PHYSICAL REVIEW B **81**, 104109 (2010)

Zircon-monoclinic-scheelite transformation in nanocrystalline chromates

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(Received 16 December 2009; revised manuscript received 12 February 2010; published 17 March 2010)

Our *in-situ* high-pressure x-ray diffraction measurements on zircon structured nanocrystalline chromates show that the structural phase transformation from zircon to scheelite phase proceeds via an intermediate monoclinic phase, i.e., zircon→monoclinic→scheelite. Though there have been speculations about zircon-scheelite phase transformation proceeding through an unstable transient monoclinic phase in $ZrSiO_4$, we have experimentally demonstrated the existence of a similar intermediate stable state in a zircon structured compound. For our nanocrystalline samples, the transformation pressure is found to be higher than the bulk.

DOI: 10.1103/PhysRevB.81.104109 PACS number(s): 81.40.Vw, 61.50.Ks, 64.70.K−

I. INTRODUCTION

Zircon ($ZrSiO_4$) is an important mineral found in the earth's crust, mainly in igneous rocks and sediments.[1] It is known to undergo a first-order crystalline phase transition from the zircon (SG $I4_1/amd$ and $Z=4$) to the reidite (scheelite $I4_1/a$ and $Z=4$) form at ~23 GPa. Several isostructural ABO$_4$-type compounds, such as the vanadates, chromates, germanates, also undergo the same high-pressure phase transition, displaying a typical density increase of ~10%.[2–6] Static as well as shock experiments on $ZrSiO_4$ support the martensitic nature of this phase transformation.[7,8]

Kusaba *et al.* suggested that zircon to scheelite transformation may be brought about by shear deformations. The suggested mechanism is based on the elongation/compression along the two equivalent (110) directions in the basal plane of the zircon phase, followed by a small displacement of the atoms and rotation of the SiO_4 tetrahedra.[9] However, based on the observations of abrupt changes observed in frequencies of the Raman internal modes across this transition, Jayaraman *et al.* argued that the transformation path cannot be this simplistic.[6] They felt that the Raman results indicate a substantial rearrangement of the cations and the anions, both in length and angle.

Recent theoretical *ab initio* and shell model calculations on $ZrSiO_4$ by Smirnov *et al.*[10] show absence of any dynamical structural instability up to ~70 GPa. Therefore they have concluded that hydrostatic compression alone cannot be responsible for this phase transition and instead it must be caused by anisotropic strains. Energy barrier heights obtained through first-principles calculations by Florez *et al.* indicate that transient states between zircon and scheelite phases are likely to be monoclinic.[11]

Though not of direct relevance in terms of mechanism, we should also mention here that a recent Raman investigation on zircon structured $TbPO_4$ shows its transformation to a monazite structured monoclinic phase at high pressure.[12] Isostructural compounds such as $YCrO_4$,[13] $LuVO_4$, $YbVO_4$,[14] YVO_4,[3] also transform to the scheelite phase at 3, 8, 5.9, and 8.5 GPa, respectively. If this phase transformation in the chromates and the vanadates is primarily due to shear strains, as proposed in Ref, 10, it is difficult to explain, why these compounds transformed even though they were well within the hydrostatic limits of the pressure transmitting media viz., 4:1 methanol:ethanol and nitrogen. All these results imply that the zircon to scheelite phase transformation path is yet not fully understood, despite a large number of studies on zircon and isostructural compounds.

Another issue which needs to be understood in this set of compounds is the dependence of their high-pressure behavior on particle size. For example, would the high-pressure behavior of the nanoparticles be the same as that of the bulk material? Would they undergo the same phase transition as that observed in the bulk or they would tend to amorphize at high pressure? It is well known that the thermodynamic properties of nanocrystalline materials may differ significantly from their bulk counterparts due to large surface to volume ratio.[1,15–17] In fact Tolbert *et al.*[18] showed that in nanocrystalline CdSe the transformation pressure for wurtzite to rocksalt transformation increased on decreasing the particle size. Further, the increase or decrease in the transformation pressure of the nanocrystalline materials has been shown to depend on the ratio of the volume collapse in bulk and nanocrystalline samples at the transformation pressure and the differences between surface and the internal energies.[19] The surface versus bulk free energy contributions also affect the stability of the crystalline phases and a whole new phase diagram can be assigned to the nanocrystalline materials.[15]

It is well known that zircon and zircon structured compounds in the bulk form, are poor glass formers and have not yet been amorphized at high pressures. Recent studies have shown that bulk $ZrSiO_4$ can be amorphized at room pressure when irradiated with heavy ions.[20] However, when bulk $ZrSiO_4$ was simultaneously subjected to high pressure and heavy ion irradiation, it fragmented into nanoparticles and then transformed to the scheelite phase at ~14.5 GPa, i.e., at much lower pressures than the bulk.[21] In contrast, another study has shown that the transition pressure for zircon-scheelite phase change is higher for nanocrystalline zircon.[22,23] Therefore, there is an ambiguity about the size and transformation-pressure correlation. The understanding of this would have implications on the usage of reidite (scheelite phase of zircon) as a peak pressure indicator in meteoric impacts.[9]

To understand some of the issues mentioned in the last two paragraphs it is important to carry out high-pressure in-

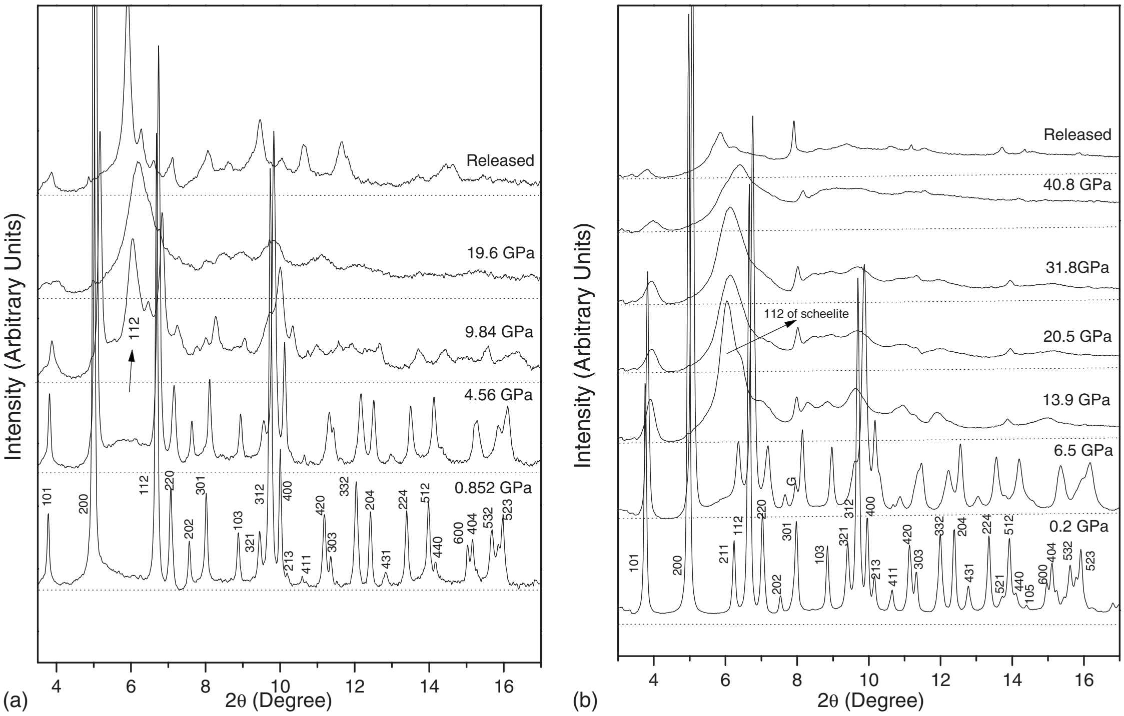

FIG. 1. [(a) and (b)] The diffraction pattern of (a) $YCrO_4$ and (b) $HoCrO_4$ collected at a few representative pressures ($\lambda = 0.308$ Å). The ambient pressure data has been indexed with respect to the zircon structure. The diffraction peaks of the high-pressure phase have been indicated by arrows. The diffraction peak marked as (112) at high pressure refers to the scheelite phase. The background of the lowest pressure phase has been subtracted from all the subsequent pressure runs. From the figure we can see that the background increases with pressure and is retained even on release of pressure suggesting partial amorphization of the nanochromates at high pressure.

vestigations on some nanocrystalline zircon structured compounds, which in the bulk show transformation to the scheelite phase at very low pressures. Since the bulk forms of $YCrO_4$ and $HoCrO_4$ transform to the scheelite phase at $P < 5$ GPa, i.e., well within the hydrostatic pressure regime of most of the pressure transmitting media employed in diamond anvil cells, we have investigated the structural behavior of the nanocrystalline forms of these chromates at high pressures. Our results show that the transition from the zircon to scheelite phase in these chromates proceeds via an intermediate monoclinic phase and hence it is not a one step process. Moreover, this intermediate monoclinic structure is distinct from the monazite structure observed earlier in $TbPO_4$ (Ref. 12) and has been observed for the first time in the zircon structured compounds. We also observed a partial amorphization of the zircon structured chromates at high pressure.

II. EXPERIMENT

Fully characterized nanocrystalline $RECrO_4$ (RE=Y, Ho) synthesized by gel-combustion process were subjected to hydrostatic high-pressure conditions in a diamond-anvil cell. In different experiments the powder samples of yttrium chromate and holmium chromate along with appropriate pressure markers (Cu) or ruby were loaded into a 100 μm hole of a preindented tungsten gasket (70 μm) in the diamond-anvil cell. 16:3:1 methanol-ethanol-water mixture was used as a pressure transmitting medium and the pressure was determined from the ruby fluorescence technique[24] or the known equation of state of copper.[25] To ensure that the sample environment was truly hydrostatic we ensured that the sample does not directly bridge the diamonds and the gasket hole has substantial amount of pressure transmitting fluid. The average crystallite size of these nanocrystalline chromates, as deduced from the Scherrer's formula was ~69 nm. The x-ray diffraction experiments were carried out at BL10XU beamline at Spring8 ($\lambda = 0.308$ Å) and at XRD1 beamline at Elletra ($\lambda = 0.67$ Å). Some of the results were also verified using Raman measurements carried out on a confocal micro-Raman experimental setup in our laboratory.

III. RESULTS AND DISCUSSION

The diffraction patterns of $YCrO_4$ and $HoCrO_4$ at a few representative pressures are shown in Fig. 1. The diffraction patterns from both these compounds show that up to ~6.5 GPa there is a monotonous shift in the diffraction peaks toward higher two-theta values. Figure 2 shows the full width at half maximum (FWHM) of some of the diffraction peaks of the samples while their diffraction patterns are still indexable as that of zircon phase. We find a large increase in the FWHM of some of the diffraction peaks such as, (321), (312), (332), etc., whereas the FWHM of the (101), (200), and (202) diffraction peaks show relatively negligible change from their ambient values. Earlier such variations have been ascribed to the shape change in crystallites across a phase transformation.[26,27]

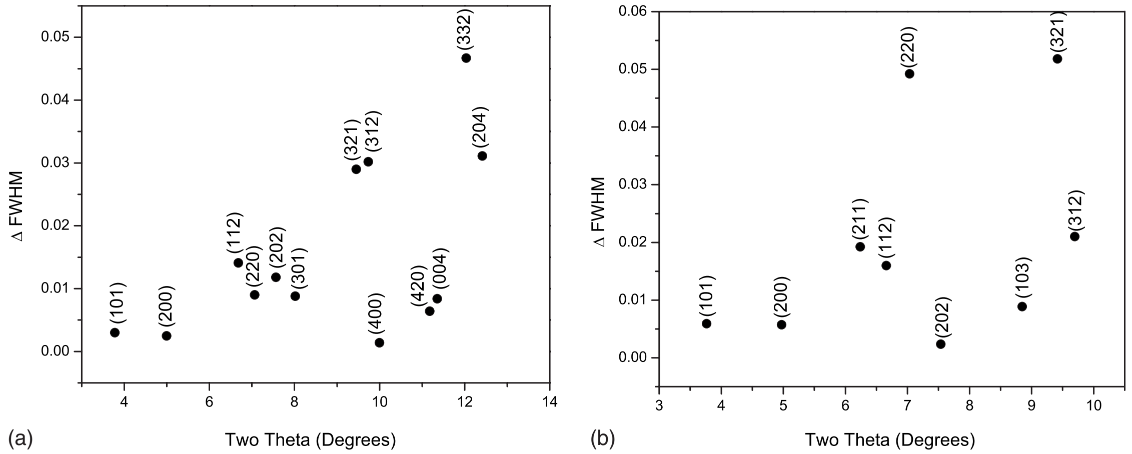

FIG. 2. The increase in FWHM of some of the diffraction peaks of (a) $YCrO_4$ at 4.6 GPa and (b) $HoCrO_4$ at 6.5 GPa. The FWHM of the (200) diffraction peak did not increase as the difference between the "a" and "b" cell constants in the monoclinic phase is ~0.01%.

To evaluate a similar possibility we note that zircon to scheelite phase transformation has been proposed to proceed through a shear in the basal plane such that the angle of intersection between (100) and (010) direction changes from 90° to 115°. If this change is not abrupt, the intermediate state would not have a tetragonal symmetry and the unit cell would be essentially monoclinic. As mentioned earlier, recent first-principles calculations also suggests a similar transient intermediate monoclinic phase.[11]

On carrying out a Rietveld analysis of the diffraction pattern of $YCrO_4$, at 4.6 GPa (Fig. 3) we could fit the high-pressure diffraction data to a monoclinic phase. (SG: No. 15; $I112/b$, $Z=4$, $\gamma=90.44°$). The structure of this monoclinic phase (MP) is similar to that of the zircon phase (ZP) except for a slight rotation of the chromate tetrahedra as shown in Fig. 4 and a change in the gamma angle from 90° to 90.44°. Similar monoclinic structure also explains the results of $HoCrO_4$ at 6.5 GPa. Thus the reduced symmetry of the high-pressure phase provides a rational explanation of unusual broadening of some of the peaks as due to unresolved split peaks. The existence of a monoclinic daughter phase has earlier been speculated, arising possibly from softening of C_{66} shear elastic constant.[28] However, recent theoretical calculations[10] have shown that this shear elastic constant is likely to soften only at ~70 GPa, making it a highly improbable cause of monoclinic distortion of the parent tetragonal cell.

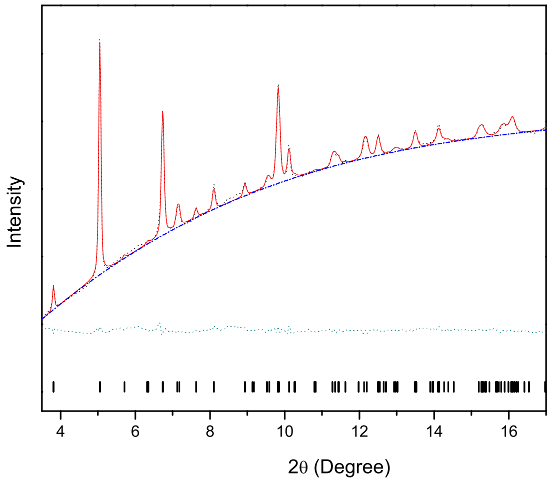

FIG. 3. (Color online) Rietveld fits to the recorded diffraction pattern of $YCrO_4$ at 4.6 GPa (red solid line) in the monoclinic structure. The blue (dot-dash) line shows the subtracted background and vertical bars give the expected positions of the diffraction peaks from the sample. The difference in the calculated and experimental diffraction pattern is given at the bottom of the graph (green dotted line).

On further raising the pressure beyond 6.5 GPa, distinct new diffraction peaks were observed in the diffraction patterns, as also indicated in Fig. 1. The diffraction patterns at these pressures could be indexed to the tetragonal scheelite phase. The Raman modes at ~7 GPa could also be assigned to the scheelite phase in agreement with the x-ray diffraction studies.[29] This shows that in nanochromates the observed monoclinic phase is not just an unstable transient phase but, has a range of stability. The scheelite structure was retained even on release of pressure. For bulk $YCrO_4$, an irreversible transformation to the scheelite phase at ~3 GPa, has earlier been established through Raman measurements.[13] Though there are no *in-situ* high-pressure studies on bulk $HoCrO_4$, the scheelite phase in this compound too has been synthesized by subjecting its zircon phase to high temperature (823 K) and pressure (4 GPa) in a belt-type press.[30] Therefore, our results suggest that the transformation to scheelite phase in

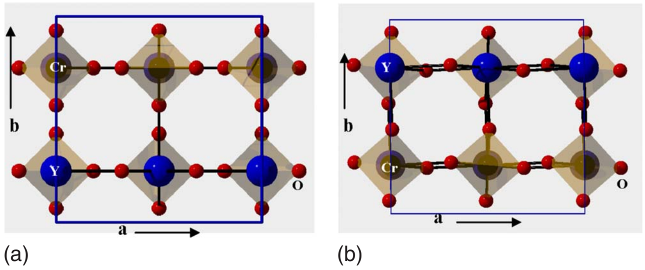

FIG. 4. (Color online) The (a) zircon and (b) monoclinic structure of $YCrO_4$ as determined from the diffraction data. The γ angle is 90.4°. The chromium, yttrium and oxygen atoms have been marked as Cr (gray), Y (blue), and O (red), respectively.

nanocrystalline chromates, is at higher pressures than observed in bulk. This is also consistent with the results of Ref. 23 on $ZrSiO_4$ which shows only traces of reidite phase even at ~36 GPa.

There are a few more useful features in the diffraction patterns shown in Fig. 1 which merit discussion. We note that the diffraction peaks of the high-pressure scheelite phase are very broad and are accompanied by an increasing background. This could be due to small crystallite size (result of multiple nucleation sites of new phase) of the new high-pressure phase. In fact from the diffraction data collected at Spring8 the calculated particle size of the high-pressure phase is ~7 nm at 10 GPa. It is known that when solid-solid phase transitions are accompanied by a volume change, single crystals fragment into much smaller crystallites.[15] Present experimental results imply that at high pressure the chromate crystallites of ~68 nm size have fragmented into smaller nanoparticles and in this process some parts of the parent crystallites may have become disordered leading to partial amorphization.

Due to the lower symmetry of the intermediate phase, one may also speculate, as proposed by Toledano *et al.*,[31] that the daughter phase may have multidomain states. This could lead to structural mismatches of the sheared domains adjacent to each other and finally result in fragmentation into still smaller nanoparticles. Moreover, the fragmentation would not necessarily be equisized and the smaller nanodomains may significantly lose translational order due to relaxations of atoms at the surfaces, contributing effectively to the observed increase in the background at high pressure.

To ascertain whether the monoclinic phase in these chromates is indeed of lower energy, we have carried out first-principles density-functional theory calculations on bulk yttrium chromate. These calculations were carried out using VASP code[32,33] with generalized gradient approximation (GGA) (Ref. 34) and plane-augmented wave (PAW) (Refs. 35 and 36) method to approximate the core electrons. A kinetic-energy cutoff of 500 eV and Monkhorst pack k-point grid of $5 \times 5 \times 5$ was found sufficient to ensure convergence. The lattice constants and fractional coordinates of the zircon and monoclinic phase of $YCrO_4$ (as determined from the Rietveld analysis) were used as the starting structures for the simulations.

Complete ionic relaxation was carried out on zircon and monoclinic structures at various volumes in antiferromagnetic spin arrangement (i.e., the magnetic moments of two chromium atoms in the primitive cell point in opposite directions) to find the lowest energy configurations. For this, symmetry and volume of the simulation box was fixed and the ionic degrees of freedom were allowed to relax to the minimum energy configurations. To determine the relative stability of the monoclinic phase compared to the zircon phase these calculations were repeated at different volumes. The optimized coordinates of the monoclinic structure are given in Table I.

The bulk modulus of zircon structured $YCrO_4$ determined from these calculations was found to be 121 GPa, in agreement with the earlier published results[37] and close to our experimentally determined value of 103 GPa.[38] The computed total energies are shown in Figs. 5(a) and 5(b) and these indicate that beyond ~3 GPa (i.e., for volume/formula unit less than ~78 Å^3), the monoclinic phase is of lower energy. Hence our experimental and theoretical studies indicate that the zircon to scheelite phase transition in these compounds may not be a one step process. Rather it may proceed via a symmetry descent and then a symmetry ascent. We have calculated the Raman modes of the zircon and monoclinic phases (optimized structures from VASP calculations were used) in the backscattering geometry with the help of PWSCF software.[39] These computations show that the Raman modes of zircon and monoclinic phases are quite similar, providing insight into the inability to identify the intermediate phase with Raman measurements.

TABLE I. The fractional coordinates of the optimized monoclinic primitive cell of $YCrO_4$ are given in this table. The lattice constants of the primitive cell are a=5.53 Å, b=5.53 Å, c=6.65 Å, α=53.3869°, β=53.3869°, and γ=64.2818°.

	Fractional coordinates		
Y	0.1242	0.3758	0.7500
Y	0.8758	0.6242	0.2500
Cr	0.6242	0.8758	0.7500
Cr	0.3758	0.1242	0.2500
O	0.7445	0.1323	0.0884
O	0.7819	0.6716	0.5846
O	0.3677	0.7555	0.4116
O	0.8284	0.7181	0.9154
O	0.2555	0.8677	0.9116
O	0.2181	0.3284	0.4154
O	0.6323	0.2445	0.5884
O	0.1716	0.2819	0.0846

IV. CONCLUSIONS

To conclude, our investigations show that the zircon structured nanocrystalline $YCrO_4$ and $HoCrO_4$ transform under hydrostatic conditions to scheelite structure, though at somewhat elevated pressures. This suggests that nonhydrostatic stresses or strains may not be vital even in other isostructural compounds where zircon-scheelite transformation has been observed. However, in the present case, an intermediate monoclinic phase (similar to the transient and hence unstable state proposed earlier[11] to delineate the path of transformation) has been observed and has also been shown to be the lower energy phase. This is similar to the case of the B1-B2 phase transition in alkaline halides and oxides where an intermediate unstable monoclinic phase describes the transition pathway but is observed only in silver chloride.[40,41] We should also note that under certain thermodynamic conditions, including the rate and step of increase in pressure, etc., it may be possible to trap the intermediate transient structures—as was also observed in quartz.[42] However, in $YCrO_4$, the observation of monoclinic phase in nanocrystalline samples may purely be incidental, as theoretical results suggest the possibility of the same for the bulk samples too,

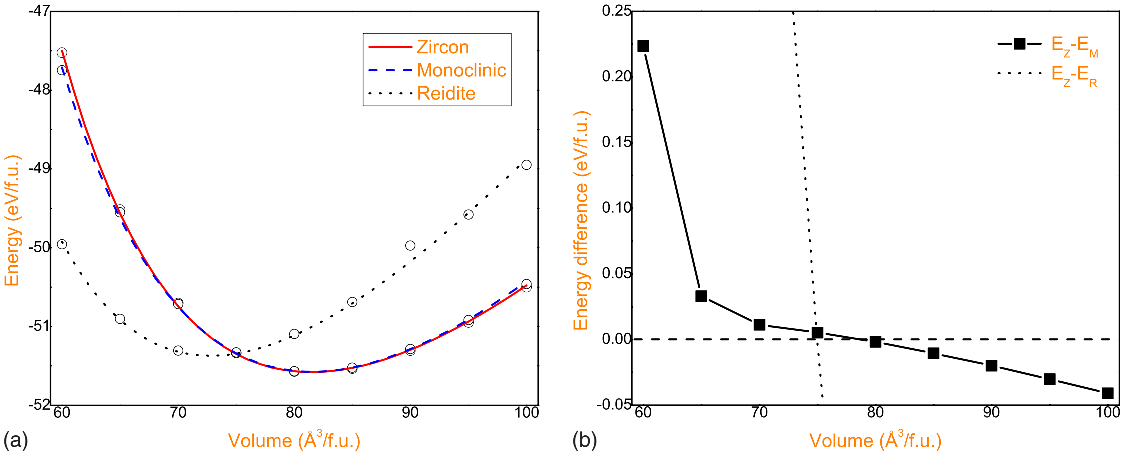

FIG. 5. (Color online) (a) Variation in computed total energy/formula unit with volume/formula unit for zircon (blue solid line), reidite (black dotted line), and monoclinic (red dashed line) phases of yttrium chromate. (b) This graph shows $(E_z - E_m)$ and $(E_z - E_R)$/formula unit versus volume/formula unit. It may be noted that $(E_z - E_m)$ variation is much larger and reidite overtakes monoclinic phase below 75 Å^3 giving the stability field of monoclinic phase between 75–78 Å^3.

for which no *in-situ* x-ray diffraction investigations have been carried out so far. It is also worth mentioning that these experiments must be carried out in very fine pressure steps as the monoclinic phase has a very small stability range (ΔV ∼3 Å^3). Hence these results should encourage more careful experiments on bulk and nano isostructural compounds to ascertain (a) if nanosize plays a role in the observability of the monoclinic phase (b) if this path is specific to chromates.

The particle size of the scheelite phase has been found to be much smaller than the parent phase, coexisting with a significant amorphous content. Also since reducing particle size increases the transformation pressure in zircon structured compounds, care must be taken when the pressures of meteoric impacts on radiation accumulated zircon sites is determined from the presence of reidite.

ACKNOWLEDGMENTS

Authors are thankful to Y. Ohishi and N. Hirao for their help during the experiments at BL10XU Spring8.

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[1] I. S. Williams, Nature **448**, 880 (2007).
[2] M. Marques, M. Florez, J. M. Recio, L. Gerward, and J. S. Olsen, Phys. Rev. B **74**, 014104 (2006).
[3] X. Wang, I. Loa, K. Syassen, M. Hanfland, and B. Ferrand, Phys. Rev. B **70**, 064109 (2004).
[4] A. Jayaraman, G. A. Kourouklis, G. P. Espinosa, A. S. Cooper, and L. G. Van Uitert, J. Phys. Chem. Solids **48**, 755 (1987).
[5] N. Garg, A. K. Mishra, and S. M. Sharma (unpublished).
[6] S. J. Duclos, A. Jayaraman, G. P. Espinosa, A. S. Oxper, and R. G. Maines, J. Phys. Chem. Solids **50**, 769 (1989).
[7] E. Knittle and Q. Williams, Am. Mineral. **78**, 245 (1993).
[8] H. Leroux, W. U. Reimold, C. Koeberl, U. Hornemann, and J.-C. Doukhan, Earth Planet. Sci. Lett. **169**, 291 (1999).
[9] K. Kusaba, T. Yagi, M. Kikuchi, and Y. Syono, J. Phys. Chem. Solids **47**, 675 (1986).
[10] M. B. Smirnov, A. P. Mirgorodsky, V. Yu. Kazimirov, and R. Guinebretière, Phys. Rev. B **78**, 094109 (2008).
[11] M. Flórez, J. Contreras-García, J. M. Recio, and M. Marqués, Phys. Rev. B **79**, 104101 (2009).
[12] E. Stavrou, A. Tatsi, E. Salpea, Y. C. Boulmetis, A. G. Kontos, Y. S. Raptis, and C. Raptis, J. Phys.: Conf. Ser. **121**, 042016 (2008).
[13] Y. W. Long, L. X. Yang, Y. Yu, F. Y. Li, R. C. Yu, S. Ding, Y. L. Liu, and C. Q. Jin, Phys. Rev. B **74**, 054110 (2006).
[14] R. Mittal, A. B. Garg, V. Vijayakumar, S. N. Achary, A. K. Tyagi, B. K. Godwal, E. Busetto, A. Lausi, and S. L. Chaplot, J. Phys.: Condens. Matter **20**, 075223 (2008); A. B. Garg, R. Rao, T. Sakuntala, B. N. Wani, and V. Vijayakumar, J. Appl. Phys. **106**, 063513 (2009).
[15] A. San-Miguel, Chem. Soc. Rev. **35**, 876 (2006).
[16] J. M. McHale, A. Auroux, A. J. Perrotta, and A. Navrotsky, Science **277**, 788 (1997).
[17] M. R. Ranade, A. Navrotsky, H. Z. Zhang, J. F. Banfield, S. H. Elder, A. Zaban, P. H. Borse, S. K. Kulkarni, G. S. Doran, and H. J. Whitfield, Proc. Natl. Acad. Sci. U.S.A. **99**, 6476 (2002).
[18] S. H. Tolbert and A. P. Alivisatos, J. Chem. Phys. **102**, 4642 (1995).
[19] J. Z. Jiang, J. Mater. Sci. **39**, 5103 (2004).
[20] W. J. Weber, R. C. Ewing, and L. M. Wang, J. Mater. Res. **9**, 688 (1994).
[21] U. A. Glasmacher, M. Lang, H. Keppler, F. Langenhorst, R. Neumann, D. Schardt, C. Trautmann, and G. A. Wagner, Phys. Rev. Lett. **96**, 195701 (2006).
[22] $ZrSiO_4$ used in this paper had small nanoislands of the zircon phase embedded in an amorphous matrix.
[23] M. Lang, F. Zhang, J. Lian, C. Trautmann, R. Neumann, and R.

C. Ewing, Earth Planet. Sci. Lett. **269**, 291 (2008).

[24] H. K. Mao, J. Xu, and P. M. Bell, J. Geophys. Res. **91**, 4673 (1986).

[25] A. Dewaele, P. Loubeyre, and M. Mezouar, Phys. Rev. B **70**, 094112 (2004).

[26] S. H. Tolbert, A. B. Herhold, L. E. Brus, and A. P. Alivisatos, Phys. Rev. Lett. **76**, 4384 (1996).

[27] J. N. Wickham, A. B. Herhold, and A. P. Alivisatos, Phys. Rev. Lett. **84**, 923 (2000).

[28] H. Ozkan and J. C. Jamieson, Phys. Chem. Miner. **2**, 215 (1978).

[29] A. K. Mishra, N. Garg, K. K. Pandey, K. V. Shanavas, Shukla, A. K. Tyagi, and S. M. Sharma (unpublished).

[30] E. Climent-Pascual, J. Romero de Paz, J. M. Gallardo-Amores, and R. Sáez-Puche, Solid State Sci. **9**, 574 (2007).

[31] P. Toledano and D. Machon, Phys. Rev. B **71**, 024210 (2005).

[32] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).

[33] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[34] J. P. Perdew, K. Burke, and Y. Wang, Phys. Rev. B **54**, 16533 (1996); J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[35] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[36] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[37] L. Li, W. Yu, and C. Jin, Phys. Rev. B **73**, 174115 (2006).

[38] The difference in bulk modulus could be because the experimental bulk modulus was determined for nano $YCrO_4$ whereas the theoretical bulk modulus was determined for bulk $YCrO_4$.

[39] S. Baroni, A. Dal Corso, S. de Gironcoli, P. Giannozzi, C. Cavazzoni, G. Ballabio, S. Scandolo, G. Chiarotti, P. Focher, A. Pasquarello, K. Laasonen, A. Trave, R. Car, N. Marzari, and A. Kokalj, http://www.quantum-espresso.org/

[40] M. Catti, J. Phys.: Condens. Matter **16**, 3909 (2004).

[41] P. T. Jochym and K. Parlinski, Phys. Rev. B **65**, 024106 (2001).

[42] M. S. Somayazulu, S. M. Sharma, and S. K. Sikka, Phys. Rev. Lett. **73**, 98 (1994).