Negative pressures in $CaWO_4$ nanocrystals

F. J. Manjón,[1,a)] D. Errandonea,[2] J. López-Solano,[3] P. Rodríguez-Hernández,[3] and A. Muñoz[3]

[1]*MALTA Consolider Team, Departamento de Física Aplicada-IDF, Universidad Politécnica de Valencia, Cno. de Vera s/n, 46022 Valencia, Spain*

[2]*MALTA Consolider Team, Departamento de Física Aplicada-ICMUV, Fundación General de la Universidad de Valencia, C/. Dr. Moliner 50, 46100 Burjassot, Valencia, Spain*

[3]*MALTA Consolider Team, Departamento de Física Fundamental II e Instituto de Materiales y Nanotecnología, Universidad de La Laguna, La Laguna 38205, Tenerife, Spain*

(Received 28 January 2009; accepted 11 March 2009; published online 8 May 2009)

Tetragonal scheelite-type $CaWO_4$ nanocrystals recently prepared by a hydrothermal method show an enhancement of its structural symmetry with the decrease in nanocrystal size. The analysis of the volume dependence of the structural parameters in $CaWO_4$ nanocrystals with the help of *ab initio* total-energy calculations shows that the enhancement of the symmetry in the scheelite-type nanocrystals is a consequence of the negative pressure exerted on the nanocrystals; i.e., the nanocrystals are under tension. Besides, the behavior of the structural parameters in $CaWO_4$ nanocrystals for sizes below 10 nm suggests an onset of a scheelite-to-zircon phase transformation in good agreement with the predictions from our *ab initio* calculations. $CaWO_4$ nanocrystals exhibit a reconstructive-type mechanism for the scheelite-to-zircon phase transition that seems to follow the tetragonal path that links both structures. This result is in contrast with the mechanism recently proposed for this transition in bulk $ZrSiO_4$ where the transition goes through an intermediate monoclinic phase. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3116727]

I. INTRODUCTION

Alkaline-earth metal tungstates (AWO_4; A=Ca, Sr, Ba) crystallizing in the scheelite structure have an increasing number of applications.[1] In the last years intense efforts have been witnessed in preparation of scheelite nanoparticles by different methods with the aim of improving the luminescence properties of scheelites.[2–9] During this search, it has been found that nanocrystals usually have different structural properties than bulk crystals and that nanocrystals can be synthesized under certain conditions in phases that are not stable for the bulk material at ambient conditions. Recently, $CdWO_4$ nanocrystals have been synthesized in a tetragonal scheelite structure despite bulk $CdWO_4$ crystallizes in the monoclinic wolframite structure.[9] On the other hand, an interesting symmetry enhancement of scheelite-type $CaWO_4$ nanocrystals synthesized by a hydrothermal method was observed when the dimensions of the nanocrystals were reduced from 31.7 to 3.4 nm.[5,6] An increase in the unit-cell volume and a decrease in the c/a ratio in the tetragonal scheelite structure was reported when decreasing the nanocrystal size below 8 nm.[5,6]

High-pressure experiments are a powerful tool to investigate the main physical properties of scheelites,[10–12] helping to improve their applications, since they depend on the structures, lattice parameters, and band structures of the different compounds, which can be tuned by varying the unit-cell volume at different pressures. In the present work, we analyze the behavior of the structural properties of the scheelite-type $CaWO_4$ nanocrystals recently reported in Refs. 5 and 6 and show that its unit-cell volume dependence on the nanocrystal size can be explained by the presence of negative pressures in them with respect to the bulk material. In order to explain the variations in the structural parameters with the nanocrystal size, we have compared the data available in the literature for bulk and nanocrystalline scheelite-type $CaWO_4$ and performed total-energy *ab initio* calculations within the framework of the density functional theory, which helped us in interpreting the structural data. Details of the calculation are given elsewhere.[10,13]

II. STRUCTURAL DATA: RELATION BETWEEN VOLUME AND PRESSURE

Li *et al.* recently reported the dependence of the unit-cell volume and c/a ratio of scheelite-type $CaWO_4$ nanocrystals as a function of nanocrystal size.[5] They found that the volume of the tetragonal unit cell increased with the decrease in nanocrystal size. Figure 1 shows the variation in the a and c lattice parameters of scheelite-type $CaWO_4$ nanocrystals with the nanocrystal size, as calculated from data of Ref. 5. It can be observed that the a lattice parameter increases monotonically as the nanocrystal size is reduced, while the c lattice parameter shows a nonmonotonous dependence on the nanocrystal size, decreasing sharply for nanocrystal sizes below 8 nm.

The increase in the nanocrystal volume reported for $CaWO_4$ nanocrystals with decreasing their size[5] can be understood if nanocrystals below a certain size feel a "negative" pressure. Since the unit-cell volume in bulk $CaWO_4$ decreases with the increase in pressure above ambient pressure (1 bar=0.1 MPa),[10,14,15] an increase in the unit-cell lattice parameters and consequently in the volume can only be

[a)]Author to whom correspondence should be addressed. Electronic mail: fjmanjon@fis.upv.es. Tel.: +34 963 877000. FAX: +34 963 877149.

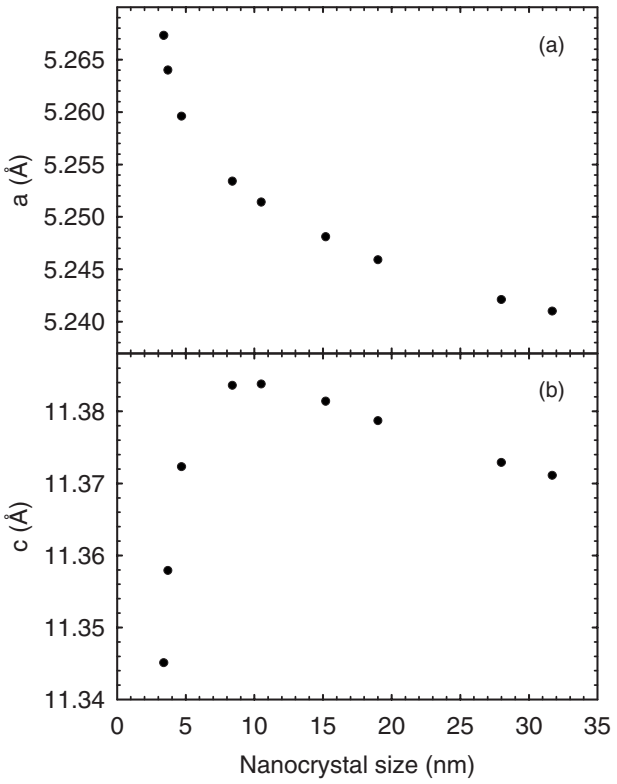

FIG. 1. Dependence of the a and c lattice parameters on the nanocrystal size in $CaWO_4$ after Ref. 5.

explained by the presence of negative pressures. However, the dependence of the a and c lattice parameters of scheelite-type $CaWO_4$ nanocrystals with decreasing nanocrystal size requires a deeper study and is analyzed later. In order to interpret the size dependence of the nanocrystal volume of Ref. 5, we assume, in a first approximation, that the scheelite-type $CaWO_4$ nanocrystals have the same volume compressibility, $\chi=-\partial \ln V/\partial P$, or equivalently the same bulk modulus, $B_0=1/\chi$ than their corresponding single crystals.[16] Under this assumption, we can use the equation of state (EOS) deduced for bulk $CaWO_4$ (Ref. 10) to calculate the negative pressures present in nanocrystals with different nanocrystal sizes. Figure 2 shows the fit of the volumes at different pressures according to the EOS obtained for bulk $CaWO_4$. We found that the smallest nanocrystal (3.4 nm) must suffer approximately a negative pressure of -0.62 GPa in order to undergo the observed volume expansion. Table I summarizes the nanocrystal sizes, their a and c lattice parameters, their unit-cell volume, and their estimated negative pressures.

III. PRESSURE EFFECTS ON THE SETTING ANGLE

It is well known that each compound crystallizing in the tetragonal scheelite structure has a characteristic setting angle (ϕ), which is the minimum angle between the W–O bond inside the WO_4 tetrahedra and the a axis. In particular, the experimental setting angle for bulk $CaWO_4$ is near 32° at ambient pressure.[14] A rather simple calculation allows the

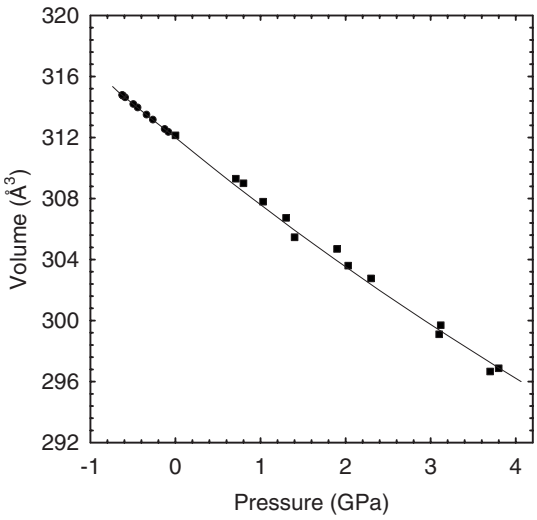

FIG. 2. Pressure dependence of unit-cell volume assumed for bulk and nanocrystalline scheelite-type $CaWO_4$. The data for the nanocrystals have been fitted to the EOS obtained for bulk (V_0=312 Å^3, B_0=72 GPa, B'_0=4.8) in order to assign a negative pressure corresponding to each nanocrystal volume. Nanocrystal data (circles) are from Ref. 5 and bulk data (squares) are from Refs. 10, 14, and 15.

setting angle to be obtained as a function of the x and y parameters of the main O atom in the tetragonal unit cell as reported by Hazen *et al.*,[14]

$$\cos\phi = \frac{0.5-2y}{\sqrt{4(x^2+y^2)+(0.25-2y)}}. \quad (1)$$

Hazen *et al.* performed single crystal x-ray diffraction (XRD) measurements in bulk $CaWO_4$ under pressure and determined the atomic positions of the O atoms in the scheelite structure with increasing pressure of up to 4 GPa.[14] In Fig. 3 we plotted the measured x, y, and z atomic positions of the O atom (symbols) as a function of pressure as taken from the work of Hazen *et al.*[14] By fitting the data of Hazen *et al.* to a straight line (solid line), we can estimate the x, y, and z parameters of the O atom that should be present in $CaWO_4$ nanocrystals according to the negative pressures present in them, as obtained from Fig. 2. It can be observed that under pressure they undergo a more or less monotonously behavior. We also plotted in Fig. 3 as black dashed lines the x, y, and z parameters obtained from our *ab initio* calculations in scheelite-type bulk $CaWO_4$ in the studied

TABLE I. Size, unit-cell volume, lattice parameters, and estimated negative pressures in the $CaWO_4$ nanocrystals of Ref. 5.

Size (nm)	V (Å^3)	a (Å)	c (Å)	P (GPa)
31.7	312.3	5.241	11.371	−0.08
28	312.5	5.242	11.373	−0.12
19	313.1	5.246	11.379	−0.26
15.2	313.5	5.248	11.381	−0.33
10.5	313.9	5.251	11.384	−0.44
8.4	314.2	5.253	11.384	−0.49
4.7	314.6	5.260	11.372	−0.59
3.7	314.7	5.264	11.358	−0.61
3.4	314.8	5.267	11.345	−0.62

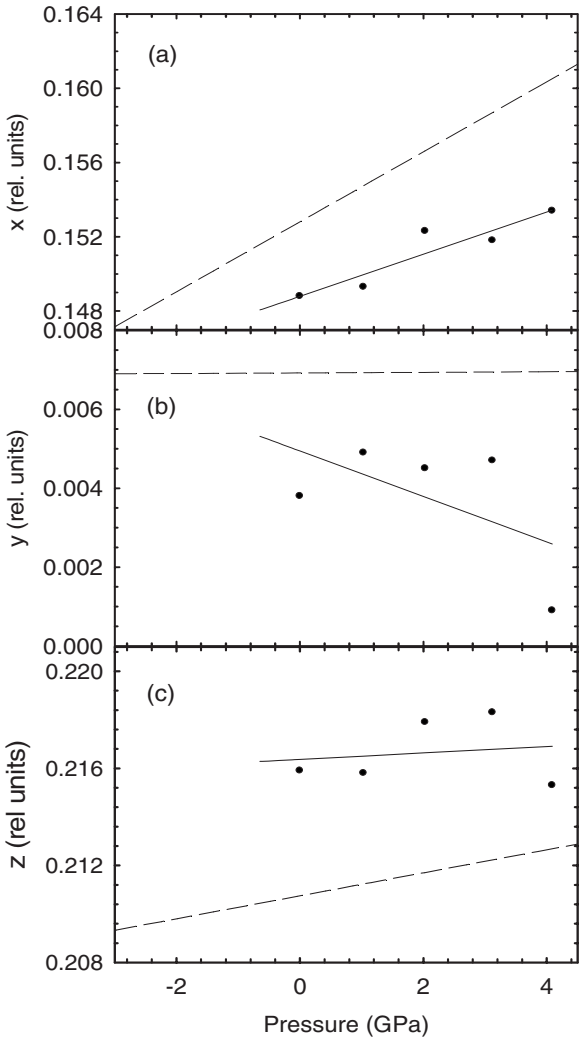

FIG. 3. Pressure dependence of the atomic parameters (a) x, (b) y, and (c) z (in relative units) of the generatrix O atom in the unit cell of bulk scheelite-type $CaWO_4$, as taken from Ref. 14. The solid line represents the linear fit of the experimental data. Dashed lines indicate the theoretical pressure dependence according to *ab initio* calculations.

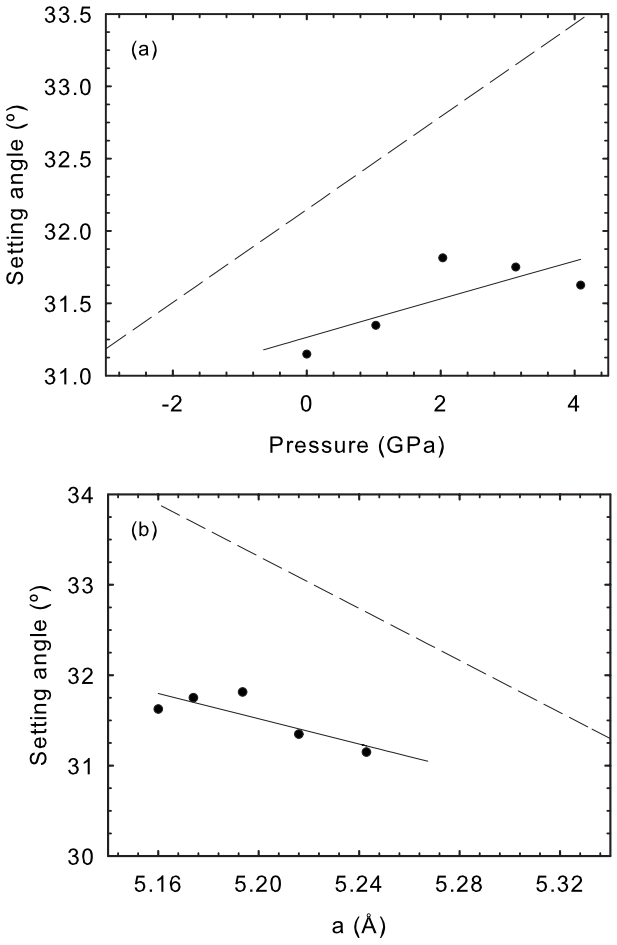

FIG. 4. Setting angle in bulk $CaWO_4$ as a function of pressure (a), and as a function of the lattice parameter (b), according to data from Ref. 14. Solid lines represent the linear fit of the experimental data. Dashed lines indicate the theoretical dependence of the setting angle according to *ab initio* calculations.

pressure range. The calculations show that, despite the difference in the absolute value, the experimental pressure dependence of the O parameters is rather well reproduced.

Figure 4(a) shows the pressure dependence of the setting angle of scheelite $CaWO_4$ in the bulk crystal that we calculated using Eq. (1) together with the experimental x and y parameters of the O atom in the unit cell of bulk $CaWO_4$ at different pressures given by Hazen *et al.* In this figure, we also plotted the *ab initio* calculated pressure dependence of the setting angle for negative pressures (dashed line). It can be observed that both experiment and theory show that the setting angle increases as a function of pressure; i.e., it decreases for negative pressures [see extrapolation of the solid line to negative pressures in Fig. 4(a)]. Note that the theoretical setting angle is slightly larger than the experimental one due to the larger values obtained for the x and y parameters of the O atom at each pressure. The increase in symmetry of the nanocrystals with reducing size reported by Li *et al.*[5] is related to the decrease in the setting angle as the nanocrystal size decreases due to the negative pressure felt by nanocrystals.[17]

Hazen *et al.* showed that the W–O bond distance in AWO_4 scheelites is rather uncompressible,[14] and, as a consequence, the decrease in the lattice parameter a with increasing pressure is mainly correlated with an increase in the setting angle. Figure 4(b) shows the evolution of the setting angle as a function of the lattice parameter a in bulk $CaWO_4$ as obtained from the data of Hazen *et al.* (symbols). A linear relationship between the setting angle and the lattice parameter a can be deduced from Fig. 4(b) in good agreement with our theoretical calculations (dashed lines). This result means that the increase in the lattice parameter a in the $CaWO_4$ nanocrystals shown in Fig. 2(a) with decreasing nanocrystal size is related to a decrease in the setting angle with decreasing the nanocrystal size in good agreement with the negative pressure present in the nanocrystals. However, the decrease in the c/a ratio in scheelite-type $CaWO_4$ nanocrystals with size smaller than 10 nm cannot be understood on the light of the negative pressure present in the nanocrystals because it was found that the decrease of pressure, i.e., increase in volume, produces an increase in the c/a ratio in the bulk material.[10,18] Therefore, one would expect an increase in the c/a ratio in scheelite-type $CaWO_4$ nanocrystals with reducing size due to their increase in the unit-cell volume with respect to the bulk.

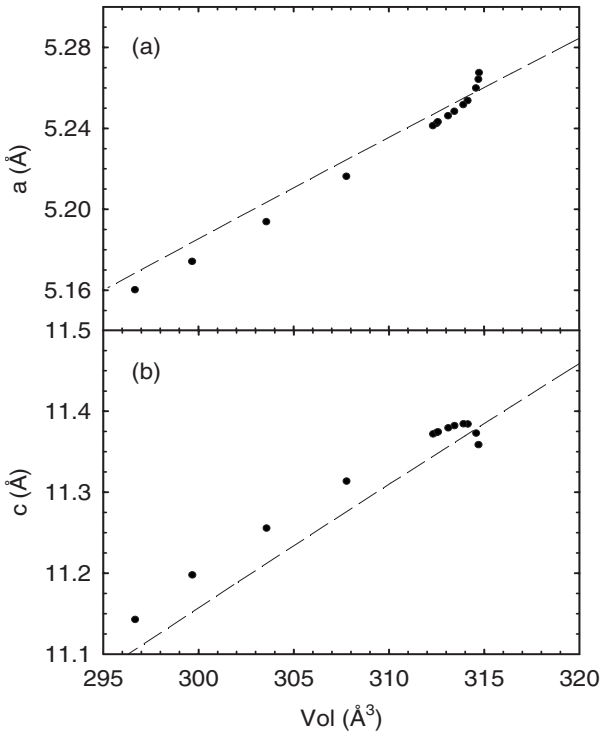

FIG. 5. Lattice parameters (a) a and (b) c of scheelite-type $CaWO_4$ nanocrystals as a function of the unit-cell volume. The dashed lines indicate the theoretical dependence of the lattice parameters as a function of the unit cell volume.

IV. HINTS OF A SIZE-INDUCED PHASE TRANSITION

In order to understand the disagreement of the pressure dependence of the experimental c/a ratio between bulk and nanocrystalline scheelite-type $CaWO_4$, we plotted in Fig. 5 the dependence of the a and c lattice parameters as a function of the unit-cell volume in the scheelite $CaWO_4$ nanocrystals as obtained from Ref. 5. For comparison, we also plotted the theoretical dependence of the lattice parameters at the same volumes in the bulk as obtained from our *ab initio* calculations (dashed lines). It can be observed that the lattice parameters of the nanocrystals with sizes below 10 nm do not behave as if they were subjected to negative pressures with their corresponding unit-cell volumes. Instead, a sudden increase (decrease) is observed for the lattice parameter a (c) for unit-cell volumes above 314 Å^3. We think that the rapid changes of the lattice parameters showed by the nanocrystals with unit-cell volumes above 314 Å^3, or equivalently for size smaller than 8.4 nm, could be indicative of a structural instability of the tetragonal scheelite structure. In the following we will discuss that the changes in the lattice parameters observed in nanocrystals with sizes below 8.4 nm are indicative of the onset of a phase transition from the scheelite to the zircon structure.

Previous *ab initio* total-energy calculations suggest that the zircon structure is a stable phase for $CaWO_4$ at negative pressures and that the negative pressure necessary to transform scheelite-type $CaWO_4$ into the zircon structure is around -2 GPa.[13] This pressure value is not far away from the negative pressure estimated to be applied to the $CaWO_4$ nanocrystals with sizes smaller than 8.4 nm (see Table I). In fact, in some materials the bulk modulus of the nanocrystals can be somewhat larger than that of the bulk.[19,20] If this was the case for the $CaWO_4$ nanocrystals, the negative pressures acting on the nanocrystals would be even higher than those estimated here and therefore closer to those necessary for the phase transition. In this case, our hypothesis would be even more confirmed than here assumed. Therefore, we think that the deviation of the lattice parameters from their expected behavior, at their associated negative pressures, is indicative of the instability of the scheelite structure and the onset of a transition to the zircon structure. A similar change in lattice symmetry with an increase in symmetry has been already observed in $CdWO_4$ nanoparticles, which crystallize in the tetragonal scheelite structure instead of the monoclinic wolframite structure of the bulk material.[9]

The zircon structure is characterized by a ratio $c/a<1$ and a setting angle $\phi=0°$. *Ab initio* calculations in $CaWO_4$ yield lattice parameters around $a=7.359$ Å and $c=6.648$ Å; i.e., with $c/a=0.9034$ for zircon-type $CaWO_4$ at the minimum of the total-energy curve as a function of unit-cell volume.[13] One could think that due to the group-subgroup relationship between the zircon and scheelite structures the phase transition between both phases should be of displacive type. The displacive-type mechanism for the scheelite-to-zircon transition could be related to the decrease in the setting angle from 32° in the scheelite phase to 0° in the zircon phase. This change in the setting angle would be simultaneous to the change in the lattice parameters a and c of the scheelite structure from $a=5.2429$ Å and $c=11.3737$ Å in bulk scheelite $CaWO_4$ to the above given values for the zircon structure. This mechanism would transform the a, b, and c axes of the scheelite structure into the a, b, and c axes of the zircon structure. However, the decrease in the setting angle from 32° to 0° involves a considerable distortion of the Ca–O distances in the CaO_8 dodecahedra and in fact four Ca–O bonds in the scheelite phase should be broken to form four new Ca–O bonds in the zircon phase. Therefore, this simple transformation mechanism through a simple tetragonal distortion is not displacive but reconstructive. The behavior of the parameters a and c in the scheelite phase shown in Fig. 1 below 8.3 nm are compatible with this type of reconstructive mechanism via a tetragonal path. An extrapolation with a logarithmic function of the data reported in Table I for nanocrystals smaller than 10.5 nm yields that $a=7.359$ Å and $c=6.648$ Å would be reached for a nanocrystal size of about 1 nm, i.e., $CaWO_4$ nanocrystals smaller than 1 nm could likely crystallize in the zircon structure.

Kusaba *et al.*[21] already studied the shock-induced zircon-to-scheelite phase transition in $ZrSiO_4$ and suggested that the mechanism for the zircon-to-scheelite phase transition was not the one described in the precedent paragraph. They suggested a reconstructive mechanism for the zircon-to-scheelite phase transition in $ZrSiO_4$ on the basis of (1) the fast transition observed between both phases in shock-wave measurements (microsecond time scale), (2) the nonreversibility of the phase transition and the rapid reversibility of the transition on increasing temperature, (3) the near 10% decrease in density when going from the zircon to the scheelite phase, (4) the large difference in the c/a ratios of

both structures, and (5) the residual strain present in the quenched crystals. The complex mechanism of the reconstructive zircon-to-scheelite phase transition that they suggested involves a two-step process: (1) a shearing deformation of the zircon tetragonal unit cell with an opening of the β angle from 90° to 115° causing a density increase of 10% and (2) a small rearrangement of atoms leading to a change of the [110] direction of the zircon phase into the [001] direction of the scheelite phase. The reconstructive zircon-to-scheelite phase transition mechanism proposed by Kusaba *et al.* can only be accomplished if a lattice with a triclinic symmetry is involved in the transition mechanism as discussed by Marqués *et al.*[22] The recent *ab initio* calculations of Marqués *et al.* that modeled the zircon-to-scheelite phase transition in $ZrSiO_4$ using an intermediate triclinic ($P\bar{1}$) structure whose β_t angle evolves from 90° at the zircon phase to 115° in the scheelite phase give support to the reconstructive mechanism of Kusaba *et al.*[22] Furthermore, Flórez *et al.* recently showed that the zircon-to-scheelite reconstructive transition in $ZrSiO_4$ occurs indeed via an intermediate structure with monoclinic $C2/c$ symmetry since the parameters of the relaxed triclinic structure obtained can be reduced to the $C2/c$ monoclinic lattice.[23] They also discussed that during the reconstructive phase transition along the monoclinic path two Zr–O bonds per ZrO_8 molecule must be broken and two new Zr–O bonds must be formed so this monoclinic mechanism is energetically favored against the tetragonal mechanism where four Zr–O bond must be broken to form four new Zr–O bonds. A similar "bond-switching" mechanism of the zircon-scheelite phase transition with two Zr–O bonds broken and two new ones formed, but with two intermediate structures (one orthorhombic and one monoclinic with $C2/c$ symmetry) has also been recently proposed giving support to the reconstructive mechanism of the zircon-to-scheelite phase transition in $ZrSiO_4$ in agreement with Kusaba *et al.*[24]

In order to investigate whether the evolution of the lattice parameters a and c of the scheelite phase for nanocrystal sizes below 8.3 nm is compatible with the scheelite-to-zircon phase transition through the monoclinic path recently proposed for bulk $ZrSiO_4$, we plotted in Fig. 6 the lattice parameters of the monoclinic intermediate cell obtained from the lattice parameters of the scheelite cell. According to Ref. 23, the lattice vectors of the monoclinic cell written in terms of the scheelite unit cell are $\mathbf{a}_m=-\mathbf{a}_s-\mathbf{b}_s$, $\mathbf{b}_m=\mathbf{c}_s$, and $\mathbf{c}_m=\mathbf{b}_s$. Therefore, the lattice parameters of the monoclinic structure given in terms of the lattice parameters of the scheelite structure are $a_m=\sqrt{2}a_s$, $b_m=c_s$, and $c_m=b_s$. Figure 6 shows that the behavior of the lattice parameters below 8.3 nm is in good agreement with the expected behavior of the scheelite-to-zircon transition through the intermediate monoclinic $C2/c$ structure reported in Refs. 23 and 24. Therefore, we can conclude that the behavior of the structural parameters a and c of the scheelite-type nanocrystals with size smaller than 8.4 nm agree with the expected behavior of the lattice parameters during the scheelite-to-zircon phase transition either by the tetragonal or by the monoclinic path. In summary, the present structural data do not allow us to determine which one is the right mechanism of the scheelite-to-zircon phase transition in $CaWO_4$ nanocrystals.

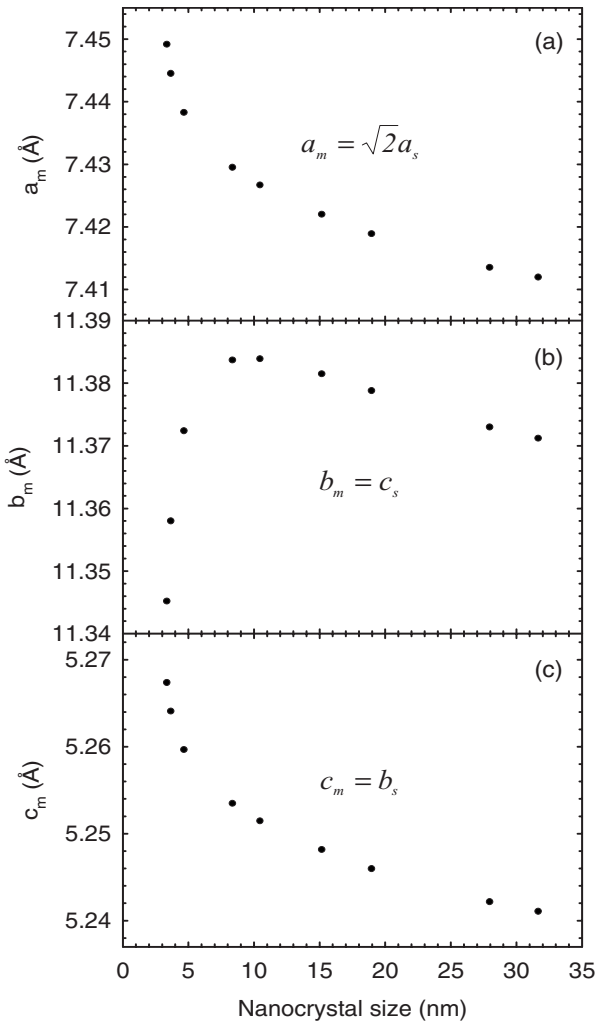

FIG. 6. Lattice parameters a_m, b_m, and c_m of the monoclinic cell of $CaWO_4$ as a function of the nanocrystal size as obtained from the lattice parameters a_s, b_s, and c_s of the scheelite cell of $CaWO_4$ plotted in Fig. 1.

The mechanism of the schelite-to-zircon phase transition in $CaWO_4$ nanocrystals can be determined if the x, y, and z parameters of the generatrix O of the scheelite phase were known for nanocrystals below 8.4 nm as they are known for bulk $CaWO_4$ (see Fig. 3). It is expected that the z parameter varies rather smoothly during the transition along the tetragonal path because the WO_4 just suffers a rotation around the c axis of the scheelite. On the other hand, the z parameter must suffer a considerable change along the monoclinic path because the WO_4 tetrahedra have to be completely reoriented during this phase transition due to the fact that in the monoclinic path the a direction of the scheelite phase transforms into the c direction of the zircon phase. Another possibility to determine the mechanism of the transition in nanocrystals is to measure their Raman scattering. These measurements could evidence the mechanism by observation or absence of Raman peaks due to the change in lattice symmetry. In the case of the tetragonal path, the Raman spectrum of the scheelite phase will not change at all until it gets the setting angle equal to 0°. At this very moment one of the phonon peaks of the spectrum will disappear since the Raman spectrum of the zircon phase has 12 Raman-active modes compared to the 13 Raman-active modes of the scheelite phase.

On the other hand, if the transition mechanism is through a monoclinic $C2/c$ structure then one would observe five additional Raman peaks compared to those of the scheelite phase or six compared to the zircon phase, since $HgWO_4$ and $CaWO_4$ above 10 GPa crystallize in the monoclinic $C2/c$ phase and exhibit 18 Raman-active modes.[25,26] A similar reasoning applies for the infrared-active modes. In fact, Raman and infrared measurements on the $CaWO_4$ nanocrystals have been already performed.[6] They show that only the Raman modes of the scheelite phase are observed even for the smallest nanocrystal sizes. This result, together with the abrupt increase (decrease) in the a (c) lattice parameter of the scheelite phase for negative pressures, could be the evidence of the scheelite-to-zircon phase transition occurring via the tetragonal path instead of through the intermediate monoclinic structure proposed for $ZrSiO_4$.[22–24] It must be noted that the only net effect observed in the Raman spectrum of $CaWO_4$ nanocrystals with 3.6 nm (Ref. 6) is a broadening of the Raman bands and a small Raman shift to lower wave numbers of most of the observed peaks.[26] This small shift is fully compatible with the negative pressure present in the nanocrystals and does not evidence any monoclinic distortion of the scheelite structure.

V. CONCLUSIONS

We have shown evidence that $CaWO_4$ nanocrystals with sizes below 30 nm reported in Refs. 5 and 6 are subjected to negative pressures that cause an instability of the scheelite phase and lead to the onset of the scheelite-to-zircon phase transition in $CaWO_4$ nanocrystals with sizes smaller than 8.4 nm. The scheelite-to-zircon phase transition in $CaWO_4$ nanocrystals is of reconstructive character and seems to proceed through a tetragonal distortion of the scheelite structure unlike in bulk $ZrSiO_4$ where it is proposed to proceed through a monoclinic path. The hypothesis for the tetragonal path for the phase transition is supported by the absence of Raman peaks corresponding to the monoclinic deformation of the scheelite structure even in the nanocrystals with smallest size. The reason for the different transition mechanism observed in the nanocrystals with respect to that proposed in the bulk could be related to the reduction in the energy barrier of the transition through the tetragonal path due to (i) the important participation of the surface energy in nanocrystals and/or (ii) the presence of impurities attached to the nanocrystals. In this respect, we want to stress that it is possible that the increase in the surface/volume ratio in the nanocrystals and/or the chemical substances attached to the nanocrystals (H_2O and $C_6H_8O_7$) might reduce the energy barrier (around 236 kJ/mol in bulk[22]) necessary for the tetragonal scheelite-to-zircon phase transition resulting in a different pressure-induced phase transition mechanism in the nanocrystals not previously found in the bulk.[27]

Further studies in scheelite-type nanocrystals are needed to confirm the mechanism of the scheelite-to-zircon phase transition in the $CaWO_4$ nanocrystals. In particular, neutron diffraction experiments in nanocrystals could help in determining the x, y, and z parameters of the O in the scheelite phase under negative pressures to give information on the behavior of the setting angle and the real behavior of the Ca–O distances in the nanocrystals. Besides, new XRD experiments could report the appearance or absence of a small peak of the monoclinic $C2/c$ phase at angles near $2\theta=4°$, the disappearance of the strong peak corresponding to the (112) and (103) Bragg reflections of scheelite $CaWO_4$ (Ref. 28) at $2\theta=27°$ in Ref. 5, and the appearance of a strong peak corresponding to the (200) Bragg reflection of zircon $CaWO_4$ at $2\theta=25°$, provided that XRD experiments are performed at the same energy used in Ref. 5. Additionally, new Raman measurements with higher resolution and covering the whole range from 50 to 1000 cm^{-1} could help in verifying whether the mechanism of the reconstructive phase transition goes along the tetragonal or monoclinic path. Finally, we want to note that a similar behavior is also expected in $CaMoO_4$ nanocrystals of similar size to those of $CaWO_4$ nanocrystals since the stability of the scheelite phase in both compounds is very similar.

ACKNOWLEDGMENTS

F.J.M. acknowledges interesting discussions with J.M. Recio and M. Flórez. This study was supported by the Spanish MCYT under Grant Nos. MAT2006-02279, MAT2007-65990-C03-01, MAT2007-65990-C03-03, and CSD2007-00045 and by the Generalitat Valenciana (Project No. GV2008/112). F.J.M. also acknowledges financial support from "Vicerrectorado de Innovación y Desarrollo de la UPV" through Project No. UPV2008-0020.

[1] D. Errandonea and F. J. Manjón, Prog. Mater. Sci. **53**, 711 (2008).
[2] A. P. A. Marques, F. V. Motta, E. R. Leite, P. S. Pizani, J. A. Varela, E. Longo, and D. M. A. de Melo, J. Appl. Phys. **104**, 043505 (2008).
[3] Y. Wang, J. Ma, J. Tao, X. Zhu, J. Zhou, Z. Zhao, L. Xie, and H. Tian, Mater. Lett. **60**, 291 (2006).
[4] A. Katelnikovas, L. Grigirjeva, D. Millers, V. Pankratov, A. Kareiva, and J. Lithuanian, Physics **47**, 63 (2007).
[5] L. P. Li, Y. G. Su, and G. S. Li, Appl. Phys. Lett. **90**, 054105 (2007).
[6] Y. G. Su, G. S. Li, Y. F. Xue, and L. P. Li, J. Phys. Chem. C **111**, 6684 (2007).
[7] T. Thongtem, A. Phuruangrat, and S. Thongtem, Appl. Surf. Sci. **254**, 7581 (2008).
[8] Z. Chen, Q. Gong, J. Zhu, Y. P. Yuan, L. W. Qian, and X. F. Qian, Mater. Res. Bull. **44**, 45 (2009).
[9] A. J. Rondinone, M. Pawel, D. Travaglini, S. Mahurin, and S. Dai, J. Colloid Interface Sci. **306**, 281 (2007).
[10] D. Errandonea, J. Pellicer-Porres, F. J. Manjón, A. Segura, Ch. Ferrer-Roca, R. S. Kumar, O. Tschauner, P. Rodríguez-Hernandez, J. Lopez-Solano, A. Mujica, A. Muñoz, and G. Aquilanti, Phys. Rev. B **72**, 174106 (2005); **73**, 224103 (2006).
[11] F. J. Manjón, D. Errandonea, N. Garro, J. Pellicer-Porres, P. Rodríguez-Hernández, S. Radescu, J. López-Solano, A. Mujica, and A. Muñoz, Phys. Rev. B **74**, 144111 (2006); **74**, 144112 (2006).
[12] D. Errandonea, D. Martinez-Garcia, R. Lacomba-Perales, J. Ruiz-Fuertes, and A. Segura, Appl. Phys. Lett. **89**, 091913 (2006).
[13] J. López-Solano, P. Rodríguez-Hernández, S. Radescu, A. Mujica, A. Muñoz, D. Errandonea, F. J. Manjón, J. Pellicer-Porres, N. Garro, A. Segura, Ch. Ferrer-Roca, R. S. Kumar, O. Tschauner, and G. Aquilanti, Phys. Status Solidi B **244**, 325 (2007).
[14] R. M. Hazen, L. W. Finger, and J. W. E. Mariathasan, J. Phys. Chem. Solids **46**, 253 (1985).
[15] A. Grzechnik, W. A. Crichton, M. Hanfland, and S. Van Smaalen, J. Phys.: Condens. Matter **15**, 7261 (2003).
[16] The bulk modulus in nanocrystals might be different to that in the bulk material. In fact, for many materials the bulk modulus in nanocrystals is usually slightly larger than in the bulk. However, the main conclusions of

this work do not depend on the value of the bulk modulus considered for the nanocrystals because a different bulk modulus would only imply a slightly different negative pressure in the nanocrystals.
[17]Note that a setting angle $\phi=0$ would be consistent with a zircon structure provided that there is a change in the lengths of the c and a axes to satisfy a $c/a<1$ ratio.
[18]D. Errandonea, F. J. Manjón, M. Somayazulu, and D. Häusermann, J. Solid State Chem. **177**, 1087 (2004).
[19]J. Z. Jiang, J. S. Olsen, L. Gerward, and S. Morup, Europhys. Lett. **44**, 620 (1998).
[20]J. E. Jorgensen, J. M. Jakobsen, J. Z. Jiang, L. Gerward, and J. S. Olsen, J. Appl. Crystallogr. **36**, 920 (2003).
[21]K. Kusaba, T. Yagi, M. Kikuchi, and Y. Syono, J. Phys. Chem. Solids **47**, 675 (1986).
[22]M. Marqués, J. Contreras-García, M. Flórez, and J. M. Recio, J. Phys. Chem. Solids **69**, 2277 (2008).
[23]M. Flórez, J. Contreras-García, J. M. Recio, and M. Marqués, Phys. Rev. B **79**, 104101 (2009).
[24]M. B. Smirnov, A. P. Mirgorodsky, V. Yu. Kazimirov, and R. Guinebretière, Phys. Rev. B **78**, 094109 (2008)
[25]G. Blasse, J. Inorg. Nucl. Chem. **37**, 97 (1975).
[26]D. Christofilos, S. Ves, and G.A. Kourouklis, Phys. Status Solidi B **198**, 539 (1996).
[27]H. Z. Liu, C. Q. Jin, and Y. H. Zhao, Physica B **315**, 210 (2002).
[28]In Ref. 5 the Bragg peaks are mislabelled, the five peaks reported are indeed (101), (112), (103), (004), and (200), see A. Zalkin and D. H. Templeton, J. Chem. Phys. **40**, 501 (1964).