Effect of partial preferential orientation and distortions in octahedral clusters on the photoluminescence properties of FeWO4 nanocrystals
Effect of partial preferential orientation and distortions in octahedral clusters on the photoluminescence properties of FeWO\(_4\) nanocrystals

M. A. P. Almeida, L. S. Cavalcante, C. Morilla-Santos, C. J. Dalmaschio, S. Rajagopal, M. Siu Li, and E. Longo

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This communication is a report of our initial research to obtain iron tungstate (FeWO\(_4\)) nanocrystals by the microwave-hydrothermal method at 170 °C for 45 min. X-ray diffraction patterns showed that the FeWO\(_4\) nanocrystals prepared with polyethylene glycol-200 have a partial preferential orientation in the (011) plane in relation to other nanocrystals prepared with sodium bis(2-ethylhexyl)sulfosuccinate and water. Rietveld refinement data indicates that all nanocrystals are monophasic with wolframite-type monoclinic structures and exhibit different distortions on octahedral [FeO\(_6\)]\(^{1-}\) clusters. High resolution transmission electron microscopy revealed an oriented attachment mechanism for the growth of aggregated FeWO\(_4\) nanocrystals. Finally, we observed that the photoluminescence properties of these nanocrystals are affected by partial preferential orientation in the (011) plane and distortions on [FeO\(_6\)]\(^{1-}\) clusters.

1. Introduction

In recent years, much research has been devoted to the synthesis of new nanomaterials with good physical/chemical properties in relation to bulk materials.\(^1\)-\(^3\) Metal tungstates with a general formula (MWO\(_4\)) represent an important group of inorganic oxides with excellent functional and electronic properties.\(^4\)-\(^6\) Their crystalline structure can be composed of M-bivalent cations with large radii (M = Ca, Sr, Ba, Pb) and small radii (M = Fe, Mn, Co, Zn). These tungstates exhibit differences in the coordination of their clusters. The first tungstate oxides have a scheelite-type tetragonal structure where cations with large radii are linked to eight oxygen atoms which form [MO\(_6\)] clusters with deltahedral coordination, while W atoms are bonded to four oxygen atoms which results in the formation of tetrahedral [WO\(_4\)] clusters.\(^7\)-\(^8\) The second tungstate oxides exhibit a wolframite-type monoclinic structure where both M and W atoms are bonded to six oxygen atoms, which results in the formation of octahedral [MO\(_6\)]\(^{1-}\) clusters.\(^9\)-\(^10\) These differences in the coordination/structure cause defects in the crystal lattice and the appearance of photocatalytic,\(^11\)-\(^12\) photoluminescence (PL),\(^13\)-\(^16\) humidity sensor\(^17\)-\(^19\) and magnetic properties\(^20\)-\(^21\) as well as electronic properties for the tungstates.

Among these tungstates, the investigation of iron tungstate (FeWO\(_4\)) has been widely reported in the literature due to good magnetic\(^22\)-\(^23\) and photocatalytic\(^24\)-\(^25\) properties. Therefore, Zhang et al.\(^26\) have developed a new synthesis method to obtain different FeWO\(_4\) meso-, micro- and nanocrystals with superior electronic properties. Several synthesis methods are used in the preparation of FeWO\(_4\) nanocrystals, but the conventional hydrothermal (CH) method has most often been employed and reported in the literature.\(^27\)-\(^30\) However, the CH method has some inconveniences, such as a long time period (typically one-half to several days) because of slow heat transfer due to the conduction and convection transport mechanism and high electric power usage (over a thousand watts). The solution to these problems is the microwave-hydrothermal (MH) method; this method facilitates the attainment of this oxide material in a shorter time and with lower energy consumption\(^31\) which is possible due to efficient internal heating (in-core volumetric heating) by direct coupling of microwave irradiation with solvent molecules, ions and hydroxides in the reaction mixture.\(^32\)

Therefore, in this communication, we have employed the MH method for the fast preparation of FeWO\(_4\) nanocrystals with different orientations by the use of surfactants. Moreover, we have analyzed their structure, size, shape, and PL properties at room temperature.

2. Experimental procedure

2.1. Microwave-hydrothermal synthesis of FeWO\(_4\) nanocrystals

A typical synthesis of FeWO\(_4\) nanocrystals was conducted as follows: 1 \(\times\) 10\(^{-3}\) mol of sodium tungstate (VI) dihydrate (Na\(_2\)WO\(_4\)\(\cdot\)2H\(_2\)O) (99.5% purity, Sigma-Aldrich) and 1 \(\times\) 10\(^{-3}\) mol of ammoniacal ferrous sulfate ([NH\(_4\)]\(_2\)Fe(SO\(_4\))\(_2\)\(\cdot\)6H\(_2\)O)]
(99% purity, Sigma-Aldrich) were dissolved in 100 mL of water (pH = 9). In separate experiments, the following quantities of surfactants were dissolved in enough ionized water to produce 100 mL of solution; a) 0.04 mol of dioctyl sodium sulfosuccinate (C_{20}H_{37}NaO_3S) (99% purity, Sigma-Aldrich), abbreviated as AOT; b) 50 mL of polyethylene glycol (C_{20}H_{44}O_{n+1}) (99% purity, Sigma-Aldrich) with a molecular mass (MW = 200), abbreviated as PEG-200. These solutions were added separately to the tungstate/iron solution, and the mixtures were placed in a Teflon autoclave which was sealed and placed inside a domestic MH system at 170 °C for 45 min. The resulting suspensions were washed with deionized water and acetone to remove residual Na⁺ ions. Finally, crystalline FeWO₄ nanocrystals (black color) were collected on a filter and dried with acetone at room temperature for several hours.

2.2. Characterizations

These FeWO₄ nanocrystals were structurally characterized by X-ray diffraction (XRD) patterns using a D/Max-2500PC diffractometer (Rigaku, Japan) with Cu-Kα radiation (λ = 1.5406 Å) in the 2θ range from 10 to 60° and from 10 to 110° both with a scanning velocity of 1° min⁻¹ in the Rietveld routine (8 h of measurement). The shape and size of these FeWO₄ nanocrystals were observed by transmission electron microscopy (TEM) and high resolution TEM (HR-TEM) using a TEM/FEI microscope operated at 200 kV. PL measurements were performed to confirm the monoclinic structure for FeWO₄ nanocrystals prepared by the MH method at 170 °C for 45 min: (a) without surfactant, (b) AOT anionic surfactant and (c) PEG-200 non-ionic surfactant. The vertical lines indicate the position and relative intensity of the JCPDS card No. 46-1446 for the FeWO₄ phase.

3. Results and discussion

3.1. XRD patterns and Rietveld refinement analyses of FeWO₄ crystals

Fig. 1 shows XRD patterns for FeWO₄ nanocrystals prepared by the MH method at 170 °C for 45 min: (a) without surfactant, (b) AOT anionic surfactant and (c) PEG-200 non-ionic surfactant.

XRD patterns in Fig. 1(a–c) indicate that FeWO₄ nanocrystals have a wolframite-type monoclinic structure with a space group of (P2₁/c) and a point group symmetry (C₃ᵥ) as described in the respective Joint Committee on Powder Diffraction Standards (JCPDS) card No. 46-1446. These crystals have a broad diffraction peak which indicates possibly the presence of nanocrystals with a reasonable degree of structural order and crystallinity at long range. Moreover, Fig. 1(c) demonstrates that FeWO₄ nanocrystals prepared with PEG-200 (non-ionic surfactant) exhibited a partial effect of crystallographic orientation in relation to other FeWO₄ nanocrystals (see Fig. 1(a–c)).

The structural refinement using the Rietveld method was performed based on the α-FeWO₄ phase with a monoclinic structure using a better approximation and indexing of the Crystallographic Information File (CIF) and employing CIF.
Therefore, Fig. 2(a–c) illustrate good agreement between the experimentally observed XRD patterns and theoretically fitted results, which indicate the success of the Rietveld refinement method (see Table 1).

In this table, the fit parameters ($R_{wp}$, $R_{bagg}$, $\chi^2$, and $S$) suggest that refinement results are very reliable. We have observed some small variations in the atomic positions related to the oxygen atoms while the iron and tungsten atoms retain their fixed positions within the structure. These results indicate major structural distortions on [FeO$_6$] and [WO$_6$] clusters of FeWO$_4$ nanocrystals prepared with the PEG-200 (polymer surfactant) which can be due to the partial effect of crystallographic orientation in the (011) plane.

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$^a$ FeWO$_4$ – without surfactant. $P2_1/c$ (13) - monoclinic, $a = 4.692(3)$ Å, $b = 5.695(5)$ Å, $c = 4.979(6)$ Å; $V = 133.08$ Å$^3$; $x = \gamma = 90^\circ$, $\beta = 89.95^\circ$; $R_{wp} = 4.81\%$; $R_{bagg} = 1.74\%$, $\chi^2 = 4.14$ and $S = 2.034$.

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$^b$ FeWO$_4$ – AOT. $P2_1/c$ (13) - monoclinic, $a = 4.684(3)$ Å, $b = 5.694(3)$ Å, $c = 4.982(1)$ Å; $V = 132.89$ Å$^3$; $x = \gamma = 90^\circ$, $\beta = 89.96^\circ$; $R_{wp} = 5.98\%$; $R_{bagg} = 4.21\%$, $\chi^2 = 6.65$ and $S = 2.578$.

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$^c$ FeWO$_4$ – PEG-200. $P2_1/c$ (13) - monoclinic, $a = 4.703(3)$ Å, $b = 5.696(5)$ Å, $c = 4.971(1)$ Å; $V = 133.19$ Å$^3$; $x = \gamma = 90^\circ$, $\beta = 89.83^\circ$; $R_{wp} = 4.87\%$; $R_{bagg} = 3.87\%$, $\chi^2 = 4.83$ and $S = 2.197$.

3.2. Representation of FeWO$_4$ unit cells

Fig. 3(a–c) illustrate a schematic representation for monoclinic FeWO$_4$ unit cells modeled from Rietveld refinement data for FeWO$_4$ nanocrystals prepared by the MH method at 170 °C for 45 min: (a) without surfactant, (b) AOT anionic surfactant and (c) PEG-200 non-ionic surfactant, respectively.

These unit cells were modeled through the Visualization for Electronic and Structural Analysis (VESTA) software version 3.1.1 for Windows using lattice parameters and atomic positions obtained from Rietveld refinement data shown in Table 1. FeWO$_4$ crystals belong to a wolframite-type monoclinic structure with a space group of ($P2_1/c$), a point-group symmetry (C$_2$h) and two formulae per unit cell ($Z = 2$) Fig. 3(a–c) verifies that bonds between O–Fe–O and O–W–O atoms were projected out of unit
cells. In these unit cells, all tungsten (W) and iron (Fe) atoms are coordinated only to six four-oxygen atoms which form distorted \([\text{FeO}_6]/[\text{WO}_6]\) clusters with an octahedral configuration, a symmetry group (\(\text{Oh}\)) and octahedral polyhedra (6 vertices, 8 faces and 12 edges).\(^{43}\) Moreover, a reasonable level of distortion on \([\text{FeO}_6]/[\text{WO}_6]\) clusters in the lattice of FeWO\(_4\) crystals prepared with PEG-200 can be verified. These differences in (O–Fe–O)/(O–W–O) bond angles can produce different levels of order–disorder and/or distortions in the FeWO\(_4\) crystal lattice.

3.3. TEM, HR-TEM and SAED analyses of FeWO\(_4\) nanocrystals

Fig. 4(a–f) show TEM/HR-TEM images and selected area electron diffraction (SAED) patterns for FeWO\(_4\) nanocrystals obtained at 170 °C for 45 min: (a,b) without surfactant, (c,d) AOT anionic surfactant and (e,f) PEG-200 non-ionic surfactant, respectively.

The TEM image in Fig. 4(a) illustrates several rods-like FeWO\(_4\) nanocrystals with an agglomerate nature as well as polydisperse shapes in a size distribution. These images also indicate that these nanocrystals are formed and grow quickly in an aqueous solution after microwave irradiation, which promotes a fast precipitation reaction.\(^{44}\) The inset in Fig. 4(a) shows that SAED patterns exhibited rings that are characteristic for rod-like FeWO\(_4\) nanocrystals. The HR-TEM image in Fig. 4(b) reveals two nanoparticles in the oriented attachment growth process that results in a nanorod. These nanocrystals have an anisotropic preferential growth along the [100] direction, which is in agreement with recent work reported in the literature for wolframite-type nanocrystals.\(^{45}\) The type of growth occurs due to differences in surface energies on each nanocrystal face. Moreover, the HR-TEM image in the inset displays some nanorods oriented in the same (001) plane (with an interplanar spacing of approximately 4.96 Å). From the counts of several nanorods, the FeWO\(_4\) synthesized in water shows an average rod size of 25.5 nm. Fig. 4(c) shows the effect of AOT surfactant on the growth of aggregated larger rods. Moreover, the inset in Fig. 4(c) exhibits some single FeWO\(_4\) nanorods. From the counts of several nanorods, the average rod size was 32.5 nm. HR-TEM images in Fig. 4(d) reveals that some of these nanorods aggregated in the same (100) plane. As a result of the oriented attachment (OA) nanoparticles grow in the [100] direction by sharing the sample crystal facet.\(^{46}\) The inset in Fig. 4(d) illustrates FFT patterns typical of FeWO\(_4\) single crystal, i.e., a well formed crystal followed by an OA growth process which results in rod-like-shaped nanocrystals. Fig. 4(e) shows the TEM image of several anisotropic rod-like FeWO\(_4\) aggregated nanocrystals prepared with PEG-200 surfactant. The counts of several nanorods reveal the growth of rods with an average size of 23.5 nm. The SAED in the inset shows the indexed polycrystalline monoclinic structure (inset of Fig. 4(f)). In addition, Fig. 4(f) illustrates the HR-TEM image of two FeWO\(_4\) nanorods with crystallographic fusion in the same (100) plane. These two nanocrystals have a specific crystallographic relationship (coincident site lattice matching) where these nanorods adhere strongly and fuse to form a large crystal.\(^{47}\) In fact, as evidence in the XRD patterns the FeWO\(_4\) nanocrystals prepared with PEG-200 have been showed a partial preferential orientation in the (011) direction. Then a fraction of the nanoparticles exhibit a preferential orientation in this direction. However, it is not possible to observe this effect in our HR-TEM images (Fig. 4f) due to the attachment oriented occurs in a plane different. Therefore, it is possible to infer that this behavior has a relationship with force bonds (O–Fe–O)/(O–W–O), fusion between the crystallographic plane with low surface energy and distorted octahedrons on [FeO\(_6\)] and [WO\(_6\)] clusters that induces an orientation in different crystallographic planes with high surface energy and effective electronic activity. However, future calculations will be performed to understand the influence of surface energies on the crystal growth process of FeWO\(_4\) nanocrystals. Moreover, Fig. 4(f) shows the HR-TEM image of two nanorods in the process of self-assembly by mean of an OA mechanism which occurs with a self-assembly by sharing a common crystallographic orientation and the docking of these nanocrystals at a planar interface.\(^{48}\) The results indicate that these rod-like FeWO\(_4\)
nanocrystals prepared with PEG-200 surfactant grew in a partial preferential orientation (XRD patterns, Fig. 1(a–c)), which is different from FeWO$_4$ nanocrystals prepared without surfactant and an AOT anionic surfactant. SAED pattern analyses indicate that FeWO$_4$ nanocrystals prepared with PEG-200 surfactant have a high crystallinity in relation to other nanocrystals. Moreover, HR-TEM images verified that the surfaces of the nanocrystals are well defined when compared to FeWO$_4$ nanocrystals prepared without and with AOT surfactant, which can exhibit a partly amorphous surface (see ESI, Fig. SI).

3.4. PL properties of FeWO$_4$ microcrystals

Fig. 5 illustrates the PL spectra at room temperature of FeWO$_4$ nanocrystals prepared by the MH method at 170 °C for 45 min: (a) without surfactant, (b) AOT anionic surfactant and (c) PEG-200 non-ionic surfactant.

According to research reported in the literature,$^{49,50}$ blue PL properties of FeWO$_4$ crystals are related to the radiative recombination of self-trapped excitons localized on a regular WO$_6^{2−}$ complex anion, whereas green PL properties are extrinsic and may be a defect-related emission. However, all these phenomena are directly associated with WO$_6^{2−}$ groups (ions), which appear only in an aqueous solution since FeWO$_4$ crystals are crystalline solids composed of interconnected clusters (–[WO$_6$]–[FeO$_6$]–[WO$_6$]–), as shown in Fig. 5(a–c). Therefore, in this communication, we assume that PL properties of FeWO$_4$ crystals are due to different types of electronic transitions between FeWO$_4$, without surfactant, FeWO$_4$-AOT, and FeWO$_4$-PEG-200.
the valence band and the conduction band. Therefore, we have observed different optical band gap values. These electronic defects were provoked by the distortion in octahedral [FeO$_6$]/[WO$_6$] clusters in the lattice (see inset in Fig. 5(a-c)). Moreover, Fig. 5(c) confirms that the PEG-200 surfactant was responsible for improvement in PL properties. This behavior is related to the partial effect of crystallographic orientation in the (011) plane which causes different distortions in octahedral [FeO$_6$]/[WO$_6$] clusters. As reported in the literature, the PL intensity enhancement may be due to the shape of the products and the improved crystallinity. Experimental results obtained by Zhang et al. indicate that luminescence properties of FeWO$_4$ are very sensitive to their morphology and strongly dependent on the size. However, in this present communication, we discovered a new factor that affects the intensity of PL emission of FeWO$_4$ nanocrystals: the effect of changes in the partial crystallographic orientation and distortions in octahedral [FeO$_6$]/[WO$_6$] clusters.

4. Conclusions

In summary, we have obtained with success rod-like FeWO$_4$ nanocrystals by the MH method at 170 °C for 45 min. XRD patterns and Rietveld refinement data indicate that these crystals are monophasic with a monoclinic structure. Structural refinement data were employed to model distorted octahedral [FeO$_6$]/[WO$_6$] clusters in the lattice of FeWO$_4$ nanocrystals. TEM and HR-TEM images show that nanocrystals grow by self-assembly, an oriented attachment process and the aggregation of small nanocrystals with a further growth of rod-like FeWO$_4$ crystals. Moreover, an effect of oriented growth was verified for FeWO$_4$ nanocrystals prepared with PEG-200. Finally, we have observed that PL properties of these nanocrystals are dependent on distortions in octahedral [FeO$_6$]/[WO$_6$] clusters and partial preferential orientation in the (011) crystallographic plane of these nanocrystals.

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References


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