

Preparation, structural and optical characterization of BaWO₄ and PbWO₄ thin films prepared by a chemical route

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Abstract

Polycrystalline BaWO₄ and PbWO₄ thin films having a tetragonal scheelite structure were prepared at different temperatures. Soluble precursors such as barium carbonate, lead acetate trihydrate and tungstic acid, as starting materials, were mixed in aqueous solution. The thin films were deposited on silicon, platinum-coated silicon and quartz substrates by means of the spinning technique. The surface morphology and crystal structure of the thin films were investigated using scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction, and specular reflectance infrared Fourier transform spectroscopy, respectively. Nucleation stages and surface morphology evolution of thin films on silicon substrates have been studied by atomic force microscopy. XRD characterization of these films showed that BaWO₄ and PbWO₄ phase crystallize at 500 °C from an inorganic amorphous phase. FTIR spectra revealed the complete decomposition of the organic ligands at 500 °C and the appearance of two sharp and intense bands between 1000 and 600 cm⁻¹ assigned to vibrations of the antisymmetric stretches resulting from the high crystallinity of both thin films. The optical properties were also studied. It was found that BaWO₄ and PbWO₄ thin films have E_g = 5.78 eV and 4.20 eV, respectively, of a direct transition nature. The excellent microstructural quality and chemical homogeneity results confirmed that soft solution processing provides an inexpensive and environmentally friendly route for the preparation of BaWO₄ and PbWO₄ thin films.

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1. Introduction

Recently crystal structures based on the scheelite-type structure, such as BaWO₄ and PbWO₄ have attracted much interest because of their approved usage as scintillating medium and use in electro-optical applications (i.e. solid-state laser and in optical fibre applications).^{1–3} On the other hand, numerous investigations on the luminescent properties of these materials, have been carried out.^{4,5} Recently, PbWO₄ has attracted special interest because of plans to use it as a

scintillator in detectors at the Large Hadron Collider in CERN.⁶

A variety of preparation techniques have been proposed to produce these materials, among these are solid-state reaction, hydrothermal synthesis, sputtering and the sol-gel processes.^{7,8} In addition, considering the importance of PbWO₄ and BaWO₄ system, thin films prepared by soft chemical processing are difficult to find in the literature. Cho et al.⁹ showed that the CaWO₄ thin films grown by an electrochemical method, consisted of grains with various sizes with an heterogeneous surface. Hence, in this paper, we shall report some experimental data based on a soft chemical method, the so-called polymeric precursor method,^{10–12} because of the liquid nature of the constituents and the relatively low processing temperatures used.

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2. Experimental procedure

The flow chart of the BaWO_4 and PbWO_4 synthesis used in this study is outlined in Fig. 1. Tungsten citrate was formed by dissolution of tungstic acid (H_2WO_4) in an aqueous solution of citric acid under constant agitation to homogenize the tungsten citrate solution. After homogenization of this solution, BaCO_3 or $\text{Pb}(\text{CH}_3\text{CO}_2)_2$ salt, was also slowly added. The complex was well stirred for several hours at 70–80 °C to produce a clear, homogenous solution. Barium carbonate or lead acetate trihydrate was dissolved in water and a stoichiometric amount added to the tungsten citrate solution. Ammonium hydroxide was used to adjust the pH of the solution (pH 5–6) and to prevent precipitation of barium citrate or lead citrate, which is favored in an acid solution. After the solution containing Ba or Pb was homogenized, ethylene glycol was added to promote the citrate polymerization by the polyesterification reaction. With continued heating at 80–90 °C, the solution became more viscous, though without any visible

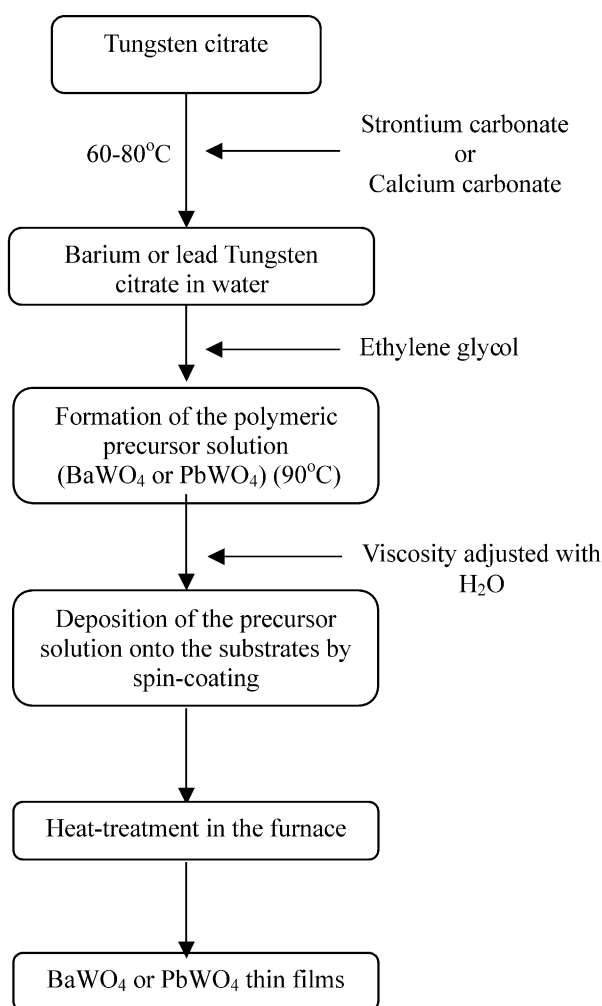


Fig. 1. Flow chart illustrating the procedure for the preparation of the PbWO_4 and BaWO_4 solutions and thin film production.

phase separation. The molar ratio between the cations barium or lead and tungsten was 1:1, the citric acid/ethylene glycol was fixed as 60:40 (mass ratio). The viscosity of the deposition solution was adjusted to 15 mPa/s by controlling the water content. The polymeric precursor solution was spin-coated on substrates by a spinner operating at 7000 rev/min for 40 s using a commercial spinner (spin-coater KW-4B, Chemat Technology). The polymeric precursor solution was deposited onto the substrates via a syringe filter to avoid particulate contamination. The substrates were silicon and quartz. After spinning onto the substrates, the films were kept in ambient air at 150 °C on a hot plate for 20 min to remove residual solvents. After the pre-annealing, the films were annealed between 200 °C and 500 °C for 4 h in air atmosphere.

The film thickness was controlled by adjusting the number of coatings and each layer was pyrolyzed at 200 °C and then crystallized before the next layer was coated. These coating/drying operations were repeated until the desired thickness was obtained.

The PbWO_4 and BaWO_4 thin films were structurally characterized by the X-ray diffraction patterns obtained using a Cu K_α radiation source in order to determine their structure evolution. The lattice parameters of the thin films were measured using the least-square method. The thickness of the coated film was measured by thin film cross-section analysis using scanning electron microscopy (SEM). The optical transmittance of the crystalline thin films was measured in the wavelength range from 200 to 800 nm, using a Cary 5G (Australia) spectrophotometer. Infrared analyses were performed by means of Equinox/55 (Bruker) Fourier Transformed Infrared (FTIR) spectrometer to observe the variation in chemical bond densities. The FTIR reflectance spectra of PbWO_4 and BaWO_4 thin films on Pt/Ti/SiO₂/Si substrates were recorded at room temperature in the frequency range of 400–2100 cm^{-1} equipped with a 30° specular reflectance accessory. FT Raman spectra for BaWO_4 and PbWO_4 powders (as reference) have been recorded by means of a Bruker RFS100 instrument, with an Nd-YAG laser (1064 nm), using 100 mW laser power, 60 scans and 4 cm^{-1} resolution.

Atomic force microscopy (AFM) was used to obtain a 3D image reconstruction of the sample's surface. These images allow for an accurate analysis of the sample's surface and the quantification of highly relevant parameters such as roughness and grain size. A Digital Instruments Multi-Mode Nanoscope IIIa was used.

3. Results and discussion

Figs. 2 and 3 show the X-ray patterns of the PbWO_4 and BaWO_4 thin films deposited onto silicon substrates after calcinations at several temperatures. A diffused

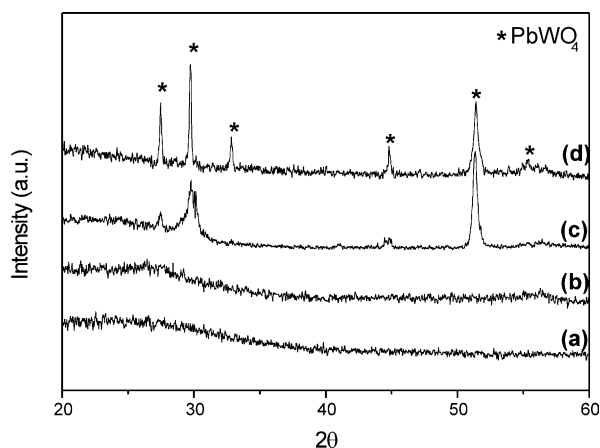


Fig. 2. X-ray diffraction patterns of PbWO₄ thin films heat-treated at different temperatures: (a) 200 °C, (b) 300 °C, (c) 400 °C and (d) 500 °C.

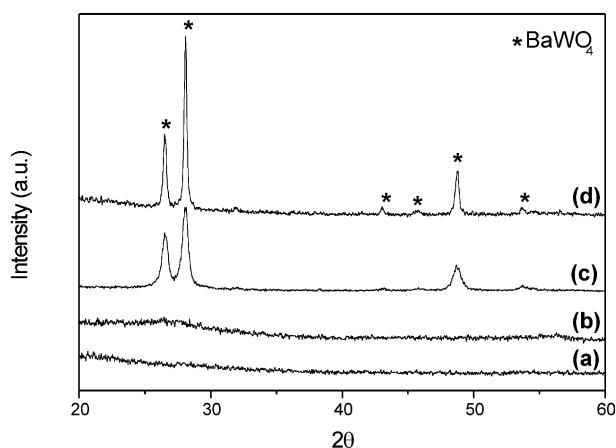


Fig. 3. X-ray diffraction patterns of BaWO₄ thin films heat-treated at different temperatures: (a) 200 °C, (b) 300 °C, (c) 400 °C, and (d) 500 °C.

X-ray diffraction (XRD) pattern is observed at 300 °C, indicating the formation of an inorganic amorphous phase after the pyrolysis process for PbWO₄ thin films. At temperatures above 400 °C, crystallization of PbWO₄ phase is observed. No intermediate phase was observed, which suggests a direct crystallization from the amorphous phase to the Scheelite-type structure. All the peaks are ascribed to a tetragonal structure having $a = 5.438 \text{ \AA}$ and $c = 12.070 \text{ \AA}$ lattice parameters. These values are close to the bulk material ($a = 5.461 \text{ \AA}$ and $c = 12.049 \text{ \AA}$). XRD patterns for BaWO₄ thin films also show the formation of an inorganic amorphous phase at 200 and 300 °C. The crystallization of the BaWO₄ scheelite phase begins at 400 °C and well crystallized structure patterns were identified in the thin films heat treated at 500 °C. Again, no intermediate phase was observed. The diffractogram reveals well-defined peaks showing a good crystallinity. All the peaks are ascribed to a tetragonal structure. A further analysis of the XRD data indicates lattice parameters of $a = 5.600 \text{ \AA}$ and

$c = 12.696 \text{ \AA}$. These values are also close to the ones of the bulk material ($a = 5.613 \text{ \AA}$ and $c = 12.720 \text{ \AA}$).

Cross-section of the films layers revealed a uniform microstructure throughout the film thickness of about 300 nm.

In addition, a more detailed observation made by atomic force microscopy (AFM) shows the difference in both thin films in terms of surface morphology of the films prepared at different temperatures. This AFM analysis showed a considerable variation in the surface morphology between the samples submitted to annealing temperatures of 200–500 °C. Table 1 shows the evolution of sample roughness measured by AFM analysis. It is evident from the AFM analysis that the BaWO₄ and PbWO₄ thin films heat treated at 200 °C and 300 °C showed a homogeneous surface morphology with very low roughness (see Table 1). There was no evidence of a granular structure (see Figs. 4a and b and 5a and b). When the sample was annealed at 400 °C, the increased roughness suggests that the material's structure became increasingly ordered. In addition, the AFM analysis showed that the BaWO₄ and PbWO₄ thin films heat-treated at 400 °C showed a homogeneous nucleation leading to a grain size distribution of approximately 20–30 and 50–60 nm, respectively, at the initial growth stage (see Figs. 4c and 5c). In addition, the BaWO₄ thin films deposited at 400 °C demonstrated a larger amount of nuclei with smaller size and more homogeneously distributed than the PbWO₄ thin films. On the other hand, the surface morphology changes dramatically at 500 °C. At this stage of growth, coalescence of nuclei occurs, with the formation of granular structures in both thin films resulting in a significant increase of roughness. This result is in agreement with the XRD analysis where at 500 °C a high crystallization can be observed. In addition, Cho et al.⁹ showed that the hydrothermal method did not produce BaWO₄ films because only discrete BaWO₄ particles appeared on the tungsten substrate.

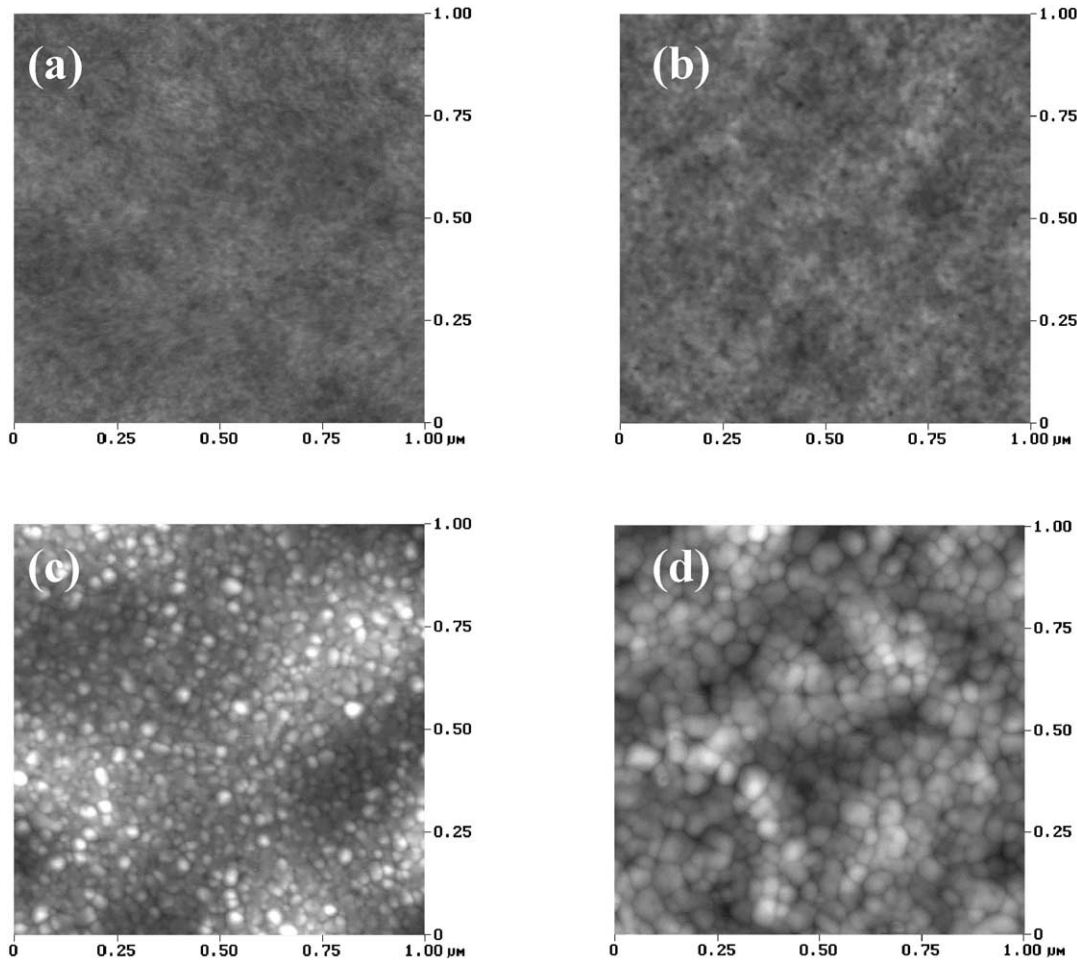
Fig. 6 shows the IR reflectance spectra of BaWO₄ and PbWO₄ thin films annealed at 150 and 500 °C. From the spectrum of PbWO₄ thin film annealed at 150 °C for 4 h in air (Fig. 6c), it is clear that undecomposed organic ligands are still present in the film. In addition, the spectrum display a very broad absorption band from 1000 to 600 cm⁻¹. This band is attributed to the M–O bonds, of a solid oxide network. Vibrations around 1718 and at 1448 cm⁻¹, which can be related to C=O stretching mode for the ester (R–COO–R) are also observed. The vibrations at 1600 cm⁻¹ and 1390 cm⁻¹ are related to a COO⁻ stretching mode for a bidentate complex (Fig. 6c). At 500 °C, the definition of two sharp bands is observed in both thin films (Fig. 6a and b), and the bands at 1718, 1600, 1448 and 1379 cm⁻¹ completely disappear. This suggests that PbWO₄ and BaWO₄ thin films crystallize at an annealing temperature of 500 °C,

Table 1

Evolution of the roughness and average grain size parameters of PbWO₄ and BaWO₄ thin films on silicon substrates

	PbWO ₄				BaWO ₄			
	200	300	400	500	200	300	400	500
Annealing temp. (°C)	200	300	400	500	200	300	400	500
Rms (nm)	0.409	0.413	1.147	9.312	0.294	0.359	1.392	2.019
A.G.S (nm)	–	–	50–60	260–270	–	–	20–30	70–80

A.G.S= average grain size; Rms=roughness.

Fig. 4. AFM images of BaWO₄ thin films heat-treated at different temperatures: (a) 200 °C, (b) 300 °C, (c) 400 °C, and (d) 500 °C.

as shown by the XRD pattern described in Figs. 2 and 3. In addition, the assumption of a tetrahedral, T_d , point group symmetry for the WO₄ units in BaWO₄ and PbWO₄ thin films, makes Γ_{T_d} , the representation for the tetrahedral symmetry as $\Gamma_{T_d} = A_1(\nu_1) + E(\nu_2) + F_2(\nu_3) + F_2(\nu_4)$, in which all four vibrational modes are Raman active (See Fig. 7), but only the $F_2(\nu_3, \nu_4)$ modes are IR active^{13,14} (See Fig. 6). Therefore, the bands at 754, 862 cm⁻¹ and 806, 887 cm⁻¹ are assigned to $F_2(\nu_3)$ antisymmetric stretches vibrations for PbWO₄ and BaWO₄, respectively.

Fig. 8 shows the optical transmission spectra of the crystalline thin films recorded in the 200–800 nm wavelength range on amorphous silica substrate because it is transparent in such spectrum region. The optical band

gap energy, E_{gap} , for the crystalline thin films was determined from the sharply falling transmission region. According to Tauc's law,¹⁵ the absorption coefficient has the following energy dependence,

$$\alpha = A(h\nu - E_{\text{gap}})^m / h\nu \quad (1)$$

where A is a constant which is different for different types of transitions indicated by different values of m ($m = 1/2, 2, 3/2$ or 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect electronic transitions, respectively), $h\nu$ is the photon energy, and E_{gap} is the Tauc optical band gap.

So the straight line plot between $(\alpha h\nu)^{1/m}$ and $h\nu$ would yield the value of the Tauc optical band gap

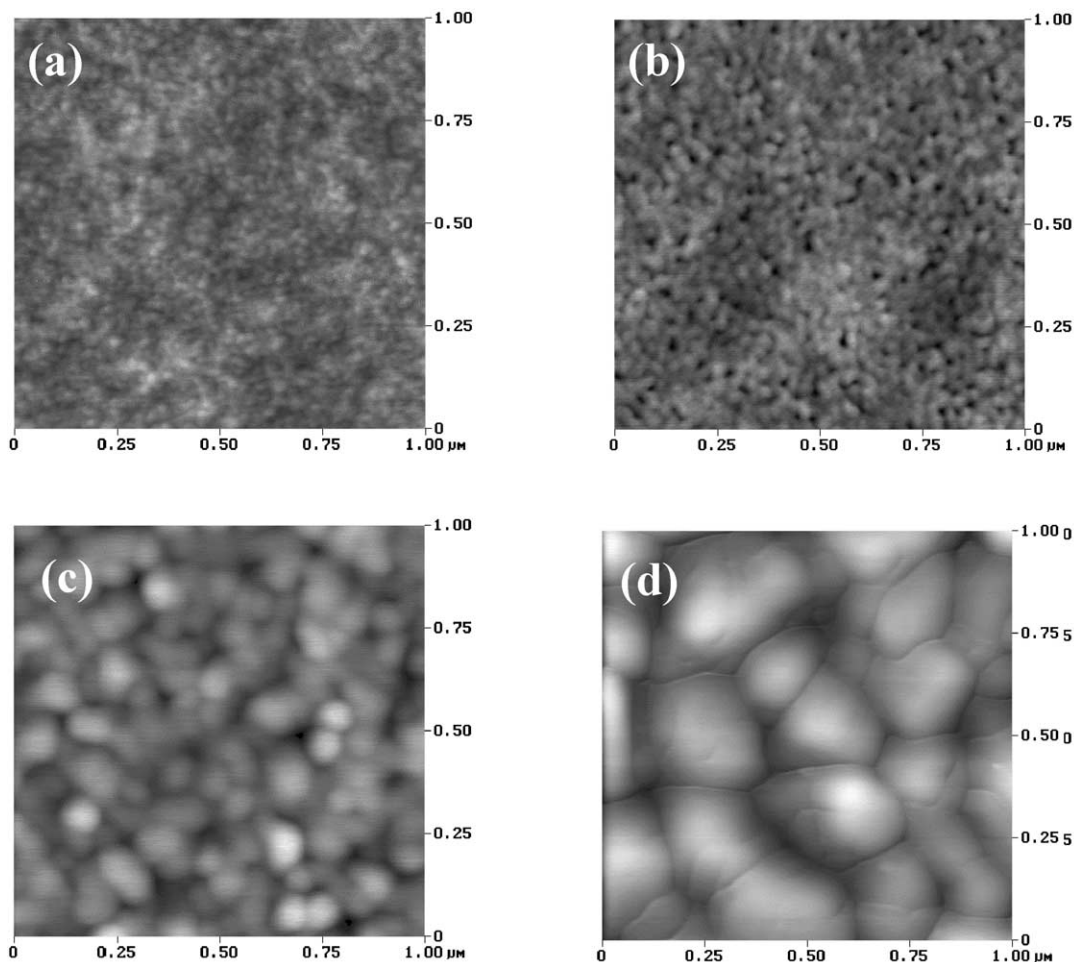


Fig. 5. AFM images of PbWO₄ thin films heat-treated at different temperatures: (a) 200 °C, (b) 300 °C, (c) 400 °C, and (d) 500 °C.

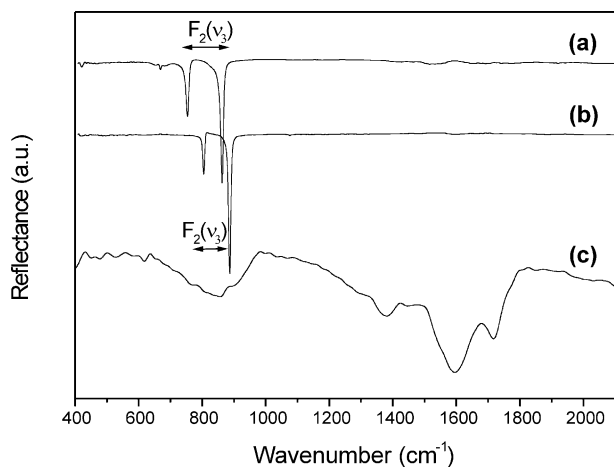


Fig. 6. The IR reflectance spectra of thin films annealed at different temperatures: (a) PbWO₄ at 500 °C, (b) BaWO₄ at 500 °C, and (c) PbWO₄ at 150 °C.

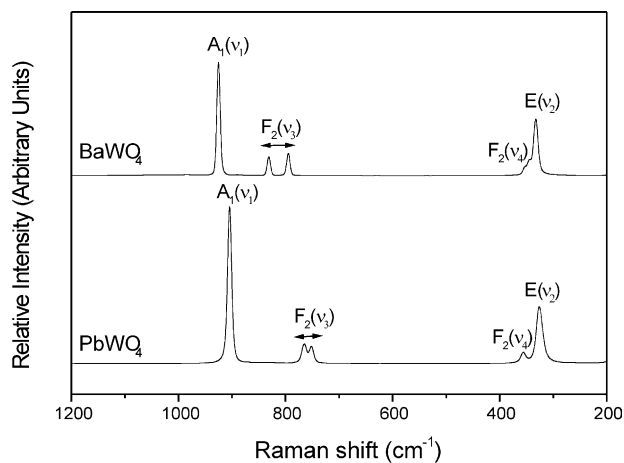


Fig. 7. Raman spectra of BaWO₄ and PbWO₄ powders prepared by the polymeric precursor method annealed at 600 °C.

(E_{gap}). The plots of $(\alpha h\nu)^2$ versus $h\nu$ for crystalline thin films are depicted in Fig. 8. The direct transition band gap of the crystalline thin films has been found to be 5.78 eV and 4.20 eV for BaWO₄ and PbWO₄ thin films, respectively, corresponding to a direct allowed

transition between valence and conduction bands. In the high energy region of the absorption edge, $(\alpha h\nu)^2$ varied linearly with $h\nu$. In the low energy region of the edge, the absorption spectrum deviated from the straight line plot. This straight line behaviour in the high energy region

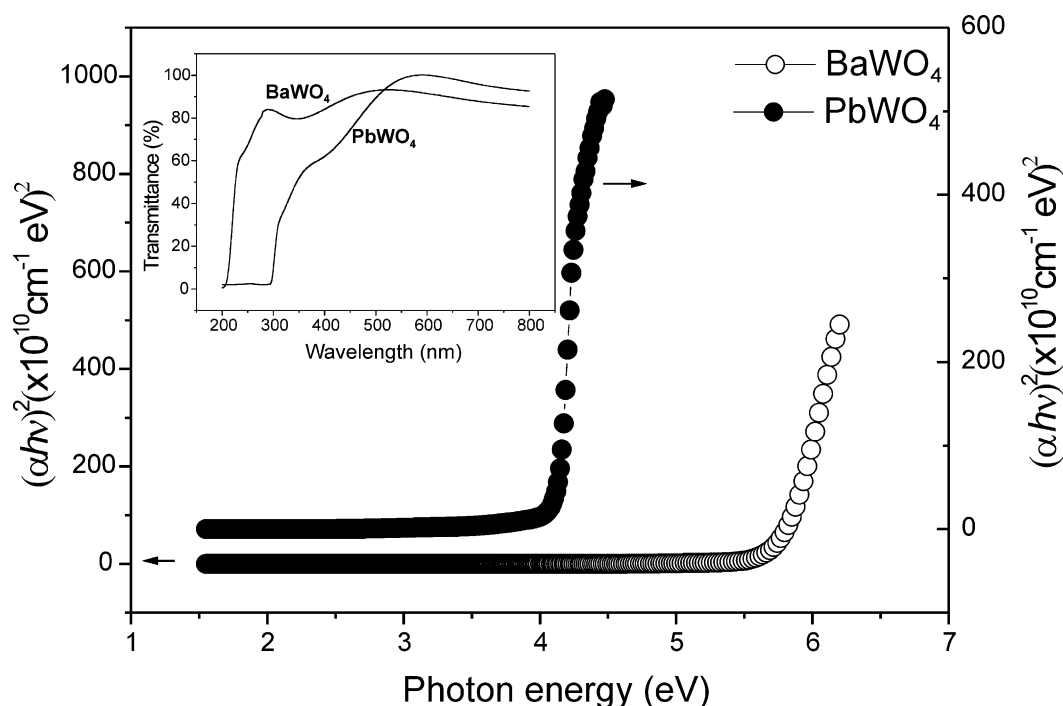


Fig. 8. Optical transmittance spectra of crystalline thin films and plots of $(\alpha hv)^2$ vs photon energy hv . The band gap energy is deduced from the extrapolation of the straight line up to $(\alpha hv)^2 = 0$.

was taken as prime evidence for the direct band gap. The optical band gap was determined by extrapolating the linear portion of the plot relating, $(\alpha hv)^2$ versus hv to $(\alpha hv)^2 = 0$ (see Fig. 8). The optical band gap of crystalline $PbWO_4$ thin film, is close to that of a $PbWO_4$ thin film determined by Xiaoling et al.¹⁶ which was 4.4 eV.

4. Conclusions

We have successfully demonstrated, for the first time, the growth of $BaWO_4$ and $PbWO_4$ thin films with scheelite-type structure by a soft chemical route the so-called polymeric precursor method. Polycrystalline, homogeneous, dense, and crack-free thin films were successfully prepared on silicon substrates using a spin-coating technique. The XRD results show that no intermediate phase was detected and a single $BaWO_4$ or $PbWO_4$ phase is crystallized from an amorphous matrix. XRD results showed a tetragonal structure of polycrystalline thin films with lattice parameters of $a = 5.600 \text{ \AA}$ and $c = 12.696 \text{ \AA}$, $a = 5.438 \text{ \AA}$ and $c = 12.070 \text{ \AA}$ for $BaWO_4$ and $PbWO_4$ thin films, respectively. The crystalline thin films presented an average grain size of approximately 260 nm and 180 nm for $PbWO_4$ and $BaWO_4$, respectively. $BaWO_4$ and $PbWO_4$ thin films presented a homogeneous nucleation since the early stage. FTIR spectra revealed complete decomposition of the organic ligands at 500 °C and the presence of the two sharp and intense bands between 1000 and 600 cm^{-1} corresponding only to the $F_2(\nu_3)$ antisymmetric

stretch modes vibrations, showing high crystallinity for both thin films. These results are in agreement with XRD patterns. The band gap energy of the crystalline thin films was found to be 5.78 eV ($BaWO_4$) and 4.20 eV ($PbWO_4$) from the Tauc approach, the linear fitting of the product $(\alpha hv)^2$ versus hv . In addition, the joint use of the IR and Raman spectroscopy powerful techniques provides comprehensive information on the vibrational structure of the thin films. It is believed that the structural and microstructural good quality is resulting from the soft solution processing that uses aqueous solutions to create shaped, sized, and oriented materials, and also emphasizes low-energy routes to the synthesis of materials with desired chemical composition and crystal structure.

Acknowledgements

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