting modes of $-\text{CH}_2$ group. The characteristic band of the stretching vibrational modes of the Mo=O double bonds is observed at 1018 cm$^{-1}$, while the vibrational stretching frequency involving single Mo-O bonds is observed at 846 cm$^{-1}$ and the scissoring mode of this bond is at 542 cm$^{-1}$.

Key words: Hydrothermal synthesis, amine-templated molybdates, molybdenum oxide-organic frameworks, one-dimensional chain.

INTRODUCTION

The great interest in the design of molybdenum(VI) oxide–organic frameworks (MOOFs) is not only due to their applications in such areas as catalysis, magnetism, sorption etc., but also due to its fascinating structural chemistry (Lysenko et al., 2010; Pope and Müller, 2001; Sencchyk et al., 2014). Various synthetic approaches have been used to isolate highly crystalline samples suitable for structural characterization by X-ray diffraction, but the synthesis of organic–inorganic hybrids using hydrothermal conditions has received special attention in the field of coordination solids based on transition-metal oxides, including transition-metal molybdate complexes (Asnani et al., 2012; Hagarman and Zubieta, 1998; Hagarman et al., 1999; Randy et al., 2001; Hagarman and Zubieta, 2000).
Hydrothermal method is a synthesis pathway in which products are produced using thermal (heat) energy and aqueous solvent. The success of this method is derived from the extremely solvating ability owing to reduced viscosity of the water under these conditions. This allows the dissolution and mixing of the solid reagents thereby minimizing differential solubility problem (Davis, 1992; Barrer, 1982; Francis and O’Hare, 1998). It has been demonstrated that the hydrothermal chemistry of polyoxomolybdates involves many interrelated reaction variables, including the pH, the molybdenum source, and the identities of other reaction species, the temperature, and time (Wu et al., 2002; Xu et al., 2000; Zhang et al., 2007; Zhang et al., 2015; Hubbard et al., 2008). Molybdophosphonates as building blocks or subunits in extended structures have been studied (Hubbard et al., 2008; Armatas et al., 2008; Jones et al., 2010; Armatas et al., 2009). A molybdenum diphosphonate network structure exhibiting reversible dehydration and selective uptake of methanol have also been reported and it is the first molybdenum diphosphonates in the absence of co-ligands (Ayi et al., 2013).

**MATERIALS AND METHODS**

The syntheses were carried out in Ace pressure tubes (15 cm³), purchased from Aldrich Chemical Co., and heated in programmable ovens. The reagents used for syntheses were obtained from Aldrich (Hexamamomioum heptamolybdate tetrahydrate (NH₄)₆Mo₇O₂₄·4H₂O; ethylenediamine,) or Epsilon Chime (4-carboxyphenylphosphonic acid) and used without further purification. In a typical synthesis of 1, (NH₄)₆Mo₇O₂₄·4H₂O (0.3088 g, 0.25 mmol) was stirred together with 4-carboxyphenyl phosphonic acid (0.101 g, 0.5 mmol) in 5 cm³ of distilled water. This was followed by the addition of 0.2 cm³ of ethylenediamine and the pH of the solution was adjusted to 3 by dropwise addition of 0.2 cm³ of Conc HCl. The resultant mixture was homogenized for 30 min before transferring into the reaction vessel and heated in an oven at 120°C for 8 h. The product, a crop of colorless crystalline material was washed with distilled water and air-dried.

**Characterization**

The surface structure and morphology of the as-synthesized compound was determined using computer controlled polarized PZP300T-8M electron microscope. The ultraviolet-visible measurements were recorded with the help of Thermo Scientific Evolution 201 UV-vis spectrophotometer. The Infrared spectra were recorded on a Shimadzu IR Affinity-1 from 400 to 4000 cm⁻¹.

**Crystal structure**

"X-ray diffraction data was collected on an Oxford Diffraction Gemini diffractometer fitted with an Atlas CCD detector using Mo-Ka radiation of wavelength 0.71073 Å at 150 K. The crystal structure and refinement parameters are given in Table 1. The structure was solved using SHELXS-97 and refined using full-matrix least squares in SHELXL-97 (Sheldrick, 2008). The final refinements were generally straightforward with all non-hydrogen atoms refined anisotropically in the final least squares run, and hydrogen atoms included at calculated positions."

**RESULTS AND DISCUSSION**

We were interested in isolating Mo (VI) oxide cluster as a building block in the preparation of molybdocarboxyphosphate frameworks. During the investigation of the (NH₄)₆Mo₇O₂₄·4H₂O–HCl Carboxyphenolphosphonic acid–ethylenediamine–H₂O–system, a new inorganic-organic hybrid material, (C₂H₇N₂)(Mo₃O₁₀) constructed from molybdenum (VI) oxide with encapsulated ethylenediammonium ions was isolated. The carboxyphenolphosphonic acid was added into the reactant mixture with the aim of obtaining molybdenum organophosphate frameworks, but was not incorporated into the final product. The ethylenediamine added to the synthetic gel exerts a significant structural role in controlling the architecture of the molybdenum oxide phase formed as well as compensating the metal oxide anionic charge. The addition of the HCl helps in maintaining acidic pH before and after the reaction. It is only in an acidic medium that the amine component gets protonated. A portion of the soluble reactant precursor was taken out for UV-Vis measurement. The UV-Vis spectrum of the reactants in aqueous solution is presented in Figure 1. The spectrum exhibits three absorption bands at 279, 284 and 286 nm. The strong band at 279 and 284 nm are attributable to π- π* transitions. These transitions involves moving electron from a bonding pi-orbital to an antibonding pi-orbital and is said to occur at high energy region of 35,842 to 35,211 cm⁻¹. The broad band at 286 nm corresponds to n – π* transitions, which involves moving an electron from a non-bonding electron pair to an antibonding pi-orbital and is found to occur at lower energy region of 34,364 to 34,965 cm⁻¹.

The surface structure and morphology of the as-synthesized product reveals colorless rod-like crystals (Figure 2). The crystal data and structure refinement parameter for compound 1 is presented in Table 1. The compound crystallizes in monoclinic space group P2₁/m (No. 14) with a = 8.08 Å, b = 14.39 Å, c = 8.89 Å; β = 97.76°. The asymmetric unit (Figure 3) consists of Molybdenum center in octahedral coordination by six oxygen atoms, and protonated amine. The bridging Mo-O bond lengths in the range of 1.592(16) to 1.693(15) Å are shorter compared with the terminal Mo-O bonds (1.994(5) to 2.429(14) Å) and the O(1)-Mo(1)-O(#2) bond angles in the range of 158.10 to 170.397° are in good agreement with similar reported compounds (Hubbard et al., 2008; Ayi et al., 2013). The structure is a one-dimensional chain consisting of (Mo₃O₁₀)²⁺ clusters interspersed by the ethylenediammonium cation (Figure 4), which also serves to compensate the framework negative charge of -2.

Figure 5 gives the infrared spectrum of compound 1. In this spectrum, the two peaks at 3657 and 3780 cm⁻¹..."
Table 1. Crystal data and structure refinement for 1.

<table>
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<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₂H₁₀N₂Mo₃O₁₀</td>
</tr>
<tr>
<td>Formula weight</td>
<td>254.91</td>
</tr>
<tr>
<td>Temperature / K</td>
<td>150(2)</td>
</tr>
<tr>
<td>Wavelength / Å</td>
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<tr>
<td>Unit cell dimensions</td>
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</tr>
<tr>
<td></td>
<td>b = 14.39(3) Å, β = 97.76(4)°</td>
</tr>
<tr>
<td></td>
<td>c = 8.89(4) Å, γ = 90°</td>
</tr>
<tr>
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<tr>
<td>Density (calculated) / g cm⁻³</td>
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<tr>
<td>Crystal size / mm</td>
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<td>Goodness-of-fit on F²</td>
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</tr>
<tr>
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<td>Largest diff. peak and hole / e Å⁻³</td>
<td>0.988 and -1.057</td>
</tr>
</tbody>
</table>

Figure 1. UV-Vis spectrum of the reactant mixture in aqueous solution for the synthesis of 1.

superimposed on the water peak can be attributed to \(-\text{NH}_2\) asymmetric stretching involved in N-H…O hydrogen bond formation. The symmetric stretching vibrational mode of the \(-\text{NH}_2\) group is observed at 3278 cm⁻¹, while
the band at 1604 cm$^{-1}$ is assigned to scissoring mode of the $-$NH$_2$ group. The peaks in the spectral range 1913 - 2492 and 2962 cm$^{-1}$ are attributed to $-$CH$_2$ symmetric and asymmetric stretching vibrations respectively. The absorption bands at 1404 cm$^{-1}$ is due to scissoring, while the one at 1149 cm$^{-1}$ is attributable to twisting modes of $-$CH$_2$ group. The characteristic band of the stretching vibrational modes of the Mo=O double bonds is observed at 1018 cm$^{-1}$ and compares well with similar compounds in the literature (Hubbard et al., 2008). The vibrational stretching frequency involving single Mo-O bonds is observed at 846 cm$^{-1}$ while the scissoring mode of this bond is at 542 cm$^{-1}$. The various assignments are made on the basis of similar work in the literature (Asnani

Figure 2. Optical microscopic image of the as-synthesized compound 1.

Figure 3. The structure of 1 showing the coordination environment of Mo and the encapsulated amine molecule.
et al., 2012; Hagrman and Zubieta, 1998; Hubbard et al., 2008; Sierka et al., 2007).

**Conclusion**

In conclusion, a new one-dimensional coordination polymer formulated as \( \text{C}_2\text{H}_{10}\text{N}_2 \) \( \text{Mo}_3\text{O}_{10} \), has been synthesized under hydrothermal conditions in the presence of ethylenediamine. The surface structure and morphology of the as-synthesized product reveals colorless rod-like crystals. The structure is a one-dimensional chain consisting of \( \text{Mo}_3\text{O}_{10} \)\(^2\) clusters of Mo (VI) octahedral interspersed by the amine molecules. In the IR spectrum, the two peaks at 3657 and 3780 cm\(^{-1}\) superimposed on the water peak can be attributed to \(-\text{NH}_2\) asymmetric stretching involved in N-H...O hydrogen bond formation. The protonated organic amine interacts with the inorganic frameworks through multiple hydrogen bonds of the type N-H...O. Efforts are
under way to use this compound as a building block in designing Mo (VI) oxide-carboxyphosphonate framework materials.

Conflict of Interest

The authors declare that there is no conflict of interest in publishing this article.

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