Dependence of structural data from sinθ/λ extension in Rietveld refinement of virtually texture-free laboratory X-ray powder-diffraction data

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Abstract

The present work analyses the effects of reducing the resolution of a data set on the structural parameters of three compounds: nitratine $NaNO_3$, gypsum $CaSO_4 \cdot 2H_2O$, and K-alum $KAl(SO_4)_2 \cdot 12H_2O$, characterized by an increasing degree of structural complexity. The unexpected result is that in the case of the near absence of preferred orientation, adequate structural information can be retrieved from data sets extending up to a minimum sinθ/λ value of ca. 0.4, corresponding to a 2θ value of ca. 75° for CuKα radiation, at least for compounds of fairly moderate complexity (ca. 25 structural parameters). Therefore, in the case of experiments collected in step-scan mode, whenever time is a limiting factor, an increase of the peak/background ratio is more advantageous than the extension of the explored reciprocal lattice.

Key words: X-ray powder diffraction; Rietveld method; structural data; sinθ/λ data extension; nitratine, gypsum, K-alum.

Introduction

Inclusion of data measured at high sinθ/λ has been claimed to positively affect the accuracy of both individual atomic displacement parameters and site populations extracted from powder diffraction experiments (Ballirano and Caminiti, 2001; Pecharsky and Zavalij, 2005). This is particularly true for structural data obtained from diffraction patterns collected on virtually texture-free samples, such as those prepared as capillary mounts. However, there as been no systematic

analysis of this effect. Accordingly, the present work investigates the effect of reducing the resolution of a data set on the relevant structural parameters of nitratine $NaNO_3$, gypsum $CaSO_4 \cdot 2H_2O$, and K-alum $KAl(SO_4)_2 \cdot 12H_2O$. The same nitratine and gypsum samples have been analysed using a different, albeit similar, instrumental setup (Ballirano and Melis, 2009; Ballirano, 2011a), obtaining structural parameters very close to those from single-crystal structure refinement (SCSR). The results of the present investigation are expected to provide information for optimizing data-collection strategies, especially at non-ambient conditions, whenever fast data-collection is required. This information is particularly useful for experiments done on laboratory instruments (Ballirano et al., 2010; Ballirano, 2011b) without the help of high intensity X-ray sources.

Experimental

The nitratine used here is an analytical-grade Merck product 6546, the gypsum is an analytical-grade Analar product 10071, and K-alum crystals were synthesised by precipitation in aqueous solution from a stoichiometric mixture of $Al_2(SO_4)_3 \cdot 18H_2O$ (alunogen: purum p.a. Fluka 06421) and K_2SO_4 (arcanite: purum p.a. Fluka 60533). Samples were ground in an agate mortar and the corresponding powders were charged in borosilicate-glass capillaries of 0.7 mm diameter. Data were collected, in transmission mode, using Cu-Kα radiation with a Bruker AXS D8 Focus operating in $\theta/2\theta$ geometry and equipped with 2.3° Soller slits placed along both incident and diffracted beams and a solid-state SolX detector. The maximum $\sin\theta/\lambda$ was 0.634 Å^{-1}, corresponding to 2θ 155° for CuKα radiation. Diffraction data were processed by the Rietveld method using TOPAS V.4.2 (Bruker AXS, 2009). This program uses the Fundamental Parameters Approach FPA (Cheary and Coelho, 1992), which is believed to improve the stability and quality of the refinement. Peak shape was modelled using a simple axial model (value refined) and the size of the divergence (0.3° = 0.6 mm) and receiving slit (0.2 mm). For modelling of microstructure effects the Double-Voigt Approach was used (Balzar, 1999), where crystallite size and strain comprise Lorentzian and Gaussian component convolutions varying in 2θ as a function of $1/\cos\theta$ and $\tan\theta$ respectively. The background was fitted with a Chebyshev polynomial of the first kind. Absorption was refined following the formalism of Sabine et al. (1998) for a cylindrical sample correcting for the resulting peaks shift. Due to the strong correlation between absorption and displacement parameters, a successful approach was used (Ballirano and Maras 2006 a,b). Initially, the absorption parameter was refined while fixing the displacement parameters to reference data and, subsequently, it was fixed allowing refinement of the individual displacement parameters. Preferred orientation was modelled with spherical harmonics following Järvinen (1993). Selection of the number of terms was done following Ballirano (2003). The values of the spherical-harmonic terms were extremely small, as expected for a capillary mount. Reference starting structural data of the samples are indicated in

Table 1. Reference starting structural data of the four analysed compounds.

Sample	Reference
nitratine	Gonschorek et al. (1995)
gypsum	Boeyens and Ichharam (2002)
K-alum	Nyburg et al. (2000)

Table 1, a list of the refined structural parameters and the number of reflections observed up to $\sin\theta/\lambda = 0.634$ Å^{-1} is shown in Table 2. For both gypsum and K-alum, hydrogen-atom positions and displacement parameters were kept fixed to the corresponding value of the reference data. The following constraints were imposed on the displacement parameters of K-alum: O3 = O3A and O4 = O4A, to reduce correlation among positional, occupancy and displacement parameters due to the occurrence of two different SO$_4$-group orientations within the structure (Larson and Cromer, 1967). For nitratine, Na and O were refined anisotropically.

Two different refinement strategies were adopted in order to evaluate the occurrence of local (instead of global) minima. The first was to expand sequentially the data, progressively increasing the maximum value of $\sin\theta/\lambda$ and refining the absorption parameter for each refinement. The second procedure was to refine of the fully extended data and then progressively reduce the maximum value of $\sin\theta/\lambda$ until a stable refinement was possible. The latter strategy implies the use of a single absorption parameter for all refinements.

Discussion

Results of the structure refinements with the fully extended data sets are consistent with the reference data. The largest discrepancy in bond distances with respect to those from SCSR reference data is 0.019 Å, but more commonly is < 0.01 Å. Conventional R indices and cell parameters of each sample are reported in Table 3. Refinement of the K alum structure reveals the occurrence of minor unreacted alunogen [3.80(11) wt.%] and tamarugite [NaAl(SO$_4$)$_2$·6H$_2$O: 0.59(4) wt.%]. Both phases were added to the refinement without

Table 2. List of the refined structural parameters, spherical-harmonic terms, treatment of displacement parameters, number of the reflections observed up to $\sin\theta/\lambda = 0.634$ Å^{-1}, and reflection/structural parameters ratio at $\sin\theta/\lambda = 0.634$ Å^{-1}.

Sample	Structural parameters	Dispacement parameters	Sph. harmonics terms	Reflections up to $\sin\theta/\lambda = 0.634$ Å^{-1}	Refl./struct. parameters
nitratine	8	anisotropic Na, O	6	90	11.3
gypsum	16	isotropic	3	536	33.5
K-alum	23	isotropic, partly constrained	4	647	28.1

Table 3. Conventional R agreement indices, space groups, and cell parameters of the four samples as obtained from the refinements of the fully extended data sets. Agreement indices as defined in Young (1993).

Sample	R_p	R_{wp}	GOF	DWd	R_{Bragg}	Space group	a (Å)	b (Å)	c (Å)	β (°)	vol. (Å^3)
nitratine	6.58	8.85	1.55	0.98	1.50	$Fd\overline{m}$	5.06757(7)	=a	16.8148(3)	90°	373.928(13)
gypsum	5.07	6.43	1.22	1.43	1.89	$C2/c$	6.28215(10)	15.1970(3)	6.52409(12)	127.4185(11)	494.681(18)
K-alum	3.48	4.74	1.56	1.00	1.46	$Pa\overline{3}$	12.15627(5)	=a	=a	90°	1796.39(2)
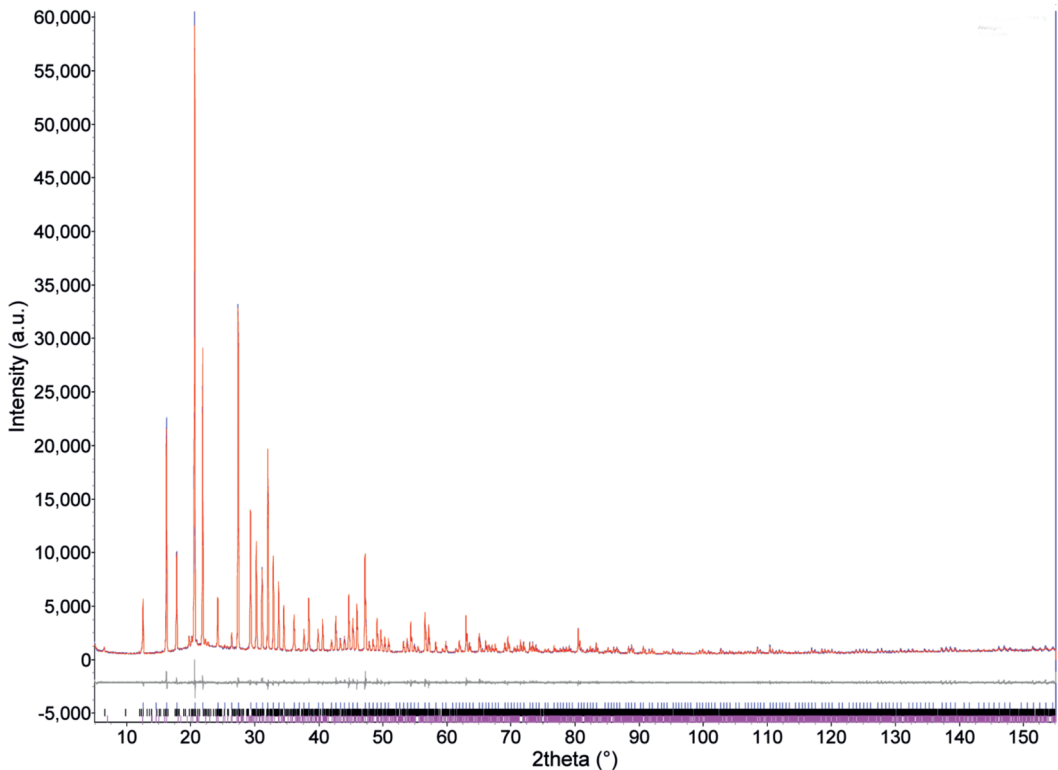
Figure 1. Conventional Rietveld plots of the refinement of the fully extended diffraction data of K-alum. Vertical bars refer to Bragg reflections of, from above to below, K-alum, alunogen, and tamarugite.

optimization of their structures, except for the cell parameters (Figure 1). The fully extended data-set consists of 647 strongly overlapping reflections due to identical $h^2 + k^2 + l^2$, leading to

31 unique Bragg peaks. In particular, 20 of the 54 reflections up to a 2θ = 50° are singlets. 23 structural parameters and 4 spherical harmonics terms up to the 8th order [k41 = -0.001(4); k61 = 0.009(4); k62 = -0.026(5); k81 = -0.002(5)] were refined.

The <S-O> bond distances for the two statistically disordered tetrahedra are 1.472 Å and 1.487 Å for the more abundant and less abundant configuration, respectively. These values are both reasonably close to 1.48 Å, reported by Bergerhoff and Brandenburg (1985) as the average S-O bond distance observed in sulphate groups occurring in inorganic compounds. Nyburg et al. (2000) obtained <S-O> distances of 1.466 Å and 1.450 Å whose shortening with respect to the expected value was attributed to the effect of libration. The Al-O bond distance is 1.8797(15) Å and compares favourably with 1.875(1) Å from reference data. The K-O bond distance is 2.9465(18) Å, slightly shorter than 2.954(1) Å reported by Nyburg et al. (2000). Finally, the k disorder parameter was refined to 0.676(3), a value that is smaller than 0.697(5) and 0.70(3) reported by Nyburg et al. (2000) and Larson and Cromer (1967), respectively. Isotropic-displacement parameters are in close agreement with the reference data, the only exception being O4 = O4A, which is moderately underestimated (ca. 40%). The effect of such underestimation could possible affect the slightly smaller k parameter obtained in the present refinement as compared to both Larson and Cromer (1967) and Nyburg et al. (2000).

Analysis of the dependence of the structural parameters from data extension provides interesting albeit unexpected results (Figures 2 a-e). First, the trend is independent at the 1σ level from the refinement strategy used, the only exception being the displacement parameters. This behaviour is due to the strong correlation between displacement parameters and absorption correction. However, the refined absorption parameter has relatively small variations, being in the range 1.41-1.59 and as a result, the corresponding differences in the displacement parameters obtained from the two refinement strategies are not relevant. The surprising result is that no significant differences (i.e. exceeding 1σ) were observed in bond distances, displacement parameters, and k disorder parameter, down to a sinθ/λ value of ca. 0.4, corresponding to a 2θ value of ca. 75° for CuKα radiation. This sinθ/λ value corresponds to a ratio of reflections/structural parameter of ca. 7. It is clear that this ratio does not have the same meaning that it takes for single-crystal X-ray or neutron diffraction (Young, 1993) due to overlapping reflections; keeping this in mind, it is reported to provide a further parameter to be evaluated. Finally, a stable and meaningful refinement was still possible at a sinθ/λ value of 0.274, corresponding to a 2θ value of 50° for CuKα radiation.

Similarly, the refinement of the gypsum structure provided similar results using both refinement strategies. The fully extended data-set consists of 536 heavily overlapped reflections. A total of 16 structural parameters were refined along with 3 spherical-harmonic terms up to 2th order [$y20$ = 0.152(7); $y22m$ = 0.013(7); $y22p$ = -0.184(5)]. The two S1-O1 and S1-O2 distances
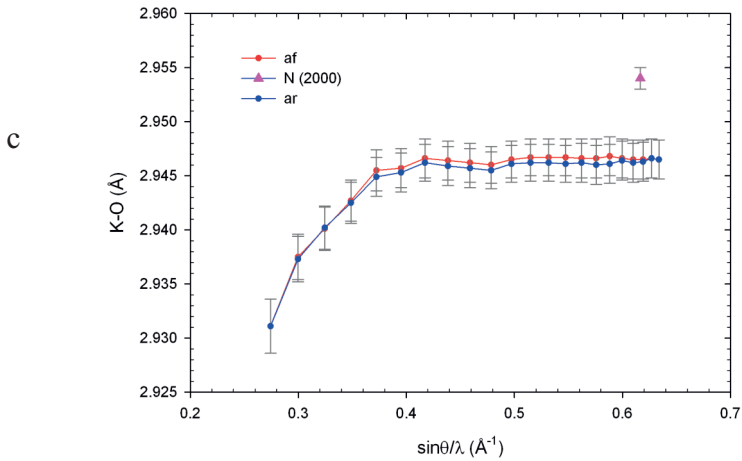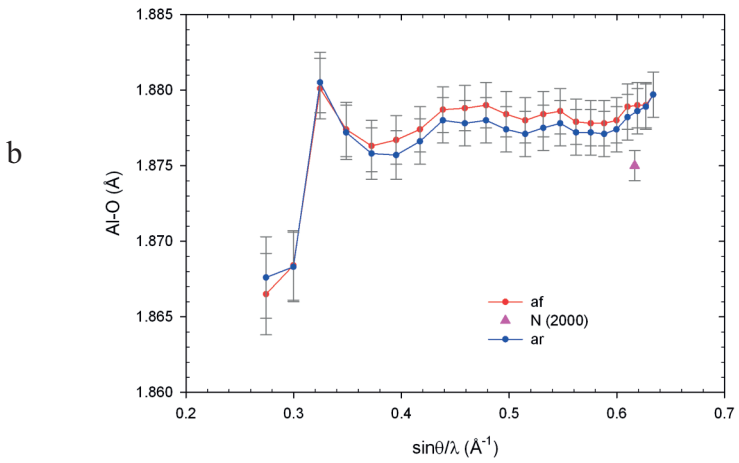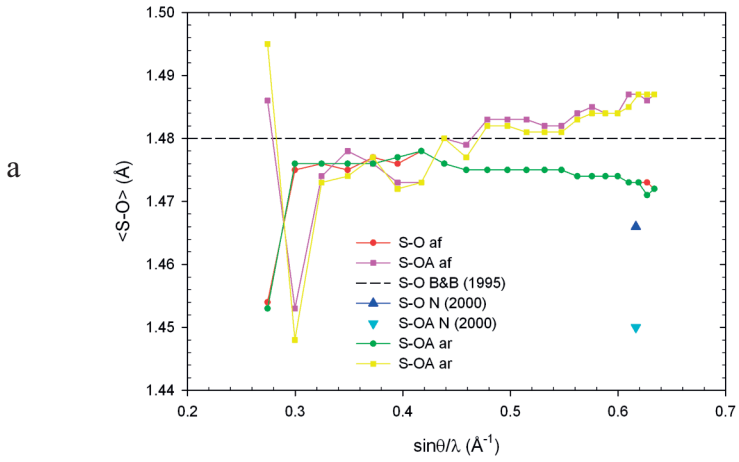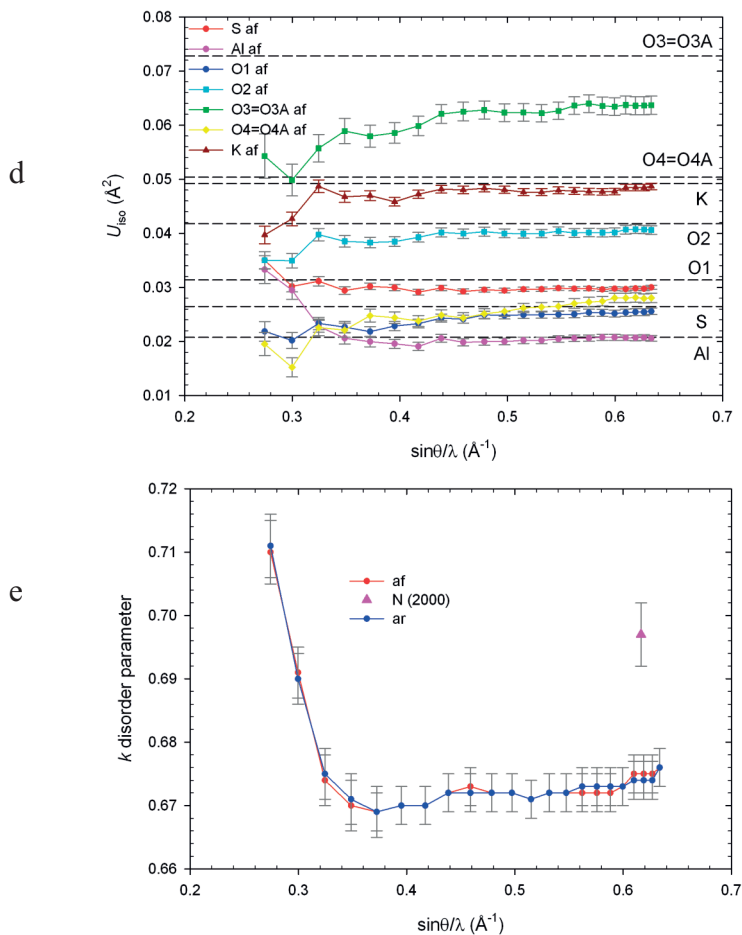
Figure 2. Dependence of the structural parameters of K-alum from data extension: a) <S-O> bond distances; b) Al-O bond distance; c) K-O bond distance; d) Uiso isotropic-displacement parameters; e) k disorder parameter. Legend: af = absorption fixed; ar = absorption refined; B&B (1995) = Bergerhoff and Brandenburg (1995); N (2000) = Nyburg et al. (2000).

are 1.472(4) Å and 1.484(3) Å, to be compared to 1.4750(10) Å and 1.4760(7) Å reported by Boeyens and Ichharam (2002). The Ca1-O bond distances of the Ca1-O$_8$ polyhedron are similar to those from SCSR, the largest differences being Ca1-O3 x2 of 2.389(4) Å relative to 2.370(1) Å

for the reference data. It is worth noting that O3 is the oxygen atom of the water molecule and the small difference (< 0.02 Å) may be possibly ascribed, at least partly, to the effect of keeping fixed in the present refinement both the hydrogen-atom fractional coordinates and

displacement parameters. The same effect could be invoked to explain the largest (albeit small) difference among all the displacement parameters shown by O3 (0.0185(8) Å^2 as compared to 0.0241(18) Å^2 of Boeyens and Ichharam, 2002). The approximation of modifying the scattering power of the water molecule oxygen atom to include the contribution of bonded hydrogen atoms (Ballirano et al., 2001) was tested. However, it produced both a worse set of agreement indices and a further lengthening of the Ca1-O3 bond distances and this approach was discontinued. As far as the dependence of the structural parameters on data extension, S-O distances are the most sensitive (Figure 3a). In fact, at a value of $\sin\theta/\lambda$ of ca. 0.4, they tend to progressively increase. Of the four independent Ca-O distances, only Ca1-O1 and Ca1-O3 show marginal shortening, which starts for a $\sin\theta/\lambda$ value of ca. 0.4 (Fig. 3b). The behaviour of the isotropic-displacement parameters is more irregular (Fig. 3c). However, below $\sin\theta/\lambda$ of ca. 0.4, the various values (excepted for O1) start to increase significantly. This behaviour is related to the progressive decrease of the refined absorption parameter from 2.91 to 2.57 as the data-set is reduced. It is worth noting that the $\sin\theta/\lambda$ value of ca. 0.4 corresponds to a ratio of reflections/structural parameter of ca. 7. As in the case of K-alum, a stable and meaningful refinement was still possible at a $\sin\theta/\lambda$ value of 0.274.

The fully extended diffraction pattern of nitratine contains 90 well-spaced reflections with only marginal overlap. 8 structural parameters and 6 spherical-harmonic terms up to 6th order [$y20 = -0.315(9)$; $y40 = -0.008(10)$; $y43m = -0.023(7)$; $y60 = 0.0077(9)$; $y63m = 0.034(7)$; $y66p = 0.002(7)$] were refined. The N-O and Na-O bond distances are in excellent agreement with those reported by Gonschorek et al. (1995): 1.2445(10) Å compared to 1.2453(7) Å, and 2.4007(5) compared to 2.4022(5) Å, respectively. Moreover, very good agreement with reference data was observed for anisotropic- and isotropic-displacement parameters. The dependence of structural parameters from data extension shows the same behaviour for both refinement strategies. Therefore, the results from the progressive reduction of the maximum $\sin\theta/\lambda$ will be presented (Figure 4a-e). In this case, the refinement becomes unstable at $\sin\theta/\lambda$ values smaller than 0.349, corresponding to a 2θ value of 65° for CuKα radiation. All structural parameters are within 2σ of those obtained from the fully extended data set up to $\sin\theta/\lambda$ of ca. 0.4. This value corresponds to a ratio of reflections/structural parameters of ca. 2. Evaluation of the dependence of the spherical-harmonic terms from data extension shows only a moderate variation starting below a $\sin\theta/\lambda$ value of 0.349 (Figure 5).

Figure 3. Dependence of the structural parameters of gypsum from data extension: a) S-O bond distances; b) Ca-O bond distance; c) U_{iso} isotropic-displacement parameters. Legend: B&I (2002) = Boeyens and Ichharam (2002).
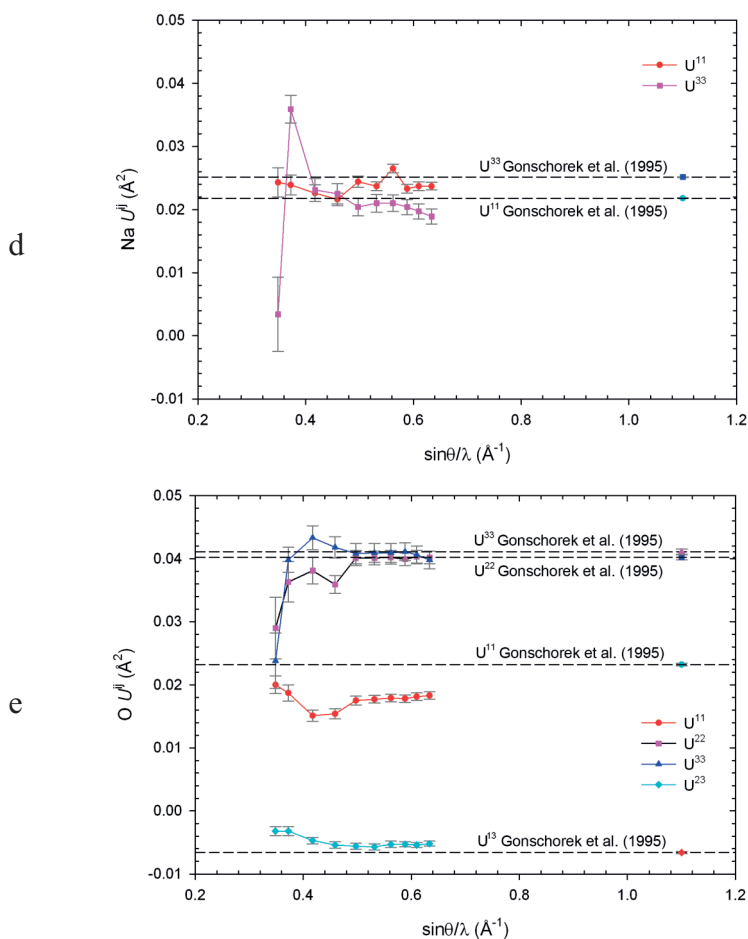
a

b

c
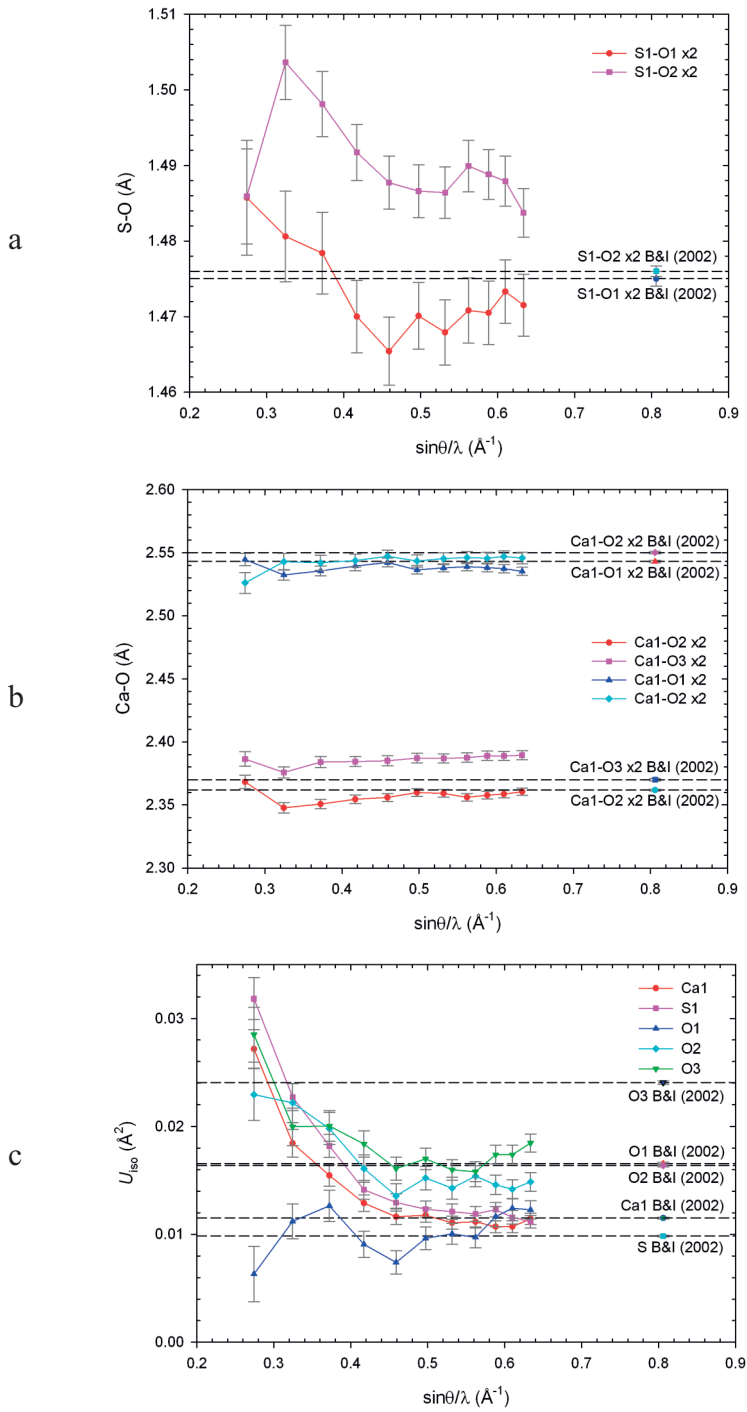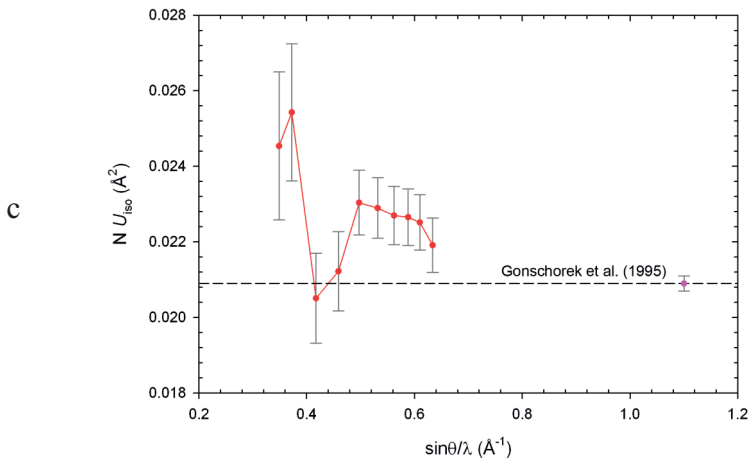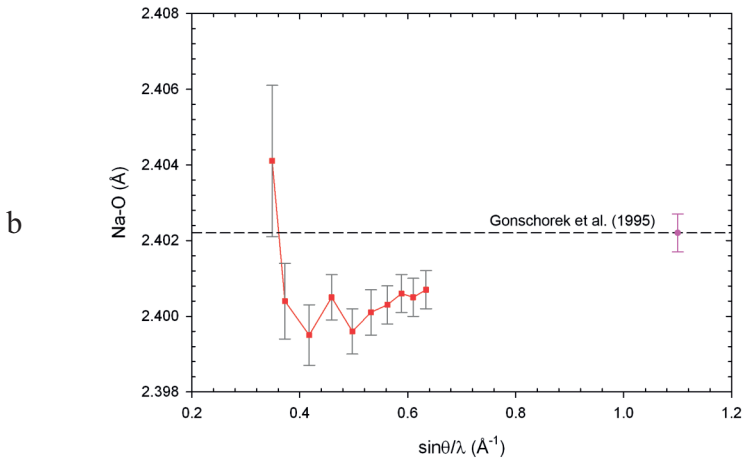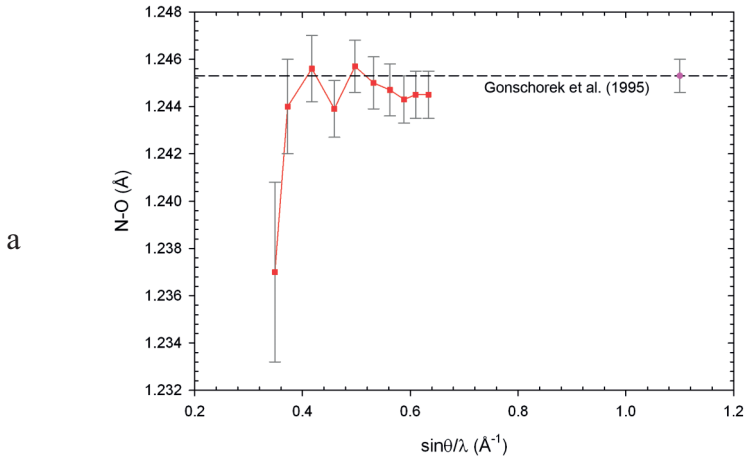
Figure 4. Dependence of the structural parameters of nitratine from data extension: a) N-O bond distances; b) Na-O bond distance; c) Na U^{ij} anisotropic-displacement parameters; d) N U_{iso} isotropic-displacement parameter; e) O U^{ij} anisotropic-displacement parameters.

Conclusions

In the case of the near absence of preferred orientation, adequate structural information can be retrieved from data sets extending up to a minimum sinθ/λ value of ca. 0.4, without imposing bond-distance constraints, at least for compounds of moderate complexity (ca. 25 refined non-hydrogen structural parameters). For K-alum and gypsum, the effect of a relatively high ratio of reflections/structural parameters (7) is partly offset by the occurrence of heavy overlapping peaks. On the other hand, for nitratine, refinement stability is still reached for
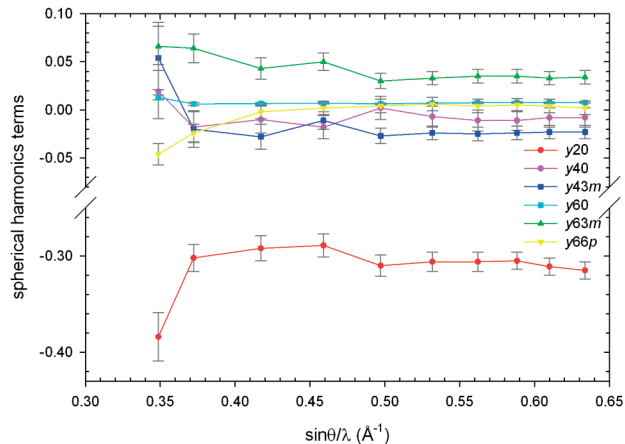
Figure 5. Dependence of spherical-harmonic terms of nitratine from data extension.

a significantly smaller over-determination ratio of 2. However, owing to the absence of overlapped peaks, this value takes a significance close to that commonly accepted in single-crystal refinement. The behaviour is expected to be significantly different whenever data are affected by texture. In this case, the intensity misfit is heavily compensated by the spherical-harmonic terms that are expected to vary significantly as a function of the maximum $\sin\theta/\lambda$ as more and more reflections influenced by preferred orientation are added to the refinement. Therefore, for experiments in step-scan mode, virtually unaffected by texture, it seems more advantageous to increase the peak/background ratio instead of extending the amount of reciprocal lattice explored.

Acknowledgments

References

Ballirano P. (2003) - Effects of the choice of different ionization level for scattering curves and correction for small preferred orientation in Rietveld refinement: the $MgAl_2O_4$ test case. *Journal of Applied Crystallography*, 36, 1056-1061.

Ballirano P. (2011a) - Laboratory parallel-beam transmission X-ray powder diffraction investigation of the thermal behaviour of nitratine $NaNO_3$: spontaneous strain and structure evolution. *Physics and Chemistry of Minerals,* 38, 531-541.

Ballirano P. (2011b) - 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. *Periodico di Mineralogia*, 80, 123-134.

Ballirano P. and Caminiti R. (2001) - Rietveld refinements on laboratory energy dispersive X-ray diffraction (EDXD) data. *Journal of Applied Crystallography,* 34, 757-762.

Ballirano P., De Vito C., Ferrini V. and Mignardi S. (2010) - The thermal behaviour and structural stability of nesquehonite, $MgCO_3 \cdot 3H_2O$, evaluated

by in situ laboratory parallel-beam X-ray powder diffraction: new constraints on CO_2 sequestration within minerals. *Journal of Hazardous Materials*, 178, 522-528.

Ballirano P. and Maras A. (2006a) - Mineralogical characterization of the blue pigment of Michelangelo's fresco "The Last Judgement". *American Mineralogist*, 91, 997-1005.

Ballirano P. and Maras A. (2006b) - In-situ X-ray transmission powder diffraction study of the kinetics of the light induced alteration of realgar (α-As_4S_4). *European Journal of Mineralogy*, 18, 589-599.

Ballirano P., Maras A., Meloni S. and Caminiti R. (2001) - The monoclinic I2 structure of bassanite, calcium sulphate hemihydrate ($CaSO_4 \cdot 0.5H_2O$). *European Journal of Mineralogy*, 13, 985-993.

Ballirano P. and Melis E. (2009) - Thermal behaviour and kinetics of dehydration of gypsum in air from in situ real-time laboratory parallel-beam X-ray powder diffraction. *Physics and Chemistry of Minerals*, 36, 391-402.

Balzar D. (1999) - Voigt-function model in diffraction line-broadening analysis. In: Defect and microstructure analysis from diffraction. (eds): R.L. Snyder, H.J. Bunge, J. Fiala, International Union of Crystallography Monograph on Cristallography n. 10, Oxford University Press, New York, pp. 94-126.

Bergerhoff G. and Brandenburg K. (1995) - Typical interatomic distances: inorganic compounds: In: International Tables for Crystallography Volume C. (ed): A.J.C Wilson, Kluwer Academic Publishers, pp. 683-684.

Boeyens J.C.A. and Ichharam V.V.H. (2002) - Redetermination of the crystal structure of calcium sulphate dehydrate, $CaSO_4 \cdot 2H_2O$. *Zeitschrift für Kristallographie - New Crystal Structures*, 217, 9-10.

Bruker AXS (2009) - Topas V4.2: General profile and structure analysis software for powder diffraction data. Bruker AXS, Karlsruhe, Germany.

Cheary R.W. and Coelho A. (1992) - A fundamental parameters approach to X-ray line-profile fitting. *Journal of Applied Crystallography*, 25, 109-121.

Gonschorek W., Schmahl W.W., Weitzel H., Miehe G. and Fuess H. (1995) - Anharmonic motion and multipolar expansion of the electron density in $NaNO_3$. *Zeitschrift für Kristallographie*, 210, 843-849.

Järvinen M. (1993) - Application of symmetrized harmonics expansion to correction of the preferred orientation effect. *Journal of Applied Crystallography*, 26, 525-531.

Larson A.C. and Cromer D.T. (1967) - Refinement of the alums structures. III. X-ray study of the α alums, K, Rb and $NH_4Al(SO_4)_2 \cdot 12H_2O$. *Acta Crystallographica,* 22, 793-800.

Nyburg S.C., Steed J.W., Aleksovska S. and Petrusevski V.M. (2000) - Structure of the alums. I. On the sulphate group disorder in the α-alums. *Acta Crystallographica*, B56, 204-209.

Pecharsky V.K. and Zavalij P.Y. (2005) - Fundamentals of powder diffraction and structural characterization of materials. Springer, New York, USA, 713 pp.

Sabine T.M., Hunter B.A., Sabine W.R. and Ball C.J. (1998) - Analytical expressions for the transmission factor and peak shift in absorbing cylindrical specimens. *Journal of Applied Crystallography*, 31, 47-51.

Young R.A. (1993) Introduction to the Rietveld method: In: The Rietveld method. (ed): R.A. Young, Oxford University Press, 1-38.