Scientific Research Publishing

Advances in Materials Physics and Chemistry, 2020, 10, 77-95
https://www.scirp.org/journal/ampc
ISSN Online: 2162-5328
ISSN Print: 2162-531X

Indentation onto Stishovite (SiO_2), MgO, and a Covered Superalloy: "Pop-In" Repair, Phase-Transition Onsets, Polymorph Energies, and Transition-Energies

Gerd Kaupp

University of Oldenburg, Oldenburg, Germany
Email: gerd.kaupp@uni-oldenburg.de

How to cite this paper: Kaupp, G. (2020) Indentation onto Stishovite (SiO_2), MgO, and a Covered Superalloy: "Pop-In" Repair, Phase-Transition Onsets, Polymorph Energies, and Transition-Energies. *Advances in Materials Physics and Chemistry*, **10**, 77-95.
https://doi.org/10.4236/ampc.2019.103007

Received: January 27, 2020
Accepted: March 24, 2020
Published: March 27, 2020

Abstract

The Berkovich indentation loading curves of the initially only extraterrestrial available polymorphs of SiO_2 are physically analyzed by applying the now well established F_N-$h^{3/2}$ plots for conical/pyramidal indentations, in view of determining the phase-transition onset forces, indentation energies, and transition energies. Two phase-transitions of synthesized Stishovite yielding 2 polymorphs (one of them is Seifertite) with these properties are characterized. A third post-Stishovite polymorph is safely projected for higher load indentation. Both of them are now available at room temperature on earth for further investigation and the projected third of them is waiting. The published "pop-ins" had to be removed by self-evident repair of the force-depth curve. The meaning of published "pop-ins" is elucidated, apparently for the first time. The reasons for them and their avoidance are manifold. They are not materials' properties but mechanical artefacts. Published pop-ins are not at all connected to phase-transitions, despite theoretical considerations claiming elastic-plastic conversion at the start of "pop-ins". Spherical indentation analyses before them are obsolete. Final support is inter alia that one of the two new MgO twinning transitions is within a published "pop-in excursion". The putting of a pop-in arrow at smooth loading curve without discontinuities is criticized, as the transfer between chemically different phases is neither phase transition nor "pop-in". The polymorph's onset forces, their energies and their endo- or exo-thermic phase-transition energies are reported. The development of the Stishovite, post-Stishovite and MgO polymorphs is mechanochemical analyzed. High pressure polymorph energetic properties are important for the earth's sub mantel investigations and for public safety of technical materials such as MgO for constructions, or covered superalloys

for e.g. airplanes, turbines, etc. Breakage and catastrophic cracks are more easily initiated at polymorph interfaces, the onset and transition energies must be above the highest possible mechanical and thermal stress for their being safe.

Keywords

Berkovich Indentation, Catastrophic Cracking, Covered-Superalloy, False Historical Concepts, MgO, Phase-Transition-Energy, "Pop-In", Post-Stishovite, Stishovite

1. Introduction

Extraterrestrial materials such as high energy polymorphs of quartz were at first detected in meteorites from Mars and later collected from Moon. These crystalline materials are tetragonal Stishovite and later also the post-Stishovite polymorphs that are orthorhombic Seifertite, and the monoclinic quartz variety. All three are metastable at room temperature. Stishovite is now also found in atomic explosion craters and world-wide in ultrahigh pressure metamorphism rocks, or even in some diamonds. High-pressure-high-temperature syntheses are now successful in crystallizing sufficiently large single crystals of Stishovite, and Seifertite has also been obtained. They are yet the second hardest oxides. The indentation of Stishovite is of particular interest, as indentations of α-quartz undergo exothermic phase-transition into an amorphous phase but not endothermic into crystalline Coesite, another high pressure polymorph of SiO_2. Apart from amorphous phases one could expect exothermic formation of Coesite or endothermic Seifertite and the monoclinic variety from Stishovite. A still higher post-Stishovite polymorph's transition energy will be expected. Two microindentations with Berkovich diamond indenters have been reported. One of them reports three small pop-ins and the other one very late broad "pop-in". But smooth loading curves are necessary before physical (not iterative fitting) analyses are enabled for phase-transition onsets (depth and load), indentation work (W_{indent}), applied work ($W_{applied}$), and transition energy (W_{trans}). Such endeavor requires correct calculation, excluding rounding errors with the already long available simple closed formulas. Iterations converging to a false exponent on the depth h and the inexcusable violation of the energy law must be avoided. Rethinking of the "pop-in's" meaning and their removal or avoidance removes the still most complicated common misinterpretations.

Phase-transitions are revealed from physically analyzed [1] smooth force-depth curves of conical-pyramidal indentations not involving "pop-ins". The differences in the penetration resistances of the formed polymorphs provide sharp unsteadiness in the normal force vs. depth$^{3/2}$ plots (F_N vs $h^{3/2}$). Some still iterating opponents have disdainfully been calling it "Kaupp-plot" but we will take it up now respectfully. The Kaupp-plot gives the penetration resistance k with dimen-

sion [N/m$^{3/2}$] as physical hardness. It is the slope from conical, pyramidal, and wedged indentations [1]. It will be shown for the first time that "pop-in" is unintended autonomous force hold, while indentation depth values are falsely extrapolated and not corrected upon force resumption. There are several reasons for the avoidable show-up of "pop-ins". Frequent speculation in the literature still claims their being essential for elastic to plastic conversions of materials, which are however not phase-transitions [1]. Particular striking misuses of the "pop-in" term are arrows labeled "pop-in" that point to smooth loading curve sites where there is none. Furthermore, one must not use the Kaupp-plot (F_N vs. $h^{3/2}$) [1] without prior removal of published "pop-ins" (e.g. [2]), and beware of using it for spherical indentations. These are not simply parabolic. Only the Kaupp-plot reveals phase-transitions with their onsets and energies. That is easy, fast, and reliable. Phase-transitions have only rarely been guessed by "pop-outs" that require particular unloading techniques for confirming spectroscopic or electric results from e.g. hydrostatic pressure experiments. Almost all actually occurring phase-transitions remain unknown, if the physical Kaupp-plot analysis [1] is avoided for historical reasons. This proved already extremely dangerous, as polymorph interfaces upon phase-transition are nucleation sites for initially small cracks that upon further force produce catastrophic cracking for example in airliners [3] [4] [5]. Remedy is indispensable for e.g. the titanium alloys of propeller blades that should be improved in composition or replaced by other improved superalloys in airliners. Their phase-transition onsets and endothermic phase-transition energies must be far beyond the maximal forces that occur during turbulent flight. After the author's complaints in [4] [5] that phase-transition under load facilitates catastrophic cracking of titanium alloys, there is now a response. The chosen faster "remedy" is apparently not replacement of the alloy by a better one. It is now the placing of devices in front of the airliners' turbine propellers for impeding rotating broken off propeller blades from exiting at their higher speed in forward direction and shortly thereafter hit penetrating at the fuselage.

This paper puts forward the physical analyses of widespread Berkovich indentations for clarifying erroneous reports in the literature on the basis of common calculation rules, but not iterations with up to 3 + 8 free parameters. It disproves the unfortunately continued toleration of the ISO (International Standardization Organization) violation of the energy law, which impedes to even think of phase-transitions, not to speak of their detecting by the F_N vs. $h^{3/2}$ curve. This paper exemplifies the new application possibilities (the phase-transition activation energy requires temperature-dependent indentations). It analyzes the indentation onto Stishovite (SiO_2), magnesium oxide, and a covered superalloy. It requires only the physical loading curve analysis for obtaining the phase-transition onset and its energy. The calculation uses basic algebraic calculation rules but no iterations for the secure use of existing and advanced materials. The ease of the indispensable physical analysis of indentations is particularly favorable. Also the necessity for precise direct calibrations will be stressed. Unfortunately, the ISO

"standards" that were obtained with false force calibration, materials' mix-up, inconsideration of the phase-transitions, and excessive multi-parameter iterations (as revealed in [5]) are unacceptable. But fortunately, these standards are not required at all. Only the absolute force and depth calibrations and the proper execution prescription of the indentation experiment are essential. That part of the calibration and its reliability is apparently in good hands at ISO or at the instrument builders, as shown by the successful physical analyses. Any occurring false calibration of instruments is fortunately immediately recognized, when experimental data do not concur with the undeniable general algebraic formulas. Examples are poor force linearity at higher loads or defective indenter tips, or manipulated published data, or iterated and fitted curves. Any false reports facilitate disastrous results when checks of their content are omitted. False experiments require repetition. Advanced materials require the use of indentations with physical analysis with all of the new possibilities for their characterization. This is exemplified in this paper.

2. Materials and Methods

When force vs depth indentation curves from the literature were analyzed for phase-transitions, all published "pop-in excursions" were removed and the falsely extrapolated depth readings were subtracted for joining the depths from before and after the shown-up distortion. A continuous smooth loading curve was obtained by joining the loading parts that were interrupted by the force hold. This self-evident repair (Section 3.1) enabled the physical analysis with the Kaupp-plot. The *k*-values (penetration resistances = physical hardness) were not affected by the repair, whatever the reasons for the "pop-in" might be because creep errors were by far too small. The original data-point pairs were taken from the printed figures that were enlarged to abscissa lengths of 15 to 20 cm for that purpose. They were directly loaded to Excel® for the calculation of **Figure 1** through **Figure 3** and listed in **Table 1**. The calculations according to the already repeatedly published short and easily proved equations (numbers 3 - 7 in [5]) must not be repeated here. Due to high sensitivity and for avoiding rounding errors, all values throughout were calculated with 10 significant figures, for reasonable rounding in **Table 1** and at the final results in the text. Due to its energy law violation of the mostly used "P" for the normally applied force we use F_N that is 0.8 P. The factor 0.8 is inherent in F_N for being compatible with the energy law. This avoids a complication of formulas. 0.2 F_N is the universal requirement for the elastic + plastic work of conical, pyramidal and wedged indentations [5].

3. Results and Discussion

3.1. "Pop-Ins": Appearance, Significance, Handling

So called "pop-ins" disturb the force-depth loading curves of indentations. If these appear, more careful repetition of the indentation experiment is required,

or repair of the printed curve from a publication becomes necessary, prior to looking for the physical force-depth and energetic relations. At every "pop-in" production, the indenter electronics go autonomously in a force hold-mode, while the penetration loop continues in a pseudo creep mode with falsely reporting somehow extrapolated "fake depth" readings (not creep depression) until resumption of the loading loop, when too deep penetration depth value readings continue. The joining together of the loading parts requires subtraction of the "fake-values". Such correction must be manually executed, as there is no automatic correction when the force loop autonomously resumes after some time. It is hard to understand why that was not seen before. The real depth is the same at both ends of the horizontal "pop-in", notwithstanding some minimal creep that is often too small for being corrected, due to the short and comparably low constant-force action. Autonomous force holding ("pop-in") is a purely instrumental error. Unfortunately, common practices still continue to concede the pop-ins a physical significance (elastic to plastic conversion) that must be urgently challenged now. For example, pop-ins have nothing in common with the onset of "a sudden and strictly plastic punching" and it is not "an entirely plastic deformation process" [6]. Correspondingly, it has been claimed that "the onset of full plastic yielding at the indenter site is to be marked at the pop-in point" or that the "Hertzian elastic stress" ends at the pop-in [7].

Published pop-ins appear primarily when nanoindentation instruments are not cased for protection from environmental influences. For example they appear upon audible, ultra and infra sound, shaking, or switching of heat sources. To say it again: the force control stops during the published pop-in, while depth values are further extrapolated and recorded instead of a creep mode switching. Other distortions of the force control can be roughness, e.g. when the descending indenter tip hits with its skew sides or edges to a terrace step or other obstacle, or when it falls into a micro-hole. These events might sufficiently arrest the very sensitive constant force increase loop. It takes thereupon some time for autonomously resuming the force loop. Remedy is repetition of the experiment at a different site of the sample, or at another time, or at a larger distance from previous impressions or sample edges. The suggested distance of 10-fold indentation width should better be 20-fold [3]. Loading curves without pop-ins are achieved when following these hints.

Nevertheless, published pop-ins have continuously been interpreted as a purely elastic to plastic conversion, even though such published pop-ins started at different forces, often occurred multiply within the same indent, and varied considerably in their time for resumption. The elastic to plastic conversion does not change at such event and that is physically proved [1]. Furthermore, the "cone-point" $\{h_{cone} = R\,(1 - \sin\alpha)$, where R is apical radius and α half-angle$\}$ is much smaller than the start of the shown-up pop-in with common Berkovich indenters ($\alpha = 70.3^{\circ}$), and spherical indentation is not simply paraboloid. Exam-

ples for such errors are manifold in the literature. Most intriguing are claims of "pop-ins" when these are not present in the smooth F_N vs h curves. Some authors even try to misuse the term "pop-in" by inserting an arrow with such label at the smooth Berkovich loading curve. And that is tried to justify with the disproved "Hertzian theory" for spheres. For example the authors of [8] try to support their false belief with a large tip radius R. By using the iterative ISO 14577 techniques for the iteration of their tip end-radius they used a fused quartz indentation and both 3 + 8 free parameter iterations for comparison with equally treated and fixed standards. But they did not consider the numerous challenging reports telling that such "calibration" leads to far too high values, when compared with direct tapping-mode AFM measurements. The published iterated "tip radius" in [8] amounts to 269 nm. Such rounding would indicate an effective cone height of 15.75 nm for a Berkovich, which is almost the same as the kink position of the Kaupp-plot in [9]. The authors of [8] assumed elastic to plastic conversion at 15.9 nm depth for their Al-covered Ni-based superalloy diffusion zone and used a so-called "Hertzian approach", falsely believing in a spherical indentation up to this point. However, as already told above, spherical indentations do not proceed with a simple parabola [9]. The rightfully found parabola with exponent 3/2 is the result of conical/pyramidal behavior [1]. The iterated tip rounding of 269 nm is thus disproved and the tried application of the "Hertzian approach" is obsolete. In fact, elastic work and all kinds of plastic work relate in the same way to force and energy [1]. The historical views are unphysical and a half-sphere indentation (calotte before the cone-point) would require the non-parabola $F_N = k\pi\,(R/h - 1/3)\,h^{3/2}$ [9]. Nevertheless, the authors of [8] put an arrow labeled with "pop-in" at their smooth loading curve where there was none. One cannot better manifest the widespread false unphysical belief than by putting a "pop-in arrow" to a smooth curve in the absence of any pop-in! Clearly, our physical analysis with the Kaupp-plot of the smooth Al-covered Ni-superalloy loading curve reveals a very minor initial surface effect and two straight lines before and after the kink position (both with R = 0.9999 regression) in **Figure 1**. That is evidence for $h^{3/2}$ parabola loading curves. This proves pyramidal (effective conical) behavior. The not spherical behavior before the kink has already graphically been shown in [9]. The Berkovich of [8] must have been sharp (commonly 50 - 100 nm) [9]. Only the correct analysis of such published curves of [8] is valid. The kink at 15.4 nm and 252 μN force does not indicate an elastic to plastic conversion and neither so a phase-transition. It clearly characterizes the crossing over two chemically different phases. This corrects the previous interpretation of the kink in **Figure 1** as a sphere to effective cone conversion in [10] when the physical analysis of spherical indentations in [9] was not yet available and the "Hertzian" parabola for spheres appeared still credible. Unfortunately, the widespread misuse of the pop-in term in connection with iterative analyses is still widely used. That's very dangerous, when used for technical materials under mechanical load.

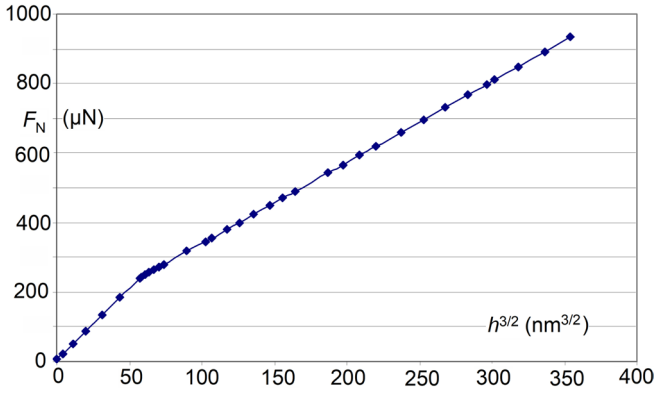

Figure 1. The physical analysis of the Berkovich indentation onto the "matrix phase" (10 μm thick) within the diffusion zone (25 μm thick) of an Al-coated Ni-superalloy; the load vs displacement curve data were taken from the figure 10 in [8] from 0 - 50 nm depth.

3.2. Stishovite, Seifertite and Monoclinic Polymorph of SiO_2

Stishovite is tetragonal SiO_2, with Rutil-type space group ($P4_2/mnm$). It is named after Sergey H. Stishov, Russia, for its first synthesis from α-quartz (density of 2.65 g/cm^3) at 20 GPa and 1100˚C [11]. A more recent synthesis treated fused quartz at 20 GPa and 1100˚C [12]. It is one of the densest (4.287 g/cm^3) polymorphs known from SiO_2 [13]. It had first been found together with Coesite in meteors from Mars and later collected from Moon [14], or from atomic bomb explosion craters, in some diamonds and now in ultrahigh pressure metamorphism rocks around the Globe.

Orthorhombic Seifertite (*Pbcn*) with unusual six-fold Si-O coordination (named after Friedrich Seifert, Bayreuth, Germany), was described in [13]. 3 years later, space group *Pbcn* or *Pb2n* and 4.29 g/cm^3 were discussed by [15], and it was synthesized in 2013 (see below). A monoclinic post-Stishovite was identified together with Seifertite (not orthorhombic $Pca2_1$, but monoclinic $P2_1/c$) was identified by [14] [16] in the Martian Shergotty meteorite. All of them are metastable at ambient conditions. It appears intelligible, that the first phase-transition of Stishovite proceeds to Seifertite with still higher density and again with the unusual 6-fold coordination of the silicon atoms. The first hint for a second phase-transition from Stishovite leads to the structurally identified $P2_1c$ polymorph again with six-fold coordination and the density of 4.30 g/cm^3. The energetic sequence of these is not certain. The minor density differences cannot secure the chosen sequence that awaits structural characterization by indentation with synchrotron X-ray analysis close to the indented Berkovich, or (less reliable) calculations of the energy and suppressiveness. It appears impossible that the about 15 known further crystalline polymorphs (known α- and ß-forms are counted) at much lower density (1.7 to 2.62 g/cm^3) and fourfold coordination could have been formed upon indentation of Stishovite. However a caveat remains, because 8 highest-pressure polymorphous structures of silica are listed with references in the Review [14] as CaF_2, Fe_2N, α-PbO_2, I2/a, $CaCl_2$, Pa-3, GeO_2, TiO_2 structures. These structures have been obtained by hydrostatic pres-

surizing or theoretical calculations, but some of them might only exist under high pressure. The orthogonal $CaCl_2$-typ (*Pnnm*) was found by a second order transition of Stishovite [17] [18] by hydrostatic pressure in a diamond anvil, but it is not quenchable and immediate first order transitions occur around 45 GPa. An inhomogenity at nearly hydrostatic pressure change in the rather gradual Raman frequency shift has been interpreted to occur from the TiO_2-structure into the non-quenchable $CaCl_2$ structure at 27˚C [18]. An earlier paper with (quasi) hydrostatic experiments reported evidence for the $CaCl_2$-structure of a post-Stishovite polymorph by synchrotron X-ray experiments. But only one phase-transition above Stishovite was found [19].

The situation changed with the detection of the quenchable Seifertite and $P2_1/c$ polymorphs. Seifertite could be synthesized from Cristobalite at 20 GPa and 900˚C [20]. Here we will rely on "quenchable" crystalline polymorph structures. The unloading curves [21] have smooth shapes, and the fast strain rate of the indentations with sharp onset would disfavor the possible $CaCl_2$ structure under these conditions and favor Seifertite and $P2_1c$ polymorphs. Indentations should be a useful tool for the formation and energetics of post-Stishovite polymorphs and the transition energies. Also the formation of still higher pressure polymorphs at room temperature can be envisaged.

3.3. The Indentation onto Stishovite

Indentations and hydrostatic compressions detect the polymorphs as they exist under pressure, and they include unquenchable (pressure-less not metastable) polymorphs. Both techniques can be performed at various temperatures. Only indentation is useful for the calculation of the important phase-transfer activation energies [22] [23], but temperature dependent indentations of Stishovite wait for their execution. Both techniques have been used for structural analysis with highly focused synchrotron X-ray analysis. The much slower hydrostatic pressure increase allows for equilibrations and the structural elucidation with X-ray analyses under pressure is easier also with various spectroscopic analyses. Raman spectroscopy has also been used with indentations. Syntheses with fast quenching (temperature and pressure) obtain only the quenchable polymorphs. Either indentation or hydrostatic pressing alone cannot distinguish all useful qualities.

3.3.1. The Indentation of Stishovite: Indentation Work and Transition Energies for 2 Post-Stishovites Despite 3 Published Pop-Ins

The Berkovich indentation onto (110) of a synthesized Stishovite single crystal [21] provided a loading curve with three short pop-ins at 0.98 mN (with 25.80 nm), at 8.53 mN (with 104.49 nm), and at 18.58 mN (with 160.13 nm) force (with depth). They are 1.0, 0.5, and 2.7 nm wide, respectively. However [21] deals only with the first of its 3 published pop-ins. Only the repaired published loading curve could be physically analyzed. The Kaupp-plot reveals a short (<40 nm) initial surface effect (including tip rounding) and two phase-transitions, in-

dicating 3 polymorphs up to 22.5 mN load. The regression line data are given as inserts in Figure 2. They contain the penetration resistance values (physical hardness) as the slopes and the force axis cuts. The equalization of the regression formulas provides the phase-transition onset kinks. The first kink (phase-transition onset) is at 9.71 mN with 110.74 nm, the second kink at 17.25 mN with 152.89 nm. There is, of course, no correspondence at all with the first of the published pop-in. The second published pop-in is 1.19 mN before the first phase-transition. The third published pop-in is 1.33 mN after the second phase-transition. Clearly, none of phase-transition values correspond with the published pop-in values. All phase-transitions occurred without any pop-in contribution, and published pop-ins are therefore not connected with phase-transitions, and they are not a prerequisite for phase-transitions. The reasons for published pop-ins have been discussed in Section 3.1, and their missing significance is again confirmed by these results. Perhaps some distortions by inhomogeneities, or disorders would have required the use of different crystal sites for indentation. The two phase-transitions indicate two post-Stishovite polymorphs as formed endothermic with higher penetration resistance (Table 1) and a third one would be at a

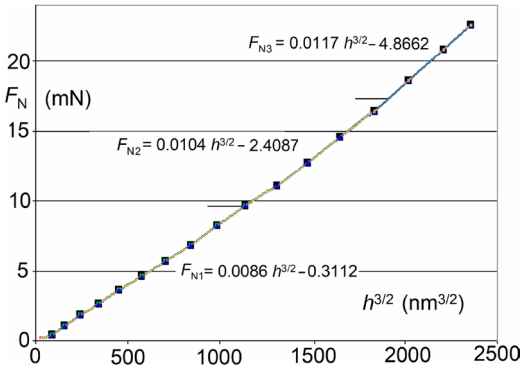

Figure 2. The physical F_N vs $h^{3/2}$ plot (Kaupp-plot) from the indentation with Berkovich onto the (110) Stishovite after removal of the pop-in excursions and correction of the penetration values with inserted regression equations; the short horizontal lines indicate the kink positions (phase-transition onsets) where the regression lines (not drawn) intersect; the original force-depth data are taken from [21].

Table 1. Berkovich micro-indentations; the arithmetically calculated indentation, application, and transition energies of Stishovite-SiO_2 with 2 post-Stishovite polymorphs and of MgO with 2 post-MgO polymorphs.

Stishovite#1 onto (110)	h_{kink} nm	F_{Nkink} mN	W_{indent}/mN mNnm/mN	$W_{applied}$ mNnm	Σ $W_{applied}$ mNnm	Full W_{appl} mNnm	W_{trans} mNnm	normalized W_{trans} mNnm/mN
#1 to #2	110.7354	9.71019	49.1884	520.40020	520.40020	537.63062	17.23042	1.77447
#2 to #3	152.8857	17.2513	32.1117	692.46215	1212.8624	1318.7383	105.87597	6.13727
#3 up to 522.588 mN	176.30[a]	22.588[b]	20.5818	581.12649	1793.9889	1991.1322	197.14335	8.72779
MgO N˚1 onto (001)								
N˚1 to N˚2	99.29877	13.8862	25.662655	705.9483	705.9483	689.43882	243.99447	17.57107
N˚2 to N˚3	243.7261	29.9345	102.93585	3851.6663	4557.6146	3647.9229	−909.691	−30.38941
N˚3 up to 70 mN	475[a]	70.0[b]	273.5352	23,934.433	28,492.047	15,771.663	−8122.15	−116.0307

[a] h_{end}; [b] F_{Nend}.

third kink as expected for an indentation at higher load. At the first kink we have #1 and #2 and at the second #2 and #3 polymorphs. The #3 polymorph compression proceeds towards a firmly predicted #4 polymorph that is however not reached at a higher force kink point, due to the cut off of the indentation load. 22.5 mN is not very high for microindentation. The regression line equations are used for the calculation of indentation work W_{indent} and transformation energies W_{trans}. These results and their normalized values are listed in **Table 1**.

The phase-transition onsets are clearly seen and marked at the sharp though shallow kinks in **Figure 2**. All transitions are endothermic and a projected third post-Stishovite is not reached due to the cupping of the indentation force. The phase-transition onset forces do not closely correlate with the transition energies. But what are the structures of these post-Stishovite polymorphs? More answers are provided by the calculated indentation work W_{indent} and the also calculated transformation energies W_{trans} that have been arithmetically calculated without iterations and without requiring the common energy-law violations of ISO-standards [22].

One has to distinguish indentation work W_{indent}, applied work W_{applied}, and transition energy W_{trans}. Before calculations, the published loading curves must be repaired from any pop-ins by removing such instrumental hold-periods with adjustment of the depth readings. Only required are the well-known formulas, as repeatedly published in [4] (their formulas 3 - 7). These correct for surface effects (axis cut F_a) of the physically analyzed loading curves. They calculate from the phase-transition onsets the balance of full $W_{\text{applied}} - \Sigma W_{\text{applied}}$ of the involved polymorphs. Such calculations have amply been published before [3] [4] [5] [22] [23]. The results are collected in **Table 1**.

The general calculation sequence is clear from **Table 1**. One obtains W_{applied1} from the triangle 0-F_{Nkink1}-depth h. The W_{applied2} requires integration of the loading curve for the corresponding range to obtain the W_{indent2} values that are multiplied with 1.25 to get the W_{applied2} values. Their corresponding sum and the full W_{applied} value are obtained as for the W_{applied1} with the corresponding triangles. The balance is obtained by subtraction (full $W_{\text{applied}} - \Sigma W_{\text{applied}}$) to obtain the W_{trans} values that are normalized by division through the corresponding force ranges. The W_{indent} values are not listed for space reasons, because they are easily obtained as 0.8 W_{applied} [22]. The normalized W_{indent}/mN values show the energy differences of the three polymorphs. It decreases from Stishovite#1 to #2 and #3. Conversely, there is much increase in the required phase-transition work the higher the energy of the polymorph. Such energetic properties are not available by other techniques and should be an empiric basis for the test of quantum mechanical calculations.

It is also seen in **Table 1**, that both phase-transitions of Stishovite (describing the three polymorphs) are highly endothermic and that the normalized transformation energies here with respect to the transition onset force are increasingly high. Every one of the three polymorphs has its particular quality that is increasing with the normal force and thus pressure. The normalized transition

energy values W_{trans} per mN of Stishovite are independent of the length of their stability ranges (the last one is cut off).

We can now ask, whether the proposed sequence of #2 before #3 is correct. The in Section 3.2 described quenchable orthorhombic Seifertite (*Pbcn*; 4.303 g/cm^3) is the first guess for #2 in **Table 1**. The second guess for #3 is the also quenchable monoclinic polymorph ($P2_1/c$; 4.30(2) g/cm^3) [16]. The reported densities are too close for deciding which one should be #2 or #3 in **Table 1**. And there is the possibility for as yet unknown unquenchable post-Stishovite polymorphs. A safe answer to these questions can only provide the onsite indentation at a synchrotron with highly focussed X-ray analyses. It is however certain that both of these endothermic formed polymorphs maintain the six-coordination of the silicon atoms. This excludes all of the numerous lower energy polymorphs with four-coordination to the silicon atoms. However, their transition energy contents are rather large in **Table 1** and that should be helpful for decisions by calculations, as long as the synchrotron studies are lacking. The multitude of proposed structures is described in Section 3.2. Further indentation experiments with higher loads than 25 mN are advisable for finding still higher polymorphs of SiO_2. The big advantage of indentation is the energetic characterization that is only possible with this technique. The reason why (post)Stishovite does not exothermic react to give the 4-fold coordination of Coesite etc, or *α*-quartz that transforms exothermally to an amorphous phase with k_1 = 2.5443 and k_2 = 1.8609 μN/nm$^{3/2}$ [5] is their enormous density due to 6-fold coordination of Si. That makes any internal expansion difficult and prefers cooperative transitions with minimal internal movements by retaining the 6-fold coordination and retaining the high density. This view is also supported by the very high penetration resistance values *k* from the Kaupp-plot (the physical hardness) of 0.0086 to 0.0117 mN/nm$^{3/2}$ (**Figure 2**). These values reach and surmount the ones of superalloys [4].

3.3.2. The Stishovite Indentation with Published Broad Late Pop-In

It appears of course appropriate to compare the indentation of Section 3.3.1 with the 3 years older indentation, again onto (110) of Stishovite, and again with a Berkovich indenter. Smaller polycrystalline Stishovite grains (50 - 200 μm wide) were used and the results "should be regarded as for single crystals" [24]. These authors published one late large "pop-in" (20 nm wide) starting at 14 mN load and 128 nm depth. After the repair of the loading curve, the Kaupp plot revealed again two phase-transitions very close to the ones in Section 3.3.1, with the very similar but slightly larger *k*-values of 0.0092, 0.0116 and 0.0133 mN/nm$^{3/2}$. The kink values are at lower loads (8.464 and 15.273 mN). After removal of the pop-in and the corresponding depth correction, the phase-transition depths (h_{kink}) are calculated lower at 97.757 and 134.136 nm than in Section 3.3.1. One of the phase-transitions is situated very far before and the other 6.8 nm behind the published pop-in from the 128 - 148 nm excursion length before the repair of the loading curve. That is again in support to the self-evident removal of pop-ins. The differences of the three *k*-values from **Figure 2** increase from +6%

to +12%. All of that points to a calibration problem of the unspecified indentation instrument due to the iterative ISO 14577 calibration [25]. An "error of ±5% for the calibration" has been claimed. As the precise conditions are not reported in [24] (e.g. sample purity, origin of instrument, compliance correction, calibration of force and depth), we refrain from the energetic calculations but rely on the apparently better defined measurements: In [21] the tip radius was measured with tapping mode AFM, the single crystal was larger, the distances between the several impressions were 20 instead of only 10 μm, and the tests were at constant strain-rate of 0.05/s. Instrument calibrations should be direct but not indirect by using ISO 14577 standards that were obtained by two consecutive iterations the first with 3 and the second with 8 free parameters [25]. And there were experimental errors at the force linearity and severe mix-up of standard materials in [25], as revealed in [5].

It is again very clear that the removal of the pop-ins from published loading curves works well, whatever their appearance might be. They might be absent, broad, or multiply narrow, early, later, and very late.

3.4. The Published Huge "Pop-In" of Periclase MgO.

While the behavior of the highly energetic and rarely available metastable materials in Section 3.3.with unusually high six-coordination to silicon atoms might appear somewhat special, one has to check at least one indentation of a normal stable material with pop-in accordingly. For example, the names Periclase for the MgO mineral (NaCl-type structure) already denotes easy cleavage all around its crystal, which can be a weak point for cracking and for pop-in production. Nevertheless, the B1 into B2 phase-transition of MgO upon hydrostatic pressure occurs between very high pressures of 429 and 562 GPa at room temperature or at much higher temperatures [26]. One could therefore not safely expect a phase-transition by a Berkovich micro-indentation onto magnesium oxide. However the reported terraces on its indented freshly cleaved (100) plane should increase the probability for pop-in production when the descending tip hits a terrace step with its skew side or edge. This has already been pointed out in Section 3.1. Micro-cracking upon Periclase indentation far from the tip edges could be excluded, as there was none of the short depressive spikes in the smooth loading curve, which are known from [3]. The authors of [6] called their published pop-in at 9.501 mN from 75 - 125 nm a "kind of accident" at the conversion from "elastic deformation" to "elasto-plastic behavior". The comparison with an indentation of Al without pop-in in [6] is misleading: there were no terraces on it. The published loading curve of MgO required therefore its elucidation. A smooth loading curve was obtained for the physical analysis after removing the published pop-in and the corresponding correction of the penetration values. Following an initial surface effect up to <30 nm depth, the Kaupp-plot from the so repaired smooth loading curve with its regression lines can now obtain the kink positions by equalizing the corresponding regression

lines (the initial effects including tip rounding are of course not part of the regression). The first exothermic phase-transition is at 99.299 nm. It is marked with the first vertical line in Figure 3. This is the depth-corrected position *within* the now removed autonomous decoupled instrumental hold period. Therefore, the phase-transition force of 13.886 mN is above the previous hold-force (9.501 mN) of the removed pop-in, as expected. Clearly, the phase-transition did neither occur at the start of the published pop-in, nor at its end. The regression lines cover data points from before and from after the force-hold-period. This observation proves: the published pop-in did not at all influence the exothermic phase-transition onset. This is an especially lucky feature. It undoubtedly confirms the new recognition of the missing significance of "pop-ins" that must be avoided or removed. It certifies the undisturbed calculation of the indentation works and the transition energies despite published pop-ins. Published loading curves with "pop-ins" must indeed be repaired for any physical analysis both for exothermic and endothermic phase-transitions (Table 1).

Our process is highly precise. While the plot from the first kink (first vertical line) to the end point might be judged uniformly (this would correlate with R^2 = 0.9996). However, the differently drawn data points of the Excel calculation indicate another very shallow kink of two regression lines (not drawn) that correlate with R^2 = 0.9998 and 0.9997, respectively. The physical analysis thus reveals three polymorphs up to at least 76 mN load. The first transition produces exothermic the first post-MgO polymorph. And this polymorph produces at higher force exothermic the second post-MgO polymorph. A projected third post-MgO kink is not reached due to the cupped off indentation force. The transition energies are listed in Table 1. The energetic data were again arithmetically calculated with the well-known closed formulas in [3] [5].

For the structures of post-MgO polymorphs we have to consider that an early B1 (NaCl type) to B2 (CsCl type) structural transformation of MgO at 13.9 and up

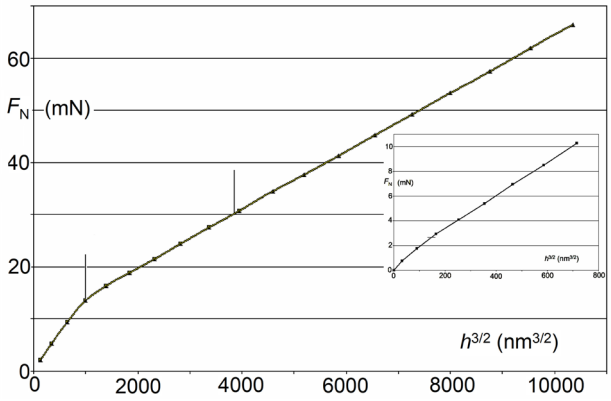

Figure 3. Kaupp-plot of the Berkovich loading data onto (100) of MgO as calculated from the F_N vs h curve of [6] after removing the pop-in and adjusting the penetration values; the vertical lines indicate the intersection of the regression lines; the insert (F_N = $0.0133h^{3/2}$ + 0.7258; R^2 = 0.9998) shows the higher resolved initial part including initial effect before the horizontal line.

to 30 and up to 70 mN load of a Berkovich indenter (Table 1) is not imaginable in view of the required super-high hydrostatic pressure for this phase-transition [26]. The early transition onset of the first transition should therefore only reach a first twinned MgO, requiring the high mechanical stress due to high crystal energy of B1-MgO (3795 kJ/mol [27]) and that the first MgO-twin upon further stress transforms exothermic to a different second twin, which is stable to more than 67 mN load at the cut-off. Further post-MgO polymorphs require higher load indentations.

Supporting evidence for these conclusions are the synthesized MgO-twins by epitaxial pulsed laser deposition from (111) faces in [111] direction [28] or by sintering of MgO (m.p. 2800˚C), at 2200-2300˚C into a structurally known monoclinic MgO-twin (a 6.443, b 5.9385, c 5.699, ß 91˚16') [29]. Two different deformation twins of MgO from {110} to [110] and from {111} to [112] slip systems have also been calculated [30]. This can provide a hint for the energetic sequence of the ones from micro-indentation in Table 1. Such twinning was apparently overlooked in the hydrostatic experiments.

The differences between the energetic data of metastable Stishovite and stable MgO are striking. While the penetration resistances are surprisingly pretty close, the first phase-transition energy W_{trans} of MgO is about 10 times higher. Conversely, the indentation energy W_{indent} of Stishovite is about twice as high. Clearly, both chemical and crystallographic effects play their decisive role. Stishovite has its unusual six-coordination of oxygen to silicon that cannot be abandoned at increasing pressure. Actually the compression of the Si-O bonds enforced the six-fold coordination of Stishovite under drastic conditions for optimal space-use. The post-Stishovite polymorphs had to retain this unusual six-fold coordination and retain that feature when producing higher energy structures with minimal internal migrations in cooperative processes. Further post-Stishovite structures will be highly interesting and should be created by indentation at higher load. Conversely, MgO with its high crystal energy retains as much as possible of its favorable structure by internal migrations for the twinning at high pressure. The further constrained first twin continues at higher load with exothermic transition to the more stable twin. Apparently more demanding internal migrations reach the more stable second twin of MgO. One does not yet know the necessary force for the transition from coordination number 6 to 8 that is required for the projected phase-transition to B2-MgO. Interestingly, all of these exothermic migrational transitions of MgO require much more applied work for exothermic transitions than the endothermic phase-transitions of Stishovite. Chemical bond energy changes upon bond-length compression and the size and electronic structure of the central atoms (Mg or Si) in combination with crystal energies play their roles for these phase-transitions.

4. Conclusions

This paper reports two phase-transitions, each of micro indentation loading

curves from the metastable Stishovite and from magnesium oxide. The projected third post-Stishovite and the projected third post-MgO are not reached due to the cupped indentation forces, but the way to them has been paved. These further polymorphs are firmly predicted for indentations up to higher loads. The published "pop-ins" within the loading curves had to be removed. The here described repair technique is highly important for the physical use of important published force vs. depth curves onto extremely precious materials, such as a good single crystal of Stishovite. Autonomous force holding ("pop-in") is a purely instrumental distortion. In the case of an Al-coated Ni-superalloy "diffusion zone" there is not a phase-transition but the crossing over two chemically different phases. It occurred without a published "pop-in", despite such strangest claim. Also in that case the widespread false belief on elastic-plastic conversion with "pop-in" had to be challenged. Unfortunately, the widespread belief in "pop-ins" is very dangerous. The change from elastic to plastic indentation does not change the smoothness of the loading parabola $F_N = kh^{3/2}$ of all normal conical or pyramidal indentations, but phase-transitions produce unsteadiness that is detected as sharp kinks in the F_N vs. $h^{3/2}$ Kaupp-plot. The so enabled search for phase-transitions for all solid materials is of practical importance. Phase transitions lead to polymorph interfaces that are sites for cracks' nucleation with catastrophic failures.

Published "pop-ins" are evidently due to the hype with them and the complicated theories about them with claiming spherical indentation just at their show-up, while spheres give no parabola and the so used exponent 3/2 on h is exclusively valid for cones, pyramids, and wedges. However, "pop-ins" are machine generated force holding with extrapolation of apparently not recognized fake depths. "Pop-ins" must be avoided by repetition of the measurement in the absence of the external or internal disturbing factors. If such distortions are published at whatever position, they are not at all indicating any materials' properties. Published "pop-ins" are not resulting from the elastic to plastic conversion. They must and can be removed with the adjustment of the depth readings by subtraction of the produced fake-depths. Such self-evident repair of published loading curves is essential and simple, as outlined in Section 3.1. Creep correction during the short force hold at low force is mostly too small for its execution requirement. The arithmetically calculated phase-transition onsets, as revealed by using the Kaupp-plots for the repaired loading curves, are before, within, and after published "pop-in excursions". Phase-transitions are not accompanied by "pop-ins". This apparently for the first time achieved new cognition replaces all false historical claims that are unfortunately still pursuit with enormously complicated untenable argumentations. Several reasons for instrumental distortions are listed for the first time in Section 3.1.

This paper also points out that the correct calibration of the indentation equipment is important for correct numerical results. Secondary calibrations with the ISO 1457 standards are unsuitable, because of the mix-up of materials

that occurred upon their generation with poor force calibration, inconsideration of their phase-transitions and iterations with at first 3 and then 8 free parameters, as revealed in [5] by checks with the Kaupp-plot. Such standards cannot be accepted for physical calibrations. But materials' standards are not necessary for the absolute physical analyses. ISO, instrument suppliers and certification agencies are required to use and enforce primary direct calibrations of the indenter instruments.

The two structurally known meteorite post-Stishovite polymorphs Seifertite and the monoclinic post-Stishovite can now easily be prepared for further investigation by microindentations onto Stishovite. Higher energy post-Stishovite polymorphs' onsets and energies are safely expected by higher force micro-indentation, and if necessary by depth sensing macro-indentation. The single crystal that has been used for **Figure 2** was already large enough for indentations at higher load micro- or macro-indentation above 25 mN. Also the B1 to B2 phase-transition onset and energies of MgO await further indentations at higher well calibrated loads.

It will be important for earth sub mantel explorations to indent all of the mayor minerals occurring in the lower earth mantle and study their high and highest energy phase-transition onsets and energies also temperature dependently. This will lead to a better understanding of the earth crust with its tectonic properties and influences. It will also be important to study all old and advanced technical and constructional materials for phase-transition onsets and energies to help avoiding catastrophic crashes of e.g. airliners, all types of fast running propellers, turbines, bridges, buildings, commodities, etc. Cracking is facilitated at polymorph interfaces. Their mechanical and thermal stress must be well below their as yet unknown phase transition onsets. As these remained undetermined for historical reasons they have now to be elucidated by physical indentation.

5. Outlook

For the future, it will be important that industry shall be enabled to use the here described results and physical analysis techniques for the correction of false characterizations of technically important materials and for producing physically correct results. To reach that goal, the independent academic teachers must abandon their very complicated historical thinking and teaching that prevents them from disagreeing with the striking energy violation of ISO. As universally deduced in [22], the violation is 20% for the correct loading exponent 3/2 on h—or it calculates to 33.33% upon use of the incorrect exponent 2 on h—of the undeniable pressure work. It cannot be created workless from nothing! However ISO 14577 still enforces to believe that all applied force is used for the penetration. ISO calls the normal force "P", which in fact means 1.25 F_N (see Section 2). This severe violation of the energy law is responsible for prescribing the false exponent 2 on h for cones and pyramids, which impedes phase-transition detections with their onsets and energies. It also falsifies dimension and value of ISO

hardness, the values of ISO modulus, and the numerous mechanical parameters that are deduced from them. This must no longer be taught in classes for students and should help for complaints against ISO 14577 and also against handbooks of the indentation equipment suppliers. Such complaints shall be directly addressed towards ISO 14577 agents in addition to the present author who continues with direct complaining at ISO in Germany. It is certainly a difficult task for worldwide ISO to thoroughly modernize their 14577-Standards for complying with the physical basis at the expense of historical belief against elementary physics. Physically sound standards are indispensable for the instruction of the certification agencies, (between agencies and for) for their requiring this states-of-the-art upon the certification of the producing industries. The latter are of course bound to their certification documents and cannot act against them. Also instrument builders must change their handbooks and provide the physical calculation routines for the physical characterization techniques and extensions to the before not even thinkable applications. This will not only increase the value of the indentation techniques, but it is a requirement for daily safety to produce physically correct data. In the meantime independent researches are urged to use the here presented and cited new physical possibilities and publish their data on phase-transition onsets and energies. That includes the here not addressed temperature dependent indentations for the activation energies of phase-transitions. After all, liability problems cannot be excused with disproved historical beliefs.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

References

[1] Kaupp, G. (2016) The Physical Foundation of $F_N = k\,h^{3/2}$ for Conical/Pyramidal Indentation Loading Curves. *Scanning*, **38**, 177-179. https://doi.org/10.1002/sca.21223

[2] Page, F., Oliver, W.C. and McHargue, C.J. (1992) The Deformation Behavior of Ceramic Crystals Subjected to Very Low Load (Nano)Indentations. *Journal of Materials Research*, **7**, 450-473. https://doi.org/10.1557/JMR.1992.0450

[3] Kaupp, G. (2018) Six Polymorphs of Sodium Chloride upon Depth-Sensing Scanning Macroindentation with Unusual Long-Range Cracks Requiring 30 N Load. *Journal of Materials Science and Engineering*, **7**, 473-483. https://doi.org/10.4172/2169-0022.1000473

[4] Kaupp, G. (2019) Physical Nanoindentation: From Penetration Resistance to Phase-Transition Energies. *Advances in Materials Physics and Chemistry*, **9**, 103-122. https://doi.org/10.4236/ampc.2019.96009

[5] Kaupp, G. (2019) Phase-Transition Energies, New Characterization of Solid Materials and Anisotropy. *Advances in Materials Physics and Chemistry*, **9**, 57-70. https://doi.org/10.4236/ampc.2019.94006

[6] Tromas, C., Girard, J.C., Audurier, V. and Woirgard, J. (1999) Study of the Low

Stress Plasticity in Single-Crystal MgO by Nanoindentation and Atomic Force Microscopy. *Journal of Material Science*, **34**, 5337-5343. https://doi.org/10.1557/JMR.1992.0450

[7] Armstrong, R.W. and Elban, W.L. (2010) Macro- to Nano-Indentation Hardness Stress-Strain Aspects of Crystal Elastic/Plastic/Cracking Behaviors. *Experimental Mechanics*, **50**, 545-552. https://doi.org/10.1007/s11340-009-9246-5

[8] Wöllmer, S., Zaefferer, S., Göken, M., Mack, T. and Glatzel, T. (2003) Characterization of Phases of Aluminized Nickel Base Superalloys. *Surface and Coatings Technology*, **167**, 83-96. https://doi.org/10.1016/S0257-8972(02)00843-5

[9] Kaupp, G. (2019) The Loading Curve of Spherical Indentions is not a Parabola and Flat Punch Is Linear. *Advances in Materials Physics and Chemistry*, **9**, 141-157. https://doi.org/10.4236/ampc.2019.98012

[10] Kaupp, G. (2013) Penetration Resistance and Penetrability in Pyramidal (Nano)Indentations. *Scanning*, **35**, 88-111. https://doi.org/10.1002/sca.21038

[11] Stishov, S.M. and Popova, S.V. (1961) A New Dense Modification of Silica. *Geokhimiya*, **10**, 837-839.

[12] Leger, J.M., Haines, J., Schmidt, M., Petitet, J.P., Pereira, A.S. and da Jamada, J.A.H. (1996) Discovery of Hardest Known Oxide. *Nature*, **383**, 401. *https://doi.org/10.1038/383401a0*

[13] Sharp, T.G., El Goresy, A., Wopenga, B. and Chen, M. (1999) A Post-Stishovite SiO_2 Polymorph in the Meteorite Shergotty: Implications for Impact Events. *Science*, **284**, 1511-1513. https://doi.org/10.1126/science.284.5419.1511

[14] Hemley, R.J., Prewitt, C.T. and Kingma, K.J. (1994) High Pressure Behavior of Silica, Chapter 2. In: Heaney, P.J., Prewitt, C.T. and Gibbs, G.V., Eds., *Mineralogy*, Volume 29, The Mineral Society of America, New York, 41-73.

[15] Dera, P., Prewitt, C.T., Boctor, N.Z. and Hemley, R.J. (2002) Characterization of a High-Pressure Phase of Silica from the, Martian Meteorite Shergotty, Alpha-PbO_2-Like. *American Mineralogist*, **87**, 1018-1023. https://doi.org/10.2138/am-2002-0728

[16] El Goresy, A., Dubrovinsky, L., Sharp, T.G., Saxena, S.K. and Chen, M. (2000) A Monoclinic Post-Stishovit Polymorph of Silica in the Shergotty Meteorite. *Science*, **288**, 1632-1634. https://doi.org/10.1126/science.288.5471.1632

[17] Tsuchida, Y. and Yagi, T. (1989) A New, Post-Stishovite High-Pressure Polymorph of Silica. *Nature*, **340**, 217-220. https://doi.org/10.1038/340217a0

[18] Kingma, K.J., Cohen, R.E., Hemly, R.J. and Mao, H.K. (1995) Transformation of Stishovite to a Denser Phase at Lower-Mantle Pressures. *Nature*, **374**, 243-245. https://doi.org/10.1038/374243a0

[19] Andrault, D., Fiquet, G., Guyot, F. and Hanfland, M. (1998) Pressure Induced Landau-Type Transition in Stishovite. *Science*, **282**, 720-724. https://doi.org/10.1126/science.282.5389.720

[20] Page, M.E., Ohtani, E., Suzuki, A., Asahara, Y. and Saxena, S. (2013) Synthesis of Seifertite and Its Applications to Shocked Meteorites. *American Geophysical Union*, No. 213, Abstract ID: P41F-1983.

[21] Dub, S.N., Brazhkin, V.V., Novikov, N.V., Tolmachova, G.N., Litvin, P.M., Lityagina, L.M. and Dyuzheva, T.I. (2010) Comparative Studies of Mechanical Properties of Stishovite and Sapphire Single Crystals by Nonoindentation. *Journal of Superhard Materials*, **32**, 406-414. https://doi.org/10.3103/S1063457610060067

[22] Kaupp, G. (2013) Penetration Resistance: A New Approach to the Energetics of Indentations. *Scanning*, **35**, 392-401. https://doi.org/10.1002/sca.21080

[23] Kaupp, G. (2014) Activation Energy of the Low-Load NaCl Transition from Nanoindentation Loading Curves. *Scanning*, **36**, 582-589. https://doi.org/10.1002/sca.21158

[24] Luo, S.N., Swadener, J.G., Ma, C. and Tschauner, O. (2007). Examining Crystallographic Orientation Dependence of Hardness of Silica Stishovite. *Physica B*, **399**, 138-142. https://doi.org/10.1016/j.physb.2007.06.011

[25] Oliver, W.C. and Pharr, G.M. (1992) An Improved Technique for Determining Hardness and Elastic Modulus Using Load and Displacement Sensing Indentation Experiments. *Journal of Materials Research*, **7**, 1564-1583. https://doi.org/10.1557/JMR.1992.1564

[26] Dubrovinskaia, N., Petitgirard, S., Chariton, S., Tucoulou, R., Garrevoet, J., *et al.* (2019) B1-B2 Phase Transition in MgO at Ultra-High Static Pressure. Cornell University, Ithaca, NY. arXiv.org>cond-mat>Xiv: 1904.00476

[27] Lide, D.R. (2005) CRC-Handbook of Chemistry and Physics. 86th Edition, CRC-Press, Taylor & Francis, Boca Raton, FL. https://www.crcpress.com

[28] Stampe, P.A. and Kennedy, R.J. (1998) X-Ray Characterization of MgO Thin Films Grown by Laser Ablation on Yttria-Stabilized Zirconia. *Journal of Crystal Growth*, **191**, 472-477. https://doi.org/10.1016/S0022-0248(98)00163-8

[29] Toda, N. (1965) On the Sintering Mechanisms of Magnesium Oxide. *Mineral Journal*, **4**, 356-373. https://doi.org/10.2465/minerj1953.4.356

[30] Yang, B., Huang, C., Yin, D., Zhao, Y., Sun, S., Yue., X., Fu.T. (2018) Investigation of Impurity Induced Twinning in MgO from First Principles Calculations. *Computational Materials Science*, **150**, 390-396. https://doi.org/10.1016/j.commatsci.2018.04.039