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CRISTOBALITE TRANSITION USING HIGH VOLTAGE
ELECTRON MICROSCOPY

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IN-SITU OBSERVATION OF THE ALPHA/BETA CRISTOBALITE TRANSITION
USING HIGH VOLTAGE ELECTRON MICROSCOPY

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ABSTRACT

A high temperature water vapor phase is expected to persist in the vicinity of high level radioactive waste packages for several hundreds of years. We have begun an investigation of the structural and chemical effects of water on cristobalite because of its abundance in the near field environment. A high voltage transmission electron microscope (HVEM) investigation of bulk synthesized α -cristobalite to be used in single phase dissolution and precipitation kinetics experiments revealed the presence β -cristobalite, quartz and amorphous silica, in addition to α -cristobalite. Consequently, this apparent metastable persistence of β -cristobalite and amorphous silica during the synthesis of α -cristobalite was investigated using a heating stage and an environmental cell installed in the HVEM that allowed the introduction of either dry CO_2 or a $\text{CO}_2 + \text{H}_2\text{O}$ vapor. Preliminary electron diffraction evidence suggests that the presence of water vapor affected the α - β transition temperature. Water vapor may also be responsible for the development of an amorphous silica phase at the transition that may persist over an interval of several tens of degrees. The amorphous phase was not documented during the dry heating experiments.

INTRODUCTION

Prediction of chemical behavior in the near-field environment of high-level radioactive waste containers requires single phase dissolution and precipitation kinetics data. Cristobalite is a common secondary mineral in the rock matrix and along fracture surfaces in the Topopah Spring Tuff, which is the host rock for the proposed high level radioactive waste repository at Yucca Mountain, Nevada. Cristobalite may also provide an analogue for certain phases in concrete that will experience a similar thermal history in the vicinity of the waste containers. In the course of obtaining dissolution rate data for α -cristobalite [1], it was noted that synthetic cristobalite dissolved at rates slightly higher than natural cristobalite. Detailed microstructural characterization of the starting and etched natural and synthetic α -cristobalite was undertaken because of this unpredicted behavior.

Cristobalite has been the subject of repeated investigations [2][3][4][5][6][7][8][9][10][11]. Its physical and chemical properties are of considerable interest because it begins a structural transition from the primitive tetragonal ($P4_12_12$) α phase to the face centered cubic ($Fd3m$) β phase at some temperature below 240°C , which is the maximum temperature expected to be attained by the host rock in the vicinity of spent fuel waste packages. The structural transition is thought to involve a slight displacive adjustment [12], but a consistently reproducible transition temperature has not been identified. It is thought that β -cristobalite is stable between the melting temperature ($\approx 1728^\circ\text{C}$) and $\approx 1450^\circ\text{C}$ [9][13][14], but can exist metastably below 200 - 275°C . It is also well known that the inversion temperature can be variable, even in the purest SiO_2 systems [15] with a transition temperature as low as 180°C . The α -cristobalite phase is known to exist between room temperature and 200 - 275°C . The effect of water vapor on the transition is unknown. This is of major concern since numerical modeling suggests that a thermal event in the vicinity of the waste packages will dehydrate the tuff, resulting in an atmosphere with a relative humidity of 100% [16]. These uncertainties have complicated attempts to develop physical and chemical models of the near-field environment. We have undertaken a reconnaissance transmission electron microscope study using an environmental cell in an effort to evaluate the roles of temperature and water vapor in the α and β -cristobalite phase transition.

EXPERIMENTAL

The transmission electron microscopy was conducted using a Kratos 1.5 MeV High Voltage Electron Microscope (HVEM). The environmental cell as described by Swann [17] was installed in the HVEM between the upper and lower objective lens pole pieces (Fig. 1). The gas flow pattern allowed maximum contact between the gas and the specimen. Gas entered the cell through the opening usually occupied by the objective aperture, and was pumped out through the specimen chamber. Dry CO_2 or $\text{CO}_2 + \text{H}_2\text{O}$ vapor were introduced to the environmental cell (Fig. 1) using a flow controller that maintained pressures between 0 and 150 mbars. The $\text{CO}_2 + \text{H}_2\text{O}$ vapor was produced by bubbling CO_2 through water maintained at 92°C . The gas flow pathway was determined by a valve upstream of the flow controller. Dry CO_2 was used to flush any remaining water vapor from the previous experiment out of the system for at

Fig. 1. Schematic of the environmental cell, and its location with respect to the objective lens of the HVEM. The location of the specimen and the gas inlet is designated as S.

Fig. 2. Scanning electron micrograph of a crushed α -cristobalite grain. The bar scale represents 10 μm .

In the absence of a diffraction pattern that was indicative of either symmetry, the relative preponderance of streaking over single reflections was used as a gauge. One to three grains were selected to monitor through the experimental sequence. When grains were lost or broken due to heating or introduction of gas, the experiment was continued with a new set of grains. Consequently, the data set is a mosaic of information from individual grains that are identified on the experiment progress diagrams (Figs. 3-7). The first two experiments, CS-2A (Table I) and (CS-2B) (Table II), were conducted to determine the applied current necessary to maintain temperature in a dry system and to establish an operating procedure for the cell. In each case the specimens were heated, cooled and reheated, but the former was cooled by the introduction of CO_2 . The second set of three experiments involved the introduction of $\text{CO}_2 + \text{H}_2\text{O}$. Experiment CS-2C (Table III) heated the specimen in vacuo beyond the transition. Introduction

least an hour before each experiment (CS-2B through CS-2E). Gas could escape from the cell and degrade the column vacuum because the four apertures through which the beam passed, two above and two below the specimen rod, were not covered in an effort to retain image quality. However, the large size of the cell chamber minimized the effect of the gas leak and the inlet pressure is considered a good estimate of the pressure at the specimen. The uneven outline of the apertures can be seen in all of the diffraction pattern images. The placement of the cell made the use of the standard objective apertures impossible. A single objective aperture fitted to the environmental cell was used for the duration of the experiments.

Cristobalite was synthesized by conventional devitrification methods [18] from 99.9% pure SiO_2 glass. The glass was crushed to $< 5 \text{ mm}$ and heated in Pt crucibles to 1530°C . The sample remained at 1530°C for eight days and was subsequently air cooled. The sample was crushed and the $< 124 \mu\text{m}$ fraction retained (Fig. 2). Sieved material was passed through a magnetic separator to remove contamination from the grinding process. X-ray diffraction (XRD) analysis indicated the presence of only α -cristobalite. No evidence of remnant glass was observed with infra-red spectra. A small amount of crushed sample was sprinkled between two halves of a folding Ni 200/100 mesh grid for HVEM observation. A carbon coat was not applied because it would evaporate during heating. The samples were heated relatively slowly ($1\text{--}2^\circ/\text{min.}$) via a small ceramic resistance heater near the tip of the specimen holder in order to reduce instability and breakage of the grains under observation. All temperatures were digitally recorded from

Pt-Pt/Rh thermocouples in contact with the sample cup. Since the quality of the thermal contact between the specimen cup, the Ni grid, and the cristobalite grain could not be ascertained during the experiment, the actual sample temperature was assumed to be equal to or less than the recorded thermocouple temperature.

Five experiments were conducted, each lasting 5-8 hours. Much of the data to be collected was crystallographic information from the diffraction pattern. In order to be able to compare intensities all diffraction patterns were exposed on negative film for three seconds. The manifestation of the displacive transition in a selected area diffraction (SAD) pattern is continuously increasing streaking. For the purpose of the experiments described in this report the β phase was identified by 3-fold symmetry and prohibited reflections. Only reflections of all even or all odd hkl indices are allowed for face centered cubic structures.

of $\text{CO}_2 + \text{H}_2\text{O}$ caused the temperature to fall. The specimen was reheated and then allowed to dehydrate. Complete dehydration was determined by comparison of the applied current to that of the dry control run. The sample was then cooled to above room temperature. Experiment CS-2D (Table IV) aged the specimen for three hours in vacuo, just below the observed transition temperature. The specimen then was heated in vacuo before dry CO_2 was introduced. Current was increased simultaneously to maintain the temperature of the specimen. Subsequently $\text{CO}_2 + \text{H}_2\text{O}$ vapor was introduced and a slightly higher temperature maintained. The specimen was then cooled to above the transition temperature before the grain was lost. During experiment CS-2E (Table V) the sample was heated in vacuo. The $\text{CO}_2 + \text{H}_2\text{O}$ was introduced at a constant temperature and then aged for one hour before cooling to approximately room temperature.

RESULTS

Transmission electron microscope analysis of the synthesized α -cristobalite indicates that the specimen is more heterogeneous than x-ray diffraction analysis would suggest. The selected area diffraction patterns represent a range of SiO_2 phases that include quartz (Fig. 3a) and β -cristobalite (Fig. 3b) in addition to α -cristobalite (Fig. 4a,b). A variety of microstructures are observed in the α -cristobalite. The antiphase boundaries (Fig. 4a) and fine (probably twin) lamellae (Fig. 4b) are imaged using in dark field techniques. The sampling procedure at the microscope was random. However, smaller grains were retained selectively on the grid and were more likely to transmit electrons. In addition, the total number of grains identified is too small for a statistical sample at this point. Therefore the data collected, in which slightly less than 33% of the grains were identified as silica phases other than well crystallized α -cristobalite, does not represent quantitative composition of the bulk specimen, but the more qualitative result that other SiO_2 phases are present.

The results of experiments CS-2A, CS-2B, CS-2D and CS-2E serve to bracket a dry forward, or heating, transition point between 200 and 250 °C. The transition temperature for the dry reverse reaction is estimated from experiments CS-2B and CS-2C as between 150 and 200 °C. Although during an

Tables I-V. Experimental conditions. The columns for CO_2 and $\text{H}_2\text{O} + \text{CO}_2$ pressures indicate the use of either pure CO_2 or an $\text{H}_2\text{O}-\text{CO}_2$ mixture in the experiment. Zeros in both columns indicate conditions indicate a vacuum in the environmental cell. Dashes indicate instances when amperage, the current applied to the resistance heater to maintain the indicated temperature, was not recorded. Significantly more current was required to maintain a given temperature if a gas phase was present. The adjacent diagrams of experiment progress illustrate the temperature and current as a function of relative time. Phases are identified as indicated by symbols defined in the legend. The symbols are lettered to identify specific grains that were monitored in the experiment. Changes in letters indicate loss of a grain and the selection of a new grain during the course of an experiment. Each experiment represents a new set of grains. Dashed lines label the point in the experiments at which the gas is introduced or varied to the gas composition and pressure indicated. The times at which specific observations were made are provided to indicate the duration of portions of the experiment.

T (°C)	P CO_2 (mbar)	P $\text{CO}_2 + \text{H}_2\text{O}$ (mbar)	amps
18	0	0	0.000
31	0	0	0.110
34	0	0	0.110
78	0	0	0.207
80	0	0	-
121	0	0	0.298
129	0	0	-
137	0	0	-
140	0	0	0.298
210	0	0	0.396
211	0	0	0.396
212	0	0	-
275	0	0	0.493
277	0	0	0.493
278	0	0	-
336	0	0	-
344	0	0	-
346	0	0	-
347	0	0	-
394	0	0	-
395	0	0	0.660
163	25	-	-
155	40	-	-
146	40	-	-
75	40	-	-
251	25	-	0.880
284	25	-	0.940
286	25	-	0.940
306	25	-	0.972

T (°C)	P CO ₂ (mbar)	P CO ₂ + H ₂ O (mbar)	amps
18	0	0	0.000
102	0	0	0.345
103	0	0	0.345
105	0	0	0.345
195	0	0	0.475
205	0	0	0.495
254	0	0	0.589
290	0	0	0.607
297	0	0	0.615
249	0	0	0.540
200	0	0	-
150	0	0	0.409
98	0	0	0.321
90	0	0	-
48	0	0	0.178
114	0	0	0.353
126	0	0	0.374
137	0	0	0.390
140	0	0	0.390
158	0	0	0.420
177	0	0	0.448

T (°C)	P CO ₂ (mbar)	P CO ₂ + H ₂ O (mbar)	amps
18	0	0	0.000
23	0	0	0.074
98	0	0	0.335
101	0	0	0.335
129	0	0	0.378
155	0	0	0.416
176	0	0	0.441
202	0	0	0.478
251	0	0	0.545
297	0	0	0.610
128	-	25	0.610
121	-	53	0.610
184	-	100	0.782
225	-	100	0.872
255	-	100	0.872
290	-	100	1.208
267	-	100	1.039
291	0	0	0.979
296	0	0	0.959
296	0	0	0.909
295	0	0	0.874
294	0	0	0.811
297	0	0	0.791
296	0	0	0.760
294	0	0	0.739
293	0	0	0.716
296	0	0	0.694
176	0	0	0.299
121	0	0	0.299
95	0	0	0.299
86	0	0	0.299
40	0	0	0.000

experiment the transition point of an individual grain is clear, these experiments cannot constrain a general transition temperature for either the forward or the reverse direction to a range of less than 50 °C. Even in view of this uncertainty, the lower temperature of the reverse transition temperature is clear. A result of dry heating in experiment CS-2B that was not expected was the apparent transition of a single crystal α -cristobalite grain to cryptocrystalline quartz (Fig. 5). Streaking increased in the diffraction patterns during heating between 114 ° and 158 °C (parallel to arrows, Fig. 5), but ultimately a polycrystalline ring pattern developed (177 °C). The polycrystalline pattern can be indexed as quartz, and so by grain size is identified as chalcedony. This has not been observed yet in any of the wet experiments.

Thus far two potential effects of the presence of a water vapor phase on the α - β cristobalite transition have been observed. The first effect was the apparent persistence of the β phase beyond the dry reverse transition temperature, in experiment CS-2E where water vapor was introduced at a temperature above the transition temperature, (>250 °C) and subsequently the specimen was cooled. The diffraction pattern sequence represented in Fig. 6 illustrates the persistence of streaking to at least 70 °C. In comparison, it can be noted that the grain dehydrated at temperature above the dry reverse transition and subsequently cooled, as represented by experiment CS-2C, undergoes the phase transition at a temperature consistent with the dry cooling experiments. The second effect is the occurrence of diffuse scatter. It

T (°C)	P CO ₂ (mbar)	P CO ₂ + H ₂ O (mbar)	amps
18	0	0	0.000
180	0	0	0.373
216	0	0	0.399
235	0	0	0.425
243	0	0	0.431
263	0	0	0.470
269	0	0	0.470
283	0	0	0.494
298	0	0	0.514
329	0	0	0.561
358	0	0	0.603
373	0	0	0.623
397	0	0	0.652
379	110	-	1.148
379	125	-	1.480
395	-	125	1.174
343	-	125	1.083
292	-	125	0.995
214	-	125	0.842

T (°C)	P CO ₂ (mbar)	P CO ₂ + H ₂ O (mbar)	amps
18	40	-	0.000
21	40	-	0.102
38	40	-	0.304
54	40	-	0.399
76	40	-	0.503
104	40	-	0.599
180	40	-	0.804
218	40	-	0.887
256	40	-	0.965
312	40	-	1.071
396	40	-	1.211
395	-	50	1.210
393	-	50	1.207
349	-	50	1.127
301	-	50	1.040
247	-	50	-
219	-	50	0.875
199	-	50	0.832
179	-	50	0.783
160	-	50	0.737
161	-	50	0.738
117	-	50	0.611
84	-	50	0.485
54	-	50	0.327
37	-	50	0.150

is clear that much of the diffuse scatter is a result of the gas environment, and its intensity should correlate directly with the molecular weight of the gas [17]. Therefore the intensity of diffuse scatter is expected to increase with the introduction of a gas into the evacuated cell, but decrease with the transition from CO₂ to H₂O + CO₂ at a given total pressure. However, comparison of diffraction patterns suggests that variations in the diffuse scatter are not always consistent with that interpretation. A sequence in experiment CS-2D (Fig. 7) follows two grains through the introduction of CO₂ and subsequently CO₂ + H₂O.

DISCUSSION

Observations conducted with HVEM document the presence of β-cristobalite quartz and amorphous silica, in samples of synthesized α-cristobalite, despite XRD analysis that suggests the presence of only α-cristobalite. The discrepancy demonstrates the difference in the quantitative resolution of the two techniques. The phase heterogeneity, which is observed using transmission electron microscopy and not observed using powder x-ray diffraction, could be responsible for some of the inconsistencies observed in the dissolution rates of synthetic and natural cristobalite specimens [1]. If so, then the dissolution experiments were sensitive to constituents present in quantities less than 2-5%. These observations demonstrate

Fig. 3. Other SiO_2 phases observed in the synthetic α -cristobalite specimen. a) Bright field image of quartz. b) Characteristically streaked electron diffraction pattern of β -cristobalite.

Fig. 4. Dark field transmission electron photomicrographs of α -cristobalite microstructures. a) Micro-lamellar structure, probably pseudo-cubic twinning. b) Anti-phase boundaries.

the necessity of characterization of a sample at a scale appropriate to the experiment that is to be performed. The same material was used for the present in-situ experiments, and must therefore be considered heterogeneous on a scale significant to these experiments.

The dry transition temperatures recorded during these experiments agree closely with those obtained from other methods and suggest that the thermal contact between the grain, the grid and the specimen cup is good. The observed rapidity of transition to a steady state at a specific temperature is consistent with earlier bulk experiments [9]. However, even at the scale of a single grain, it seems impossible to define a transition point more precisely. The apparent hysteresis is also consistent with earlier observations [9][19]. Hysteresis of as much as 30°C has been documented for a single specimen [9]. The $\alpha \Rightarrow \beta$ and $\beta \Rightarrow \alpha$ transitions are certainly complex, and may follow no consistent path as presently defined, even with dry heating. The path may be determined by microstructures such as those illustrated in Figs 8 a and b. The experimental dry heating sequence of an apparent transition from single crystal cristobalite through a more disordered state to cryptocrystalline quartz (Fig. 5) suggests that the end product may not always be cristobalite. The persistence of β phase at low temperature due to cation impurities [20] is well known and utilized industrially in the synthesis of ceramics. The results of experiment CS-2E (Fig. 6) suggest that the presence of water vapor may have the same effect. One could argue that water is responsible for the presence of β -cristobalite in the synthetic α -cristobalite specimen since it was synthesized from SiO_2 with few cation impurities. The apparent return to the dry transition point (CS-2C) upon dehydration suggests that water integrated into the structure is easily lost again.

Fig. 5. Sequence of diffraction patterns from experiment CS-2B. The numerals indicate the temperature at which each diffraction pattern was recorded. The sequence records the transition from single crystal α -cristobalite to cryptocrystalline quartz upon heating.

Fig. 6. Sequence of diffraction patterns from experiment CS-2E. The numerals refer to the temperature at which each diffraction pattern was recorded. The sequence records the persistence of streaking associated with the β -cristobalite phase during cooling to at least 84°C in the presence of water vapor.

Fig. 7. Sequence of diffraction patterns from experiment CS-2D. The numerals indicate experimental temperature. Pure CO_2 was added between 397°C and 379°C . An amorphous phase is apparent upon the addition of $\text{CO}_2 + \text{H}_2\text{O}$. Compare the diffuse scatter of X with the diffuse scatter of Y under the same conditions. The diffuse scatter in both X and Y are too intense to determine whether the amorphous phase also existed in the CO_2 environment.

The microstructural diversity of the α -cristobalite grains identified during the original characterization of the material and at the outset of the in-situ experiments is consistent with earlier suggestions that microstructure may be responsible for the wide range of documented transition temperatures [9]. Peacor [9] suggested that the transition temperature for different subvolumes of crystal could vary. The single crystal to polycrystal transition (Fig. 5) is an example of the potential microstructural complexity of this transition. However, due to the factors mentioned in the experimental section, conclusive microstructural information is difficult to obtain during the in-situ experiments. Clearly each phase possesses a range of energy states that represent microstructural state. These energy differences could be sufficient to account for differences in dissolution rate.

A qualitative estimate of the diffuse scatter due to the gas environment can be obtained from the results of experiment CS-2D (Fig. 7). A comparison between the diffraction patterns of grain X and grain Y indicates a variation in the intensity of diffuse scatter upon introduction of CO_2 , even though both are more diffuse than the evacuated chamber. However, the difference is immediately apparent with the introduction of $\text{CO}_2 + \text{H}_2\text{O}$. There, the intensity of diffuse scatter in X and Y are different. The diffuse scatter due to the $\text{CO}_2 + \text{H}_2\text{O}$ environment at 125 mbars at 379° and 292° can be no more than that represented by the least intense scatter, which is Y in each case. Therefore the remainder of diffuse scatter in X can be attributed to an amorphous phase. Unless the relative partial pressures of gas admitted to the system varies significantly but undetectably, these results suggest that an amorphous phase may exist at the transition between α and β -cristobalite in the wet system. The appearance of the β phase during the dehydration experiment (see experimental section) CS-2E (Fig. 6) further supports this possibility. The experimental sequences that should be pursued in order to arrive at conclusive results have not been exhausted and will be explored further in the future.

CONCLUSIONS

A combination of results from these experiments allows us to bracket the forward $\alpha \Rightarrow \beta$ transition at $230^\circ \pm 20^\circ\text{C}$, and the reverse $\beta \Rightarrow \alpha$ transition at $170^\circ \pm 20^\circ\text{C}$. Although this is necessarily an approximation due to the experimental inability to have direct thermal contact with the grain in question, our results lie within the range of the results obtained by other techniques. In addition to the transition point hysteresis, which is consistent with earlier observations β -cristobalite appears to persist beyond the reverse transition temperature when water vapor is present.

The possible development of an amorphous phase at the transition temperature and its persistence over a temperature interval of tens of degrees, suggests that within the transition temperature range amorphous silica may be preferred over either α or β -cristobalite if a water vapor phase is present. This temperature interval overlaps that expected in the vicinity of high level waste packages. The geochemical and mechanical properties of amorphous silica are distinct from those of either α or β -cristobalite and may have consequences for the chemical environment generated by interaction of water and water vapor with the waste package host rock. The experimental sequences described in this paper do not represent the exhaustive set required for conclusive results. However, the observations have ramifications that deserve further attention. In addition, borehole stability may be influenced by volume changes and dissolution associated with development of an amorphous phase along fractures. Of further concern is the stability of crystalline and amorphous constituents of grout and concrete, which are expected to be used in the proposed repository. Further work on the microstructural properties of amorphous calcium-silicate-hydroxide compounds over a range of temperatures and vapor phase conditions is advisable because the humid, high temperature environment may affect their aging and modify their structural transformations in a manner analogous to that observed for the $\alpha \Rightarrow \beta$ cristobalite transition.

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REFERENCES

1. G. Murphy, W. E. Glassley and P. Larson. (in prep).
2. C. N. Fenner. *Am. J. Sci.* **36** 331-384 (1913).
3. W. L. Wyckoff. *Amer. Jour. Sci.* **9** 448-459 (1925).
4. T. F. W. Barth. *Amer. Jour. Sci.* **23** 350-356 (1932).
5. T. F. W. Barth. *Amer. Jour. Sci.* **24** 97-110 (1932).
6. W. Nieuwenkamp. *Z. Kristallogr.* **92** 35 (1937).
7. W. Nieuwenkamp. *Z. Kristallogr.* **96** 454-458 (1937).
8. W. A. Dollase. *Z. Kristallogr.* **121** 369-377 (1965).
9. D. R. Peacor. *Z. Kristallogr.* **138** 274-298 (1973).
10. A. F. Wright and A. J. Leadbetter. *Philos. Mag.* **31** 1391-1401 (1975).
11. A. J. Leadbetter, T. W. Smith and A. F. Wright. *Nature Phys. Sci.* **244** 125-126 (1973).
12. M. J. Buerger. in Phase Transformations in Solids edited by R. Smoluchowski, J. E. Mayer and W. A. Weyl (Wiley, Chapman and Hall, London 1951).
13. W. A. Deer, R. A. Howie, and J. Zussman. An Introduction to the Rock Forming Minerals (Longman Group Ltd., London 1975).
14. G. L. Hua, T. R. Welberry, R. L. Withers and J. G. Thompson. *J. Appl. Cryst.* **21** 458-465 (1988).
15. V. G. Hill and R. Roy. *J. Am. Ceram. Soc.* **41** 532-537 (1958).
16. J. J. Nitao. UCID-21414 (UCID Lawrence Livermore National Laboratory, Livermore, California 1988).
17. P. R. Swann. in Electron Microscopy and Structure of Materials, edited by G. Thomas, R. M. Fulrath and R. M. Fisher (University of California Press, Los Angeles, California, 1972), pp. 878-904.
18. R. O. Fournier and J. J. Rowe. *Am. Min.* **47** 897-902 (1962).
19. L. H. Cohen and W. Klement Jr. *Phil. Mag.* **39A** 399-401 (1979).
20. A. J. Perrotta D. W. Grubbs, E. S. Martin, N. R. Dando, H. A. McKinstry, and C.-Y. Huang. *J. Am. Ceram. Soc.* **72** 441-447 (1989).

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