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Size-induced symmetric enhancement and its relevance to photoluminescence of scheelite CaWO₄ nanocrystals

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This work explores size-induced lattice modification and its relevance to photoluminescence properties of scheelite nanostructures. CaWO₄ nanocrystals, a prototype scheelite compound, exhibited a lattice expansion and an increased symmetry of structural units with physical dimension reduction, which is in contradiction to the trend previously reported in bulk CaWO₄ at high pressures or high temperatures. Lattice variations in CaWO₄ nanocrystals are probably due to the "negative pressures" that originated from strong defect dipole interactions on surfaces. The increased structural symmetry along with surface citric modifications produced a significant enhancement in photoluminescence of CaWO₄ nanocrystals, indicating a quantitatively structural control over the electronic properties. © 2007 American Institute of Physics. [DOI: 10.1063/1.2450659]

Alkaline metal tungstates of scheelite-like structures have broad applications in fundamental and applied sciences including photoluminescence, microwave devices, optical fibers, and next generation of hybrid cryogenic phononscintillation detectors.^{1–5} All these applications are highly dependent on the lattice dimension and band structures. From the solid state physics viewpoint, details of the band structure are primarily determined by the static potential within unit cells, and any symmetry perturbation in unit cell can have consequences on the electronic structures and physical properties. Nanocrystals show properties that depend strongly on structure. Variations in lattice dimension and symmetry often accompany particle size reductions.⁵⁻⁷ Therefore, an experimental identification of the nanoscale lattice modifications is advantageous for tuning the band structure and moreover physical properties of nanocrystals. Photoluminescence is sensitive to the local lattice symmetry and could be used as an intrinsic probe to map out such variations in scheelite nanocrystals. Sample quality and nanoparticle sizes currently limit this approach.

For instance, particle size control of scheelite CaWO₄ nanocrystals has been extensively studied,⁸⁻¹¹ it is still very difficult to get the diameter smaller than 10 nm for pronounced size effects without loss of sample quality. Using ethylene glycol at 180 °C, Chen et al.,⁸ obtained CaWO₄ nanoparticles of 40 nm in diameter, which is too large to result in apparent changes in band structures and physical properties. Ryu et al.9 prepared a small diameter of 12-35 nm using a microwave irradiation as followed by a heat treatment at high temperatures, while some amounts of amorphous phases are still observed to coexist with 12 nm CaWO₄. The difficulties in diameter control of high quality CaWO₄ nanocrystals and the lack of experimental knowledge about the relevant lattice dimensions impose obvious limitations regarding the application to the interpretation of the band structures and the entire set of physical properties.

CaWO₄ represents a prototype scheelite compound that shows a closely structural link to many materials such as CaMoO₄, PbMoO₄, PbWO₄, YLiF₄, and high pressure phases of TbVO₄ and DyVO₄. A systematic study on the physical dimension control and size-related photoluminescence properties of CaWO₄ nanocrystals is expected to provide information on the band-gap tailorings of a broad class of nanoscale materials for many applications. In this work, we report on the synthesis of CaWO₄ nanocrystals at sizes ranging from 3.4 to 31.7 nm. We investigated the sizeinducted lattice variations and their correlation to the photoluminescence properties of CaWO₄ nanocrystals. Our highly crystalline CaWO₄ nanocrystals luminesced more intensively than those samples prepared by other synthetic techniques.

Highly crystalline CaWO₄ nanocrystals were prepared by a hydrothermal method. 0.5M Na₂WO₄ solution was mixed with 80 ml of CaCl₂ and citrate acid solution at given concentrations. A well-controlled amount of NaOH solution was then carefully added to the clear solution until pH=8. After aging at room temperature for 12 h, a white dispersion (CaWO₄ seeds) was homogeneously formed. The mother solution containing CaWO₄ seeds was sealed in Teflon-lined stainless steel autoclaves which were allowed to react at different temperatures for 12 h. Sample structures were characterized by x-ray diffraction (XRD). Lattice parameters were calculated using Retica Rietveld program with peak positions that are calibrated by internal standard of nickel. Average sizes were calculated using Scherrer formula and were further confirmed by transmission electron microscope (TEM). Chemical species bonded to sample surfaces were examined by infrared spectra, while their amounts were quantitatively determined by a combustion analysis method. Photoluminescence (PL) spectra of the samples were recorded using FLS920 luminescence spectrometer under an excitation line of 243 nm.

All samples gave diffraction peaks (Fig. 1) that are essentially identical to the standard data for bulk $CaWO_4$,¹² which indicates the formation of single-phase tetragonal *scheelite* structure. The internal strains were very small and ignored here. The average size for $CaWO_4$ seeds was calcu-

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FIG. 1. XRD patterns for $CaWO_4$ nanocrystals at given particle sizes. The vertical bars represent the standard diffraction data for bulk $CaWO_4$ from JCPDS file (Ref. 12). The inset is a high resolution TEM image for 15.1 nm $CaWO_4$.

lated to be 3.4 nm from peak broadening, which seems to be the only example of preparation of CaWO₄ with dimension smaller than 5 nm. With increasing the reaction temperatures to 190 °C, the diffraction peaks became narrowed (Fig. 1), and the physical dimension of CaWO₄ seeds grew up to 31.7 nm. TEM observations (inset of Fig. 1) indicated that all particles were tiny single crystals in a spindly shape with average diameters being much closer to those calculated from broadened diffraction line. The spacing between adjacent lattice fringes along the orientation direction is 0.282 nm, which is comparable with d spacing of 0.285 nm for (004) plane as calculated for 15.1 nm $CaWO_4$. Therefore, CaWO₄ nanocrystals were oriented along *c*-axis direction. The surfaces of CaWO₄ nanocrystals were confirmed by IR spectra (not shown) to be chemically bonded with citrate species and hydration layers. The chemical formula of CaWO₄ nanocrystals is thus described as CaWO₄ xH_2O . yC₆H₈O₇. Our careful chemical analysis of carbon and hydrogen clearly demonstrated that the molar ratios of citrate species (y) and absorbed water (x) increased with particle size reduction (Fig. 2).

Figure 3 illustrated the lattice parameters of CaWO₄ nanocrystals as a function of particle sizes. Lattice volume increased monotonically with particle size reduction [Fig. 3(a)], while the axial ratio of c/a decreased from 2.169 to 2.154 [Fig. 3(b)], tending to c/a=2 for an ideal structure of scheelite phase with equal cation coordination.¹³ This observation clearly indicated that the symmetry of structural units increased with physical dimension reduction (or lattice



FIG. 2. Particle size dependence of molar ratios of absorbed water molecules and citric species in CaWO₄ nanocrystals. The chemical formula of CaWO₄ nanocrystals is described as CaWO₄ · $xH_2O \cdot yC_6H_8O_7$.



FIG. 3. Particle size dependence of (a) lattice volume and (b) axis ratio of c/a for CaWO₄ nanocrystals.

expansion). Consequently, the lattice dimension dependence of structural symmetry for CaWO₄ nanocrystals [Fig. 3(b)] is opposite to what is observed in bulk under high pressures¹³ or at high temperatures.¹⁴ For the latter cases, a decrease in lattice volume gives rise to an increased symmetry (or c/a axis ratio decrease).

The lattice expansion observed in Fig. 3(a) could arise from a number of possible sources. An unlikely source would be surface stresses, since these give a lattice contrac-tion in metal nanocrystals.¹⁵ We proposed that the causes of lattice expansion in CaWO₄ nanocrystals are primarily due to the chemical bonding variations of framework ions under "negative pressure" effects. In a tetragonal scheelite structure, one tungsten atom is coordinated with four oxygen atoms and formed an isolated tetrahedron.¹¹ The bonding between Ca^{2+} and WO_4^{2-} is mainly ionic, whereas inside WO_4 polyhedron, the W-O bonds are primarily covalent with almost equal bond lengths. The outmost surfaces of CaWO₄ nanocrystals could be terminated with a large fraction of unsaturated calcium ions and/or tungstate groups, most likely creating an imbalance of the charges at solid boundaries/or surfaces. Consequently, a defect dipole layer is expected to occur.³ Though these dipole moments on surfaces could be partially removed by chemical bonding of citrate species and absorbed water molecules, the repulsive interactions among these dipoles might be strong enough to yield negative pressure by varying the chemical nature of ionic $Ca^{2+}-WO_4^{2-}$ bonds for lattice expansion [Fig. 3(a)]. Size-dependent covalency/ionicity data are unavailable for the present nanocrystals, nevertheless Boerio-Goates et al.⁵ have argued that lattice expansion in ionic rutile TiO₂ nanocrystals is correlated with the negative pressure and the resulting covalency enhancement.

With regards to the symmetry enhancement in $CaWO_4$ nanocrystals [Fig. 3(b)], it has to take into account the influences of hydrated surfaces on surface energies. Just like what is observed in many nanoscale oxides and mineral oxides,¹⁶ the surfaces of CaWO₄ nanocrystals were highly hydrated (Fig. 2). According to a theoretical work on bulk CaWO₄,¹⁷ surface hydration gives rise to decreased surface energies



FIG. 4. PL spectra of $CaWO_4$ nanocrystals with diameters of (a) 31.7 nm, (b) 15.1 nm, (c) 9.3 nm, and (d) 3.4 nm.

depending on the crystal planes. Consequently, size reduction may have impacts on the symmetry of structural units and the resulting properties. In bulk, WO₄ units are directly aligned along a axis, whereas along c axis there is a Ca cation located between two WO₄ tetrahedra. As a result, the variability of axis length along c and a directions is reasonable to occur, owing to the different arrangements of hard WO₄ tetrahedra. Consistent with the oriented growth of CaWO₄ nanocrystals along the c-axis direction (Fig. 1), the hydrated {001} plane exhibits the lowest surface energy of 0.36 J m⁻² among all exposed planes, while the surface energy for hydrated {100} and {010} planes is comparatively large, being around 1.06 J m⁻².¹⁷ Therefore, a decreased c/aaxis ratio is expected since the dipole-dipole interactions on the polar end surfaces (001) might have very limited influence on the lattice dimension, which explains the enhanced structural symmetry in CaWO₄ nanocrystals.

Photoluminescence is sensitive to the lattice variations and surface modifications. All CaWO₄ nanocrystals gave a dominant emission centered at 421 nm (Fig. 4), which is attributed to the intrinsic electronic transfer of WO₄ (Ref. 18) or to the self-trapped centers with exciton energies being located within the band gap.¹⁹ PL emission for the present nanocrystals persisted smaller than 10 nm, while those for other nanocrystals are hard to see even at particle sizes of about 20 nm.¹⁹ To understand the nature of this apparent inconsistency, an analysis of microstructural factors of CaWO₄ nanostructures is required. As stated above, the symmetry of structural units of CaWO₄ nanocrystals increased with particle size reduction, which would decrease the luminescence intensity.²⁰ Surface hydration may weaken to certain extent the luminescence intensity because OH⁻ groups from the absorbed water could act as the luminescent quenchers.²¹ These results do not mean that the luminescence intensity can be always decreased with particle size reduction, since CaWO₄ nanocrystal surfaces are also chemically bonded with citric species (Fig. 2) which may reduce dangling bond density on surfaces and hence the number of trap sites for nonradiative recombination. For the latter case, the quantum efficiency of photoluminescence could be significantly enhanced,²² somewhat like what has been observed for sulfide nanocrystals with surfaces being modified by organic materials.²³ The balance of all these factors might be the primary cause for the enhanced photoluminescence emission of CaWO₄ nanocrystals even at a small size of 3.4 nm.

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- ¹V. Pankratov, L. Grigorjeva, D. Millers, S. Chernov, and A. S. Voloshinovskii, J. Lumin. **94**, 427 (2001).
- ²I. H. Park, B. S. Kim, K. Y. Kim, and L. H. Kim, Jpn. J. Appl. Phys., Part 1 **40**, 4956 (2001).
- ³P. Mogilevsky, T. A. Parthasarathy, and M. D. Petry, Acta Mater. **52**, 5529 (2004).
- ⁴D. S. Kim, M. Ostromecki, and I. E. Wachs, J. Mol. Catal. A: Chem. **106**, 93 (1996).
- ⁵G. Li, J. Boerio-Goates, B. F. Woodfield, and L. Li, Appl. Phys. Lett. **85**, 2059 (2004).
- ⁶X. D. Zhou and W. Huebner, Appl. Phys. Lett. **79**, 3512 (2001).
- ⁷D. Schroeer and R. C. Nininger, Phys. Rev. Lett. **19**, 632 (1967).
- ⁸D. Chen, G. Z. Shen, K. B. Tang, H. G. Zheng, and Y. T. Qian, Mater. Res. Bull. **38**, 1783 (2003).
- ⁹J. H. Ryu, J. W. Yoon, C. S. Lim, W. C. Oh, and K. B. Shim, Ceram. Int. **31**, 883 (2005).
- ¹⁰A. Senyshyn, H. Kraus, V. B. Mikhailik, and V. Yakovyna, Phys. Rev. B **70**, 214306 (2004).
- ¹¹M. I. Kay, B. C. Frazer, and I. J. Almodovar, J. Chem. Phys. 40, 504 (1964).
- ¹²JCPDS card No. 41-1431.
- ¹³D. Errandonea, F. J. Manjón, M. Somayazulu, and D. Häusermann, J. Solid State Chem. **177**, 1087 (2004).
- ¹⁴S. N. Achary, S. J. Patwe, M. D. Mathews, and A. K. Tyagi, J. Phys. Chem. Solids **67**, 774 (2006).
- ¹⁵A. Taneda and Y. Kawazoe, J. Magn. Soc. Jpn. **23**, 679 (1999); E. Anno and M. Tanimoto, Phys. Rev. B **73**, 155430 (2006); W. H. Qi and M. P. Wang, J. Nanopart. Res. **7**, 51 (2005).
- ¹⁶H. A. Al-Abadleh and V. H. Grassian, Surf. Sci. Rep. **52**, 63 (2003).
- ¹⁷T. G. Cooper and N. H. de Leeuw, Surf. Sci. **531**, 159 (2003).
- ¹⁸A. Jayaraman, B. Batlogg, and L. G. VanUitert, Phys. Rev. B **31**, 5423 (1985).
- ¹⁹S. J. Chen, J. Li, X. T. Chen, J. M. Hong, Z. L. Xue, and X. Z. You, J. Cryst. Growth **253**, 361 (2003).
- ²⁰J. W. Stouwdam, M. Raudsepp, C. J. M. Frank, and van Veggel, Langmuir 21, 7003 (2005).
- ²¹Y. Haas and G. Stein, Chem. Phys. Lett. **15**, 12 (1972); W. Di, X. Wang, B. Chen, S. Lu, and X. Zhao, J. Phys. Chem. B **109**, 13154 (2005).
- ²²M. Konishi, T. Isobe, and M. Senna, J. Lumin. **93**, 1 (2001).
- ²³M. Jones, J. Nedeljkovic, R. J. Ellingson, A. J. Nozik, and G. Rumbles, J.

Phys. Chem. B 107, 11346 (2003).