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Laboratory parallel-beam transmission X-ray powder diffraction investigation of the thermal behavior of calcite: comparison with X-ray single-crystal and synchrotron powder diffraction data

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Abstract

Thermal behavior of calcite has been analyzed in the 303-1098 K thermal range by laboratory parallel-beam transmission X-ray powder diffraction. Present results provide a clear indication of the possibility to extract high-quality structural data from such instrumental set up. Such quality has been proved to be at the same level of a mid eighties X-ray single crystal investigation. Analysis of the spontaneous strain e_{33} provides a critical exponent β of 0.2499(5) consistent with the value of ¼ expected for a tricritical behavior. Structure refinements seemengly support the Ising model of disorder.

Key words: high-temperature X-ray powder diffraction; Rietveld method; calcite; nitratine; order/disorder phase transition; spontaneous strain.

Introduction

In the last decades much effort has been devoted to the development of instrumentation especially suited for non-ambient measurement of X-ray powder diffraction data. Synchrotron radiation has been the source of choice for such experiments exploiting the very high intensity as compared to conventional sealed-tube radiation. This crucial advantage, apart for a very fast acquisition time, allows the use of a large beam-path, ultimately leading to an improved resolution over conventional laboratory instrumentation. However, the recent improvement on fast detectors, coupled with the use of transmission geometry on capillary samples, has pushed toward the limits of laboratory X-ray powder diffraction. The aim of this paper is to define such limits by comparing the results of a non-ambient structure investigation carried out with one of such instruments with those of a very recent synchrotron radiation investigation and with a mid eighties X-ray single-crystal structural analysis on the same material. A paper discussing such limits for RT measurements has been recently published (Ballirano, 2003). The sample object of this investigation is calcite that has been, together with isotypic nitratine, $NaNO_3$, the object of a number of investigations of the temperature dependence of crystal structure (for a thorough bibliographic list see: Harris, 1999; Antao et al., 2009). The interest is due to the fact that such relatively simple materials undergo an order/disorder transition related to an orientational disorder of the $CO_3^=$ or NO_3^- groups. Because of experimental difficulties (CO_2 overpressure of at least 2 atm is required to avoid calcite decomposition; Jacobs et al., 1981; Dove and Powell, 1989; Dove et al., 2005) the thermodynamic modeling of such transitions has been preferentially investigated on nitratine, extrapolating the results to calcite. However, as stated by Harris (1999) "…attempts to assign the phase transitions to standard models have been largely unsuccessful…".

The well-known structure of calcite consists of layers of carbonate groups and calcium cations alternating along [001]. Each Ca is bonded to three oxygen atoms pertaining to the upper carbonate layer and three pertaining to the lower one, leading to an octahedral coordination. At RT in the same layer the carbonate groups have the same orientation. This mutual orientation of the carbonate groups in the two successive layers is opposite (rotated by 60°). At temperatures exceeding that of decomposition an order/disorder transition related to an orientational disorder of the $CO_3^=$ group takes place. This transition should lead to a *c* halving connected to the symmetry change $R\bar{3}c$ (low temperature, LT phase) → $R\bar{3}m$ (high temperature, HT phase). A very interesting question is related to the mechanism of such a transition. An increased librational amplitude L_{33} acting in the *a, b* plane has been claimed to be the relevant *precursoring* effect. As the libration reaches the value of 30°, the difference in the orientation of neighbouring planes of $CO_3^=$ disappears and the carbonate group becomes disordered (Swainson et al., 1998). Such model should represent a rotational analogue of Lindemann melting (Dove et al., 2005). Another candidate transition model is a 2D Ising-like one, with the oxygen atoms distributed between two sites at ± *x*, 0, ¼. In the case of the ordered RT phase, the *x*, 0, ¼ site has a 100% occupancy that decreases upon heating until, at the transition temperature T_c, each one has a 50% occupancy. This leads to a symmetry reduction to $R\bar{3}m$. Available reference non-ambient full structural data are from the X-ray single-crystal study of Markgraf and Reeder (1985) and from the synchrotron powder investigation of Antao et al. (2009). The two different data apparently support different models, as Markgraf and Reeder (1985) did not find any additional in-plane 60° rotated oxygen site up to 1073 K, the highest investigated temperature, whereas Antao et al. (2009), starting at 764 K, were able to refine the structure using the Ising model.

The latter results are in disagreement with those from neutron powder diffraction, not reported in full, of Dove et al. (2005) that were unable to find any appreciable population of the anti-ordered orientation until T_c. It should be pointed out that the structural investigation of Antao et al. (2009) was based on a relatively limited angular range, extending up to $\sin\theta/\lambda \cong 0.42$ Å^{-1}. This reduced data set forced the authors to adopt a few approximations, e.g. the use of partly constrained isotropic displacement parameters, in particular O U_{iso} = C U_{iso}. Such an approximation introduces severe bias on the electron density distribution. In fact, Effenberger et al. (1981), Markgraf and Reeder (1985), and Maslen et al. (1993; 1995) indicated a pronounced anisotropy of the oxygen thermal ellipsoid at each analyzed temperature. This fact has been indirectly confirmed by Antao et al. (2009) as well by a RT refinement based on synchrotron high-resolution powder X-ray diffraction (HRPXRD) extending up to $\sin\theta/\lambda \cong 1.05$ Å^{-1}. Therefore, it is expected that the ability to refine at least the anisotropic displacement parameters (adp's) for oxygen could produce a significant improvement on the results of structural analysis.

Experimental

A single-crystal of prismatic calcite from Bohemia was crushed in an agate mortar and the resulting powder was loaded in a 0.7 mm diameter SiO_2-glass capillary that was glued to a 1.2 mm diameter Al_2O_3 tube by means of an high-purity alumina ceramic (Resbond 989). The capillary/tube assembly was subsequently aligned on a standard goniometer head. Data were collected on a parallel-beam Bruker AXS D8 Advance automated diffractometer operating in θ-θ geometry using Cu Kα radiation. It is fitted with diffracted-beam radial Soller slits and a PSD VÅNTEC-1 detector set to a 6° 2θ aperture and a prototype of capillary heating chamber (Ballirano and Melis, 2007). Thermal calibration of the chamber was carried out using MgO (periclase) as standard (Reeber et al., 1995). Diffraction data were collected in the angular range 20-140° 2θ ($\sin\theta/\lambda$ = 0.61 $Å^{-1}$) with a step-size of 0.022° 2θ, and 2s of counting time. The 26° < 2θ < 27° angular range was excluded from the refinement because of the occurrence of a very small Cu Kβ component of the strong 103 reflection arising from a non perfect monochromatization of the incident beam by the Göbel mirror. Within this angular range no reflections of calcite occur.

Thermal behavior of calcite was investigated in the 303-1098 K temperature range at steps of 15 K. The value of the high-temperature limit was forced by the failure of the capillary due to incipient re-crystallization of the glass to quartz. A view of the complete data set is reported in Figure 1 as a pseudo-Guinier plot.

Diffraction data were evaluated by the Rietveld method using TOPAS v. 4.2 (Bruker AXS, 2009) operating in launch-mode. This program implements the Fundamental Parameters Approach FPA (Cheary and Coelho, 1992). FPA is a convolution approach in which the peak-shape is synthesized from a priori known features of the diffractometer and the microstructural features of the specimen. This approach has been demonstrated to improve the stability and the quality of the refinement. Peak shape was modeled through FPA imposing a simple axial model (12.6 mm) and the size of the divergence slit (0.2 mm). Peak broadening was assumed to follow a Lorentzian (size) and a Gaussian (strain) behavior (Delhez et al., 1993). Peaks position was corrected for sample displacement from the focusing circle. The background was fitted with a 33-term Chebyshev polynomial of the first kind. Such a large number of terms were required for a proper fit of the amorphous contribution of the glass-capillary. Absorption was refined at 303 K considering the contribution of the aluminum windows of the

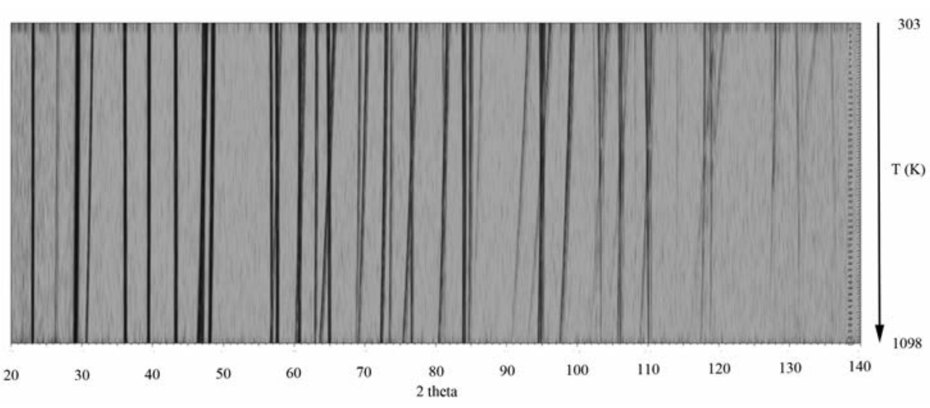

Figure 1. Complete experimental data set displayed as a pseudo-Guinier plot.

heating chamber following the formalism of Sabine et al. (1998) for a cylindrical sample. This value was kept fixed for all the remaining patterns.

Preferred orientation was modeled by means of spherical harmonics (nine refinable parameters up to the 8th order). The choice of the order was performed following the procedure of Ballirano (2003). A first series of refinements was carried out allowing optimization of spherical harmonics terms that were found to be extremely small (as expected for a capillary mount) and constant throughout the analyzed thermal range. The final structural data set was obtained keeping the spherical harmonics terms fixed to the corresponding averaged values.

Starting structural data were those of the Ising-model of Antao et al. (2009) with the oxygen atoms distributed between two sites at $\pm x$, 0, ¼ and allowing refinement, a part of the oxygen sites $\pm x$ coordinate and occupancy, of anisotropic displacement parameters adp's for Ca and O, and isotropic for C. Such approximation was forced by the presence of strong correlations among C and O U_{ij} tensors leading to a general instability of the refinements. However, reference single crystal data indicate a substantial isotropy of adp's of the carbon atom at each temperature. Therefore, it is expected that such approximation should have very limited effects on the final quality of the refinements. A scrutiny of the correlation matrix indicates that occupancy is substantially independent from adp's the largest elements being 0.52 for O U_{22} , 0.37 for O U_{11} , and -0.36 for O x).

Table 1. Range of the conventional agreement indices, defined as in Young (1993), obtained for the various refinements.

wRp (%)	6.40-7.47
Rp (%)	5.03-5.93
R_{Bragg} (%)	0.64-1.19
χ^2	1.22-1.31
DWd	1.31-1.51

Conventional agreement indices obtained for the various refinements are listed in Table 1.

Discussion

Thermal expansion and spontaneous strain

Calcite has a very anisotropic dependence of cell parameters from T (Figure 2). In fact, the *c* axis expands significantly whereas the *a* axis slightly contracts. The latter behavior is different from nitratine for which the *a* axis slightly expands. Data are in substantial agreement with those of Markgraf and Reeder (1985), Dove and Powell (1989), Dove et al. (2005), and Antao et al. (2009). Systematic slightly larger values of the *a* cell parameter have been found for the present data set as compared to those of Antao et al. (2009). Dependence from T in the investigated thermal range can be fitted with great accuracy with a second-order polynomial of type $p = a_0 + a_1\mathrm{T} + a_2\mathrm{T}^2$. Unfortunately, we were not able to confirm the more significant contraction of the *a* axis at temperatures near T_c reported by Dove et al. (2005) and Antao et al. (2009). Moreover, there is an almost perfect superposition for the *c* axis data with those of Antao et al. (2009) and also in this case the temperature dependence has been successfully fitted with a second order polynomial. Results of non-linear fitting are reported in Table 2.

Among the different properties used for thermodynamic analysis of phase transitions, spontaneous strain *e* variation as a function of T has received special attention. This second-rank tensor, constrained by symmetry, has been largely used as a determinant of thermodynamic properties for phase transitions (Carpenter et al., 1998). Clearly, a very stringent request for a modeling of the spontaneous strain data is the availability of very accurate cell parameters. However, because there are no available experimental data for the dependence of cell parameters from T for the HT, ordered polymorph, each proposed dependence has been derived at the

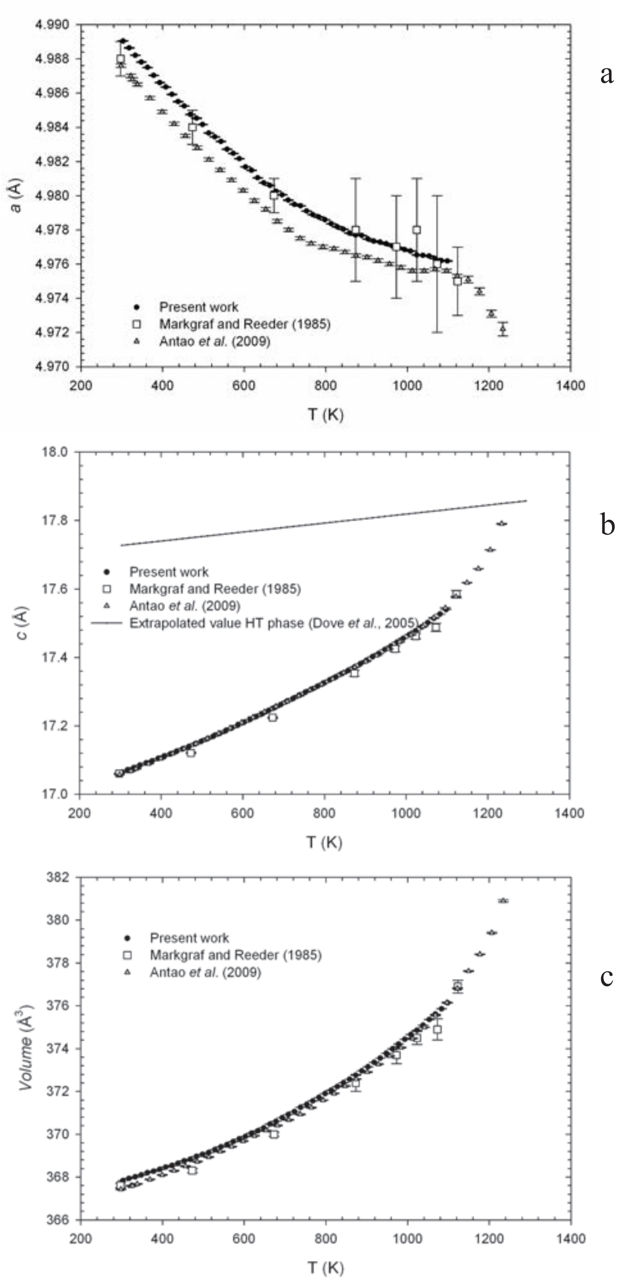

Figure 2. Cell parameters and volume dependence from temperature; a) *a* cell parameter; b) *c* cell parameter; c) cell volume. Reference data from Markgraf and Reeder (1985) and Antao et al. (2009) are reported for comparison.

Table 2. Results from data-fitting procedures using the polynomial $p = a_0 + a_1T + a_2T^2$ for thermal expansion data in the 303-1098 K thermal range.

	a	c	V
R^2	0.9994	0.9999	0.9999
a_0	5.0000(1)	16.961(2)	367.21(4)
a_1	-4.05(4) x 10^{-5}	2.79(6) x 10^{-4}	7(11) x 10^{-5}
a_2	1.73(3) x 10^{-8}	2.22(4) x 10^{-7}	7.27(8) x 10^{-6}

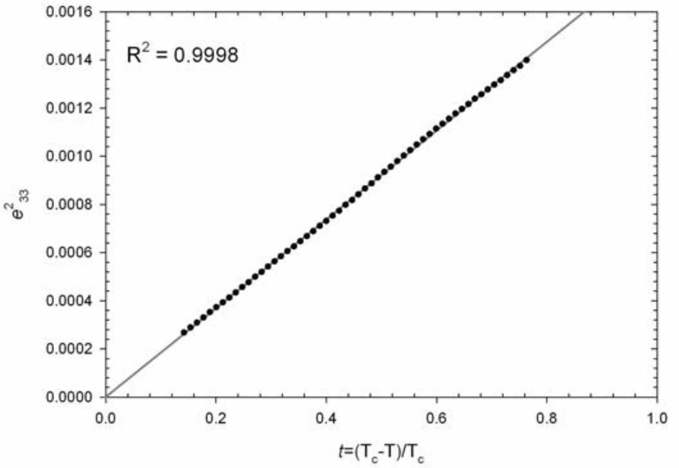

Figure 3. Test of the linear $e_{33}{}^2$–t dependence for the present analyzed thermal range. A T_c of 1280 K provides zero strain at the transition.

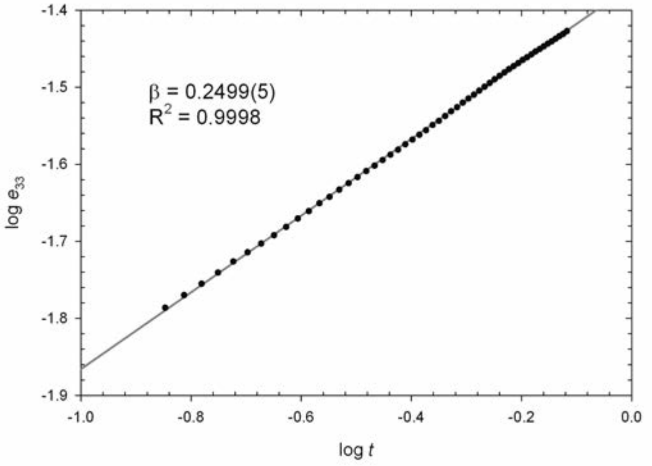

Figure 4. Test of linearity for the log e_{33} vs log t plot. The critical exponent was found to be 0.2499(5) from the slope, expected to be equal to 2β. This value is consistent with a tricritical behavior.

expenses of a few arbitrary assumptions.

A linear extrapolation of the c_0 cell parameter of the HT polymorph below T_c, calculated with the best estimate reported by Dove et al. (2005) indicates the presence of significant spontaneous strain consistent with reference data. By the way, the equation $c_0 = 2 x (8.8438 + 6.5527 x 10^{-3} T)$ reported by Dove et al. (2005) should be, in effect read as $c_0 = 2 x (8.8438 + 6.5527 x 10^{-5} T)$.

However, the absence of direct measurements of the cell parameters for the HT phase renders unreliable a quantitative evaluation of strain. In fact, it can be shown that there is a strong dependence of both the extension of e_{33}^2-t [(t=(T-T_c)/T_c)] linearity region and the value of the critical exponent β on the selection of the dependence function of c_0 from temperature and of the T_c (Ballirano, 2011).

Different T_c values were iteratively tested and evaluated from a purely statistical point of view. An almost perfect linear e_{33}^2–t dependence (R^2=0.9998) has been obtained for the present analyzed thermal range using a T_c of 1280 K (Figure 3). Such value has the advantage of providing a zero strain at T_c, hypothesizing a linear behavior extending up to the transition temperature. This value is greater than 1240 K reported by Antao et al. (2009) and 1260 K by Dove and Powell (1989). However, it should be reminded that Dove and Powell (1989) reported the occurrence of a well defined 113 superlattice reflection still at 1258 K. Therefore, it is reasonable to hypothesize that its complete disappearance, indicating the symmetry change $R\bar{3}c \rightarrow R\bar{3}m$, could occur some degrees above 1260 K.

The critical exponent *β*, giving the temperature dependence of the macroscopic order parameter Q, was derived from the slope, expected to be equal to 2*β*, of the log e_{33} vs log t plot (Figure 4). The resulting critical exponent was found to be 0.2499(5) perfectly fitting the expected value of ¼ for a tricritical behavior (Harris, 1999). Such value is in agreement with 0.240(8) obtained by Harris (1999) from simultaneous fitting of the intensities of the 113 and 211 superlattice reflection originally reported by Dove and Powell (1989).

No crossover in the value of the critical exponent *β*, as reported in isotypic nitratine (Reeder et al., 1988), has been observed up to t = 0.14.

Within the investigated thermal range,

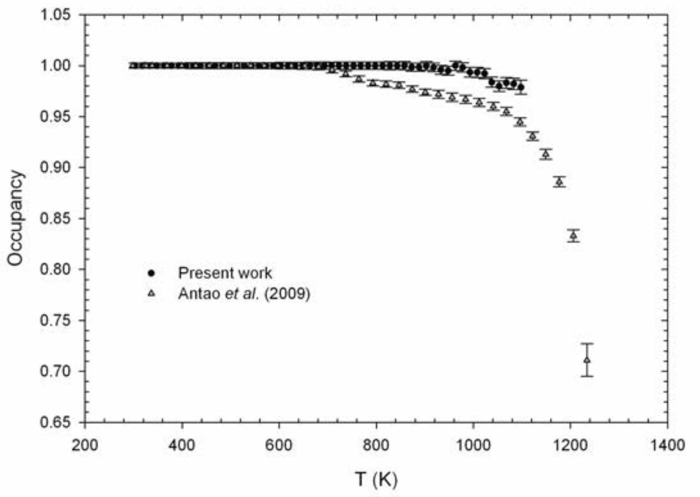

Figure 5. Oxygen site occupancy dependence from temperature. Reference data from Antao et al. (2009) are reported for comparison.

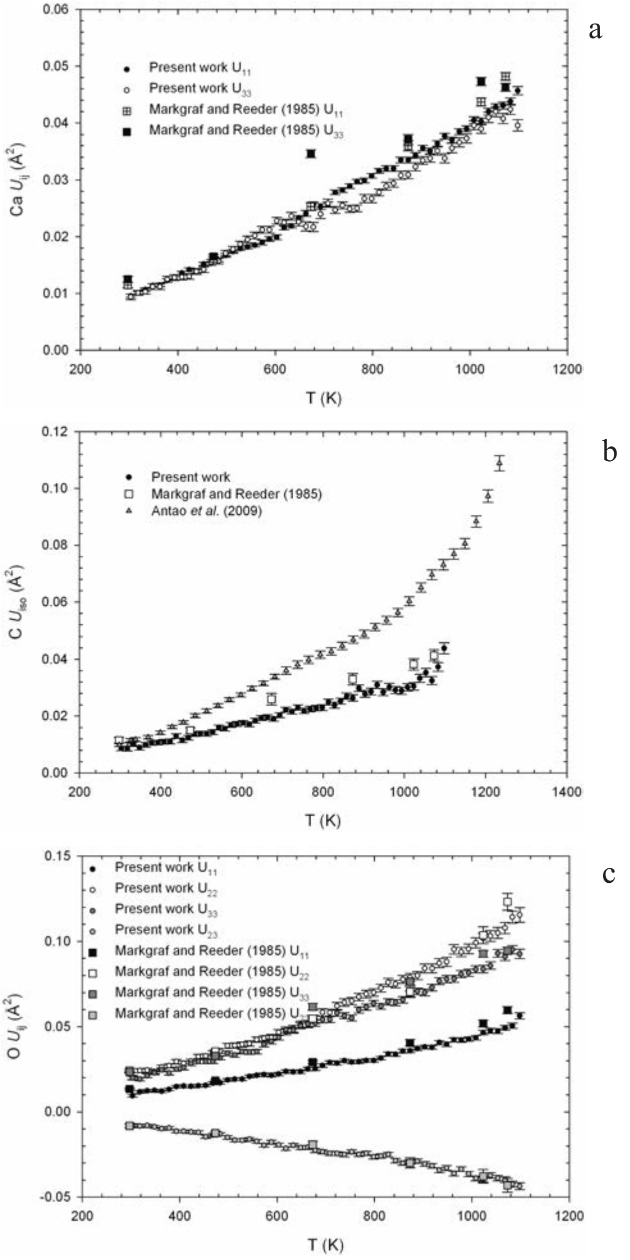

Figure 6. Adp's (for Ca and O) and isotropic displacement parameter (for C) dependence from temperature; a) Ca; b) C; c) O. Reference data from Markgraf and Reeder (1985) (Ca, C, O) and Antao et al. (2009) (C = O) are reported for comparison.

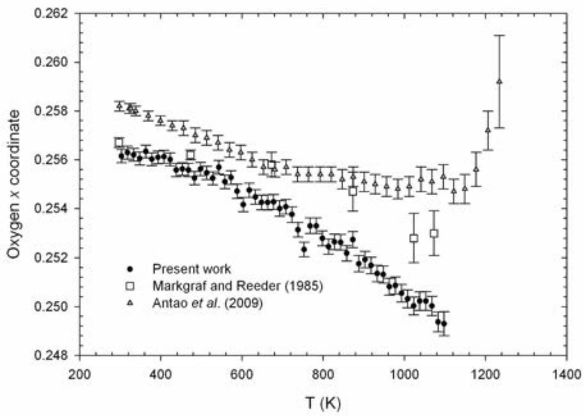

Figure 7. Oxygen *x* fractional coordinate dependence from temperature. Reference data from Markgraf and Reeder (1985) and Antao et al. (2009) are reported for comparison.

quantitative analysis of the microstructural parameters does not indicate any variation as a function of temperature.

Structure evolution

Structure refinements of calcite using the Ising-model were stable at each temperature differently from Dove et al. (2005). However, the occupancy of the oxygen site at the "disordered" position refined to a value greater than 3σ only at T exceeding 1038 K (Figure 5). This is a value significantly higher than 764 K reported by Antao et al. (2009). The present results are more in accordance with those of Markgraf and Reeder (1985) who were not able to detect any extra peak in difference Fourier maps at 1073 K. The use of F_{obs} by Dove et al. (2005) to demonstrate the absence of the oxygen site at the "disordered" position may have failed, as pointed out by Antao et al. (2009), because of bias effects from the starting structural model. The large discrepancy of the present results to those of Antao et al. (2009) could be due to the crude O U_{iso} = C U_{iso} approximation used in the latter work.

Displacement parameters are in remarkable agreement with those from single-crystal analysis (Figure 6) and lattice-dynamical calculations (Pilati et al., 1998). The isotropic displacement parameter for the carbon atom is only slightly smaller than the equivalent isotropic displacement parameter recalculated from the adp's of Markgraf and Reeder (1985).

The evolution of the oxygen site *x* fractional coordinate is reported in Figure 7. The general behavior of the oxygen site *x* fractional coordinate dependence from T follows approximately that of reference data, a part for a slight systematic displacement. Such displacement is more significant with respect to the data of Antao et al. (2009). However, it should be noted that the *x* fractional coordinate from the latter article differs significantly already at RT from that reported by several authors from single-crystal data (Effenberger et al., 1981; Markgraf and Reeder, 1985; Maslen et al., 1993; 1995). The *x* coordinate regularly decreases within the investigated thermal range. As a result the Ca-O bond distance lengthens (Figure 8) and the C-O bond distance has a strong apparent reduction (Figure 9) as a function of T. However, after correction for rigid-body motion (Downs et al., 1992) the C-O bond distance showed a slight increase from 1.290 to 1.300 Å. Because it is expected that the C-O bond

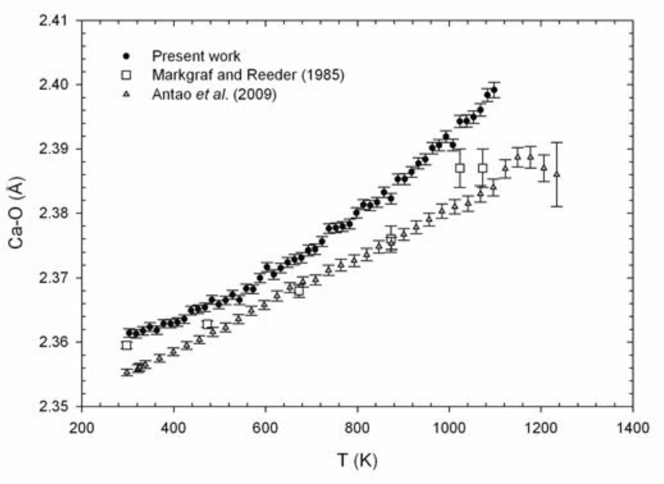

Figure 8. Ca-O bond distance dependence from temperature. Reference data from Markgraf and Reeder (1985) and Antao et al. (2009) are reported for comparison.

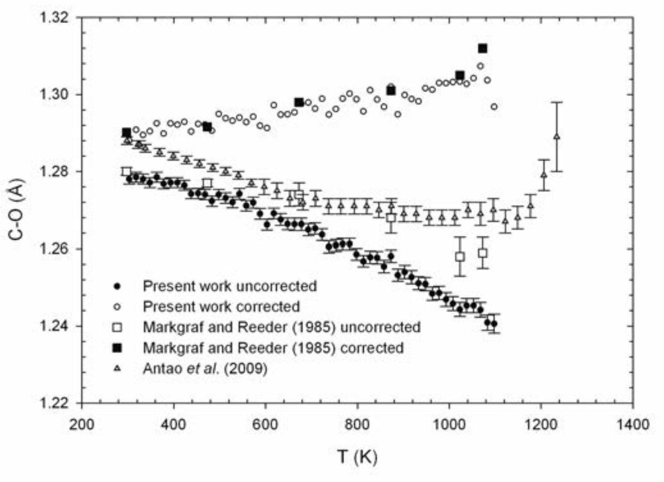

Figure 9. C-O bond distance dependence from temperature. Reference data from Markgraf and Reeder (1985) and Antao et al. (2009) are reported for comparison. Whenever possible, data corrected for rigid-body motion are also plotted.

distance is substantially independent from T (approximately 1.290 Å with oxygen positions corrected for riding motion) we may possibly attribute such behavior to the inability to refine anisotropically the carbon atom. However, it should be remarked that the dependence from temperature of the C-O bond distance, corrected for riding motion, reported by Markgraf and Reeder (1985) is almost perfectly superimposed to the present powder diffraction data. On the contrary, data reported by Antao et al. (2009) show significant deviation from the expected trend. In particular, C-O decreases from *ca*. 1.29 Å at RT up to ca. 1.27 Å at approximately 750 K. Subsequently, it remains constant up to 1200 K before increasing back to ca. 1.29 Å. Note that, because of the adopted constraint O U_{iso} = C U_{iso}, no correction for rigid-body motion is applicable in the present case.

Conclusions

Present results provide a clear indication of the possibility to extract high-quality structural data from laboratory parallel-beam transmission X-ray powder diffraction. It has been found that such quality is comparable with that of an X-ray single-crystal analysis of the mid eighties, at least in the present case of calcite. From the analysis of the spontaneous strain e_{33}, a critical exponent β of 0.2499(5), perfectly consistent with the expected value of ¼ for a tricritical behavior, was obtained using a T_c of 1280 K. However, it should be observed that such value is strongly dependent on the choice of the T_c and the dependence of c_0 from temperature. In this work, the dependence of the c_0 cell parameter of the HT polymorph below T_c proposed by Dove et al. (2005) was used. Such arbitrary choice is justified by the absence, to date, of experimental data for the cell parameters of the HT phase. Structure refinements seemingly support the Ising model of disorder. However, because of the very small (ca. 3%) refined population of the "disordered" oxygen site at the highest accessible temperature, it would be greatly desirable to extend further the analyzed thermal range in order to confirm the stability of the refinements in the presence of rapidly increasing adp's. It should be noticed that, at least up to 1073 K, the TLS rigid body refinement of Markgraf and Reeder (1985) produced similar values for both L_{11} and L_{33} corresponding to librational amplitudes of approximately 10°. On the contrary, Dove et al. (2005) obtained different values with L_{33} significantly greater than L_{11}, from neutron powder diffraction, with no screw component refined, a feature apparently supporting the free-rotational model of phase transition. Moreover, both anisotropic and rigid-body refinements by Markgraf and Reeder (1985) produced the same adp's. Therefore, we may speculate that the present adp's are consistent with the TLS tensors refined by Markgraf and Reeder (1985) instead of those reported by Dove et al. (2005). Therefore, it is possible that such differences observed for the TLS tensors (and therefore displacement parameters) could be the reason for the failure to detect oxygen atoms at the "disordered" site of Dove et al. (2005).

As a final remark, the present data set is of better quality that that obtained very recently by Antao et al. (2009) from synchrotron powder X-ray diffraction experiments, primarily because of the extended sinθ/λ range analyzed resulting in 81 instead of 28 observed reflections. In fact, cutting the maximum sinθ/λ value to 0.42 Å^{-1}, to produce a data set consistent with that used by Antao et al. (2009), a significant decaying of the quality of the structure refinements was observed. The main problem was the difficulty to properly refine the absorption correction. However, also in this case anisotropic refinements were stable throughout the investigated thermal range.

Acknowledgments

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