

# A neutron powder investigation of the structure of $\text{KCaCO}_3\text{F}$ at various temperatures

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Received 10 August 2005; received in revised form 8 September 2005; accepted 8 September 2005

Available online 25 October 2005

## Abstract

The structure of  $\text{KCaCO}_3\text{F}$  is reinvestigated to unambiguously determine the K and Ca sites by neutron powder diffraction. The powder neutron diffractions at temperatures (295 K, 373 K, 473 K, 573 K and 673 K) are also performed to reveal the thermal expansions for this compound. No structural transition in this compound is found in the experimental temperature range. The Rietveld refinements indicate that the unit cell parameters and the cell volume of the compound increase linearly with the increasing temperature. Large anisotropic thermal expansions are found in this compound. The thermal expansion coefficient along  $a$  ( $b$ ) axis is over two times as large as that parallel to the  $c$ -axis. The possible reasons for the large anisotropic thermal expansions are briefly discussed.

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**Keywords:** Chemical synthesis; Crystal structure and symmetry; Neutron diffraction; Anisotropic thermal expansion; Fluoride carbonate

## 1. Introduction

Fluoride carbonates are known to occur in minerals for a long time. Recently, some transition metals [1–5] and rare earths fluoride carbonates [6–8] were successfully synthesized through hydrothermal reactions.  $\text{KCaCO}_3\text{F}$  was first identified by West and Fletcher [9] through solid-state reaction. But its crystal structure was unknown since the single crystals are difficult to obtain probably due to the decomposition of  $\text{CaCO}_3$ . Recently, its structure has been determined from X-ray powder diffraction by Chen et al. at room temperature [10]. The crystal structure was determined to possess a hexagonal symmetry with space group  $P\bar{6}m2$ . The cell constants are  $a = b = 5.101 \text{ \AA}$  and  $c = 4.4551 \text{ \AA}$ . The compound consists of infinite Ca–F–Ca chains parallel to the  $c$ -axis and planar  $\text{CO}_3$  group perpendicular to the  $c$ -axis, with the apices of the hexagonal cell occupied by K ions. The structure is only tentative. As the atomic numbers for Ca ( $Z = 20$ ) and K ( $Z = 19$ ) only differ by 1, their atomic scattering factors are so close to each other that X-ray diffraction cannot clearly distinguish them. In this paper, neutron powder diffraction study

is performed to redetermine this structure, in particular, the Ca and K sites. In addition, variable-temperature neutron powder diffraction data are collected to investigate the thermal expansion property of the compound. A strong anisotropic thermal expansion from room temperature to 673 K is found in this compound. The thermal expansion along the  $a$  ( $b$ ) axis is over two times as large as that parallel to the  $c$ -axis. Possible reasons for the large anisotropic thermal expansion are briefly discussed in this paper according to the structural mode and thermal expansion of different bonds.

## 2. Experimental

The titled compound is obtained by solid-state reaction as described by Chen et al. in Ref. [10]. The starting compounds, high purity  $\text{CaCO}_3$  (A.R), KF (99.9%) are mixed homogeneously in the appropriate molar ratios and fired at 600 °C for 24 h under flow  $\text{CO}_2$  atmosphere. The obtained powders of  $\text{KCaCO}_3\text{F}$  obtained are well crystallized, containing only a tiny amount of  $\text{Ca}_5(\text{SiO}_4)_2\text{F}_2$  (1–3 mol%). The silicon element probably came from the quartz tube in which the syntheses were performed.

Neutron diffraction data are collected using the BT-1 32-detector high-resolution powder diffractometer with a  $\text{Cu}(311)$  monochromator at the NIST center for Neutron Research. A wavelength of  $1.5402(1) \text{ \AA}$ , and  $15'$  incident collimation are employed. Data were collected with a counting time of approximately 12 h for each sample. The  $2\theta$  scan range was  $10^\circ$ , with a step size of  $0.05^\circ$ , so that each data point is collected in two adjacent detectors with a total

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scan range of 3–168° ( $2\theta$ ). The data from the 32 detectors are then processed to yield a single histogram using interpolations between adjacent observations to correct for zero-point offsets and detector sensitivities. The details for BT-1 instrument are described at the NIST Center for Neutron Research Center Web site, <http://webster.ncnr.nist.gov/xtal/>.

The program Fullprof [11] is used for the Rietveld refinement of crystal structures of the compound, using the following values of the scattering amplitudes:  $b(\text{K})=0.3670 \times 10^{-12}$  cm,  $b(\text{C})=0.6646 \times 10^{-12}$  cm,  $b(\text{O})=0.5803 \times 10^{-12}$  cm and  $b(\text{Ca})=0.4700 \times 10^{-12}$  cm,  $b(\text{F})=0.5654 \times 10^{-12}$  cm [12].

A DTA/TG measurement is conducted with a home-made CR-G type high temperature  $\mu$ -DTA apparatus.  $\alpha\text{-Al}_2\text{O}_3$  is used as a reference substance. Pt–PtRh thermocouples were used for measurement. The precision of measurement was  $\pm 3^\circ\text{C}$ . The heating rate was  $10^\circ\text{C}/\text{min}$ .

### 3. Results and discussion

The neutron powder diffraction patterns at different temperatures are presented in Fig. 1, in which the open circles stand

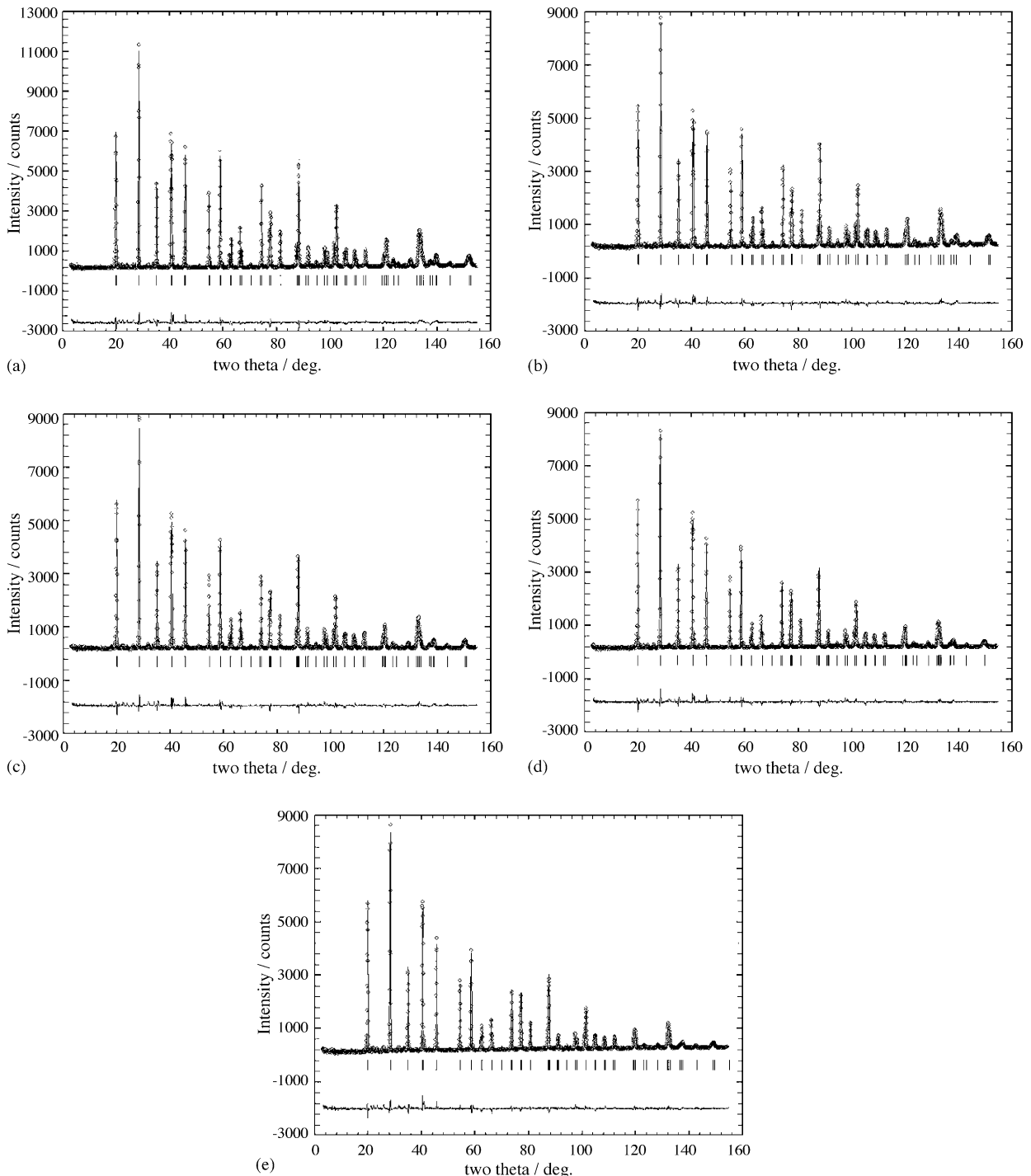


Fig. 1. Neutron diffraction patterns of  $\text{KCaCO}_3\text{F}$  at 295 K (a), 373 K (b), 473 K (c), 573 K (d), 673 K (e). Circles correspond to observed values, solid lines correspond to calculated patterns. The bottom trace depicts the difference between the experimental and the calculated intensity values.

Table 1  
Crystal data and data collection parameters in the different measured temperatures

Chemical formula	KCaCO <sub>3</sub> F				
Chemical formula weight	158.170				
Space group	<i>P</i> $\bar{6}$ <i>m</i> 2				
Z	1				
Calculated density at room temperature (Mg/m <sup>3</sup> )	2.619				
Wavelength (Å)	1.5402(1)				
2θ range (°)	3–168				
Profile function	Pseudo-Voigt				
Number of parameters refined	24				
Excluded regions (°)	155–168				
	Experimental temperature (K)				
	295	373	473	573	673
<i>a</i> (Å)	5.09724(10)	5.10556(11)	5.11615(11)	5.12562(12)	5.13338(13)
<i>c</i> (Å)	4.45539(10)	4.45803(11)	4.46165(11)	4.46475(13)	4.46751(13)
<i>V</i> (Å <sup>3</sup> )	100.251(4)	100.638(4)	101.136(4)	101.583(5)	101.954(5)
<i>R</i> <sub>p</sub> (%)	5.98	5.98	5.81	6.17	5.82
<i>R</i> <sub>wp</sub> (%)	8.64	8.48	8.22	8.68	8.56
<i>R</i> <sub>exp</sub> (%)	4.56	5.05	5.12	5.34	5.18
<i>S</i>	1.9	1.7	1.6	1.6	1.6
<i>R</i> <sub>B</sub>	5.07	5.41	5.06	5.56	5.66
<i>R</i> <sub>F</sub>	3.48	3.91	3.63	4.06	4.18

Note:  $R_p = \sum |y_{io} - y_{ic}| / \sum |y_{io}|$ ;  $R_{wp} = [\sum w_i (y_{io} - y_{ic})^2 / \sum w_i y_{io}^2]^{1/2}$ ;  $R_{exp} = [(N - P_1 - P_2) / \sum w_i y_{io}^2]^{1/2}$ ;  $S = \sum [w_i (y_{io} - y_{ic})^2 / (N - P_1 - P_2)]^{1/2}$ .

for the observed intensities and the solid lines are calculated patterns. The angular region for all data sets  $2\theta = 155\text{--}168^\circ$  is excluded because of the strong noise in this region. That will not influence the refinement accuracy [13]. The initial structures are refined by the Fullprof program [11] based on the structural model of KCaCO<sub>3</sub>F solved by Chen et al. at room temperature. The result at room temperature (295 K) is consistent with that reported by Chen et al. [10]. The calculated patterns are in good agreement with the experimental ones. Table 1 shows the experimental data and refined results of KCaCO<sub>3</sub>F. The final positional parameters are listed in Table 2. The site of K is determined to occupy 1a and Ca 1d. Moreover, no disorder in occupancy in K and Ca sites is found. Trying the site exchange of K and Ca only leads to unacceptable values of agreement factors. These results confirm the structural model of Chen and coworkers. The structure is built from planar CO<sub>3</sub> groups perpendicular to *c*-axis, with K ions occupying the apices of the hexagonal cell, an infinite F–Ca–F chain parallel to *c*-axis, and Ca ions also lying in the same plane of CO<sub>3</sub> groups (Fig. 2). To further check the reliability of the structure, the bond valences calculated according to the Brown and Altermatt parameters [14] are listed in Table 3. It can be seen that the bond valence sums in our structure are very reasonable for both cations and anions.

No structural transformation patterns are found from variable-temperature neutron powder diffraction. The DTA/TG experimental result also confirms no structural transition in this compound from room temperature to about 700 °C, and the absorption peak at 774 °C indicates that the sample decomposed at this temperature (Fig. 3). According to the TG curve, the thermal decomposition is also characterized by the apparent decrease in the sample weight near the temperature 774 °C.

Table 2  
Refined atomic positions and thermal parameters of KCaCO<sub>3</sub>F at different temperatures

Atoms	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )	Temperature (K)
K	1a	0	0	0	1.332(30)	295
					1.736(35)	373
					2.129(40)	473
					2.560(51)	573
					2.720(60)	673
C	1f	0.66667	0.33333	0.5	1.052(19)	295
					1.156(21)	373
					1.200(21)	473
					1.400(25)	573
					1.489(28)	673
F	1c	0.33333	0.66667	0	2.107(27)	295
					2.477(31)	373
					2.964(35)	473
					3.381(42)	573
					3.796(49)	673
Ca	1d	0.33333	0.66667	0.5	1.230(26)	295
					1.382(28)	373
					1.694(30)	473
					1.845(36)	573
					2.129(43)	673
O	3k	0.81094(7)	0.18906(7)	0.5	1.555(12)	295
		0.81044(8)	0.18957(8)	0.5	1.844(14)	373
		0.80974(9)	0.19026(9)	0.5	2.211(16)	473
		0.81060(10)	0.19182(10)	0.5	2.575(19)	573
		0.80948(12)	0.19052(12)	0.5	2.869(23)	673

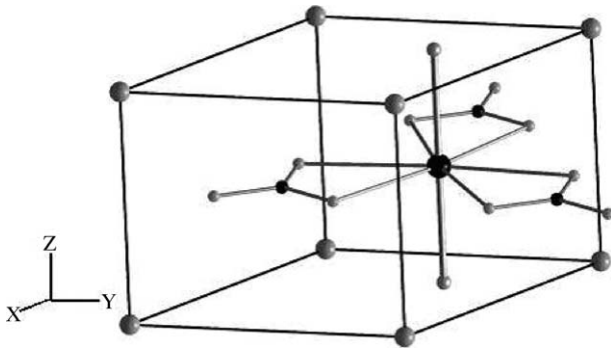


Fig. 2. The structure of  $\text{KCaCO}_3\text{F}$ . Big black balls stand for Ca atoms, and small ones for C atoms. Big grey balls stand for K atoms, medium ones for F atoms and small ones for O atoms.

Table 3  
Ca–O, C–O, K–O, Ca–F and K–F bonds valence of  $\text{KCaCO}_3\text{F}$

	Ca	C	K	$\sum s$
O	0.203	1.369	0.172	2.1202
	0.203	1.369	0.172	
	0.203	1.369	0.172	
	0.203		0.172	
	0.203		0.172	
	0.203		0.172	
F	0.353		0.077	0.927
	0.353		0.077	
			0.077	
$\sum s$	1.924	4.107	1.263	

Note: The summation of bond valence for O only accounts for two “0.203”, two “0.172” and one “1.369”, according to their coordination numbers.

$d$  spacing values of some strong diffraction peaks at different temperatures are listed in Table 4. The shifts of the  $d$  spacing values of peaks reveal the change of the lattice of the crystal, which indicates the unit cell parameters expand with the increasing temperatures. The variations of the cell parameters and cell volumes with temperature normalized to those at room temperature are shown in Fig. 4. It exhibits an approximately linear relationship between the expansion of lattice parameters and temperature. The unit-cell parameters and the cell volume increase on heating. The thermal expansion coefficient values  $\alpha_T^a$ ,  $\alpha_T^c$  and  $\alpha_T^V$  of  $\text{KCaCO}_3\text{F}$  are  $1.9(\pm 2) \times 10^{-5} \text{ K}^{-1}$ ,  $7.9(\pm 2) \times 10^{-6} \text{ K}^{-1}$  and  $4.5(\pm 5) \times 10^{-4} \text{ K}^{-1}$ , respectively, which are calculated from the

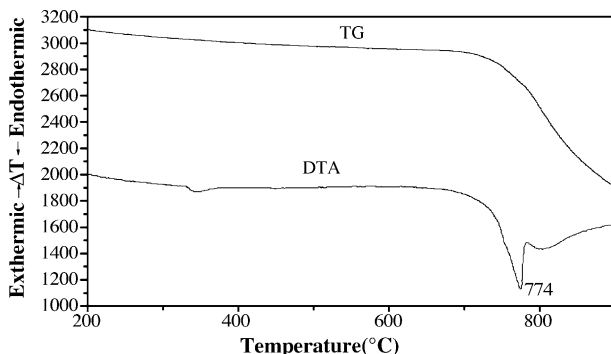


Fig. 3. The DTA/TG curves of  $\text{KCaCO}_3\text{F}$ .

Table 4  
Experimental result of  $d$  values of part diffraction peaks at different temperatures

$hkl$	$d_{hkl}$ (Å)				
	295 K	373 K	473 K	573 K	673 K
0 0 1	4.4678	4.4682	4.4690	4.4700	4.4791
1 0 1	3.1402	3.1450	3.1465	3.1513	3.1562
1 1 0	2.5513	2.5550	2.5615	2.5654	2.5691
0 0 2	2.2305	2.2308	2.5615	2.5654	2.5691
2 0 1	1.9796	1.9819	1.9859	1.9897	1.9920
1 1 2	1.6783	1.6807	1.6824	1.6849	1.6865
2 0 2	1.5691	1.5704	1.5728	1.5750	1.5764

following equation [15]:

$$\alpha(T) = \left[ \frac{1}{l(T)} \right] \left[ \frac{dl(T)}{dT} \right] \quad (1)$$

where  $l(T)$  is the length of sample at the temperature  $T$  as defined in the reference, but here we define it as the lattice constants because they obey the same principle. The lattice expansion coefficient along the  $a$  ( $b$ ) axis is over two times as larger as that along the  $c$ -axis. The difference between them reveals the anisotropic thermal expansion of this crystal, which maybe result from the different expansion of the bonds in this compound [16,17].

From Table 5, we can see that the thermal expansion rate of C–O bond is the smallest among all bonds, indicating that  $\text{CO}_3$  group is very rigid with the temperature, just like  $\text{CO}_3$  group behaved in the Calcite crystal [18]. Hence, the thermal expansions in the  $a$ – $b$  plane should in a large part depend on the Ca–O bonds, and K–F bonds that are also parallel to the  $a$ – $b$  plane and have a similar expansion rate. Because of the existence of the infinite chain formed by Ca–F–Ca, the thermal expansion along the  $c$ -axis should be determined mainly by the thermal expansion rate of Ca–F bonds. The thermal expansion rate for Ca–F is only one third of that for Ca–O or K–F bonds. Therefore, the large anisotropic thermal expansions are due to the significant difference in thermal expansion rate of bonds and the atomic configuration in this structure.

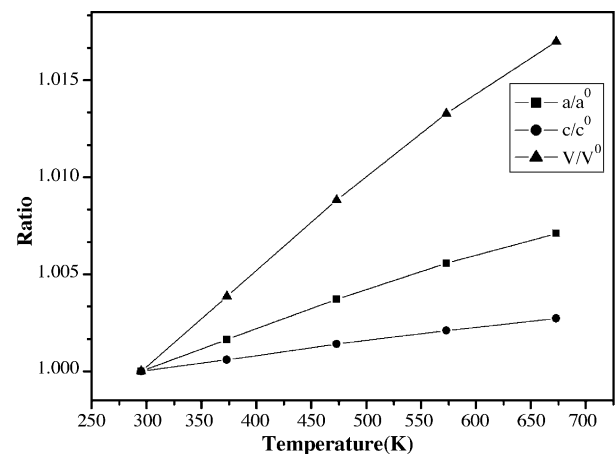


Fig. 4. Variations of  $\text{KCaCO}_3\text{F}$  cell parameters and cell volume with temperature. Cell parameters and cell volume are normalized to those at room temperature (295 K).

Table 5  
Selected interatomic distances (Å) and thermal expansion coefficients of bonds

	Bond length (Å)					Thermal expansion coefficient ( $10^{-5}$ Å/K)
	295 K	373 K	473 K	573 K	673 K	
C–O	1.2737(4)	1.2714(5)	1.2678(5)	1.2670(6)	1.2698(7)	–1.0
Ca–O	2.5563(1)	2.5608(4)	2.5666(4)	2.5716(5)	2.5754(6)	5.1
Ca–F	2.2277(1)	2.2290(1)	2.2308(1)	2.2324(1)	2.2338(1)	1.6
K–O	2.7836(3)	2.7890(2)	2.7962(3)	2.8013(4)	2.8034(4)	5.2
K–F	2.9429(1)	2.9477(1)	2.9538(1)	2.9593(1)	2.9638(1)	5.5

## Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (NSFC) under the grant number of 50372081 and 100 talents project sponsored by the Chinese Academy of Sciences. We thank T. Zhou and M. Zhao for technical help. W.Y. Wang and J.K. Jian are thanked for their critical reading of the manuscript.

## References

- [1] N. Mercier, M. Leblanc, *Eur. J. Solid State Inorg. Chem.* 30 (1993) 217.
- [2] N. Mercier, M. Leblanc, *Eur. J. Solid State Inorg. Chem.* 31 (1994) 423.
- [3] H. Park, J. Barbier, *J. Solid State Chem.* 155 (2000) 354.
- [4] A. Ben Ali, V. Maisonneuve, L.S. Smiri, M. Leblanc, *Solid State Sci.* 4 (2002) 891.
- [5] A. Ben Ali, V. Maisonneuve, S. Kodjikian, L.S. Smiri, M. Leblanc, *Solid State Sci.* 4 (2002) 503.
- [6] N. Mercier, M. Leblanc, E. Antic-Fidancev, M. Lemaître-Blaise, P. Porcher, *J. Alloys Compd.* 225 (1995) 198.
- [7] E. Antic-Fidancev, M. Lemaître-Blaise, P. Porcher, N. Mercier, M. Leblanc, *J. Solid State Chem.* 116 (1995) 286.
- [8] E. Antic-Fidancev, G. Corbel, N. Mercier, M. Leblanc, *J. Solid State Chem.* 153 (2000) 270.
- [9] A. West, J. Fletcher, ICDD PDF 44-0085, International Centre for Diffraction Data, 1992.
- [10] X.L. Chen, M. He, Y.P. Xu, H.Q. Li, Q.Y. Tu, *Acta Cryst. E60* (2004) 50.
- [11] J.R. Carvajal, Fullprof, Version 2.45, Institut Laue Langevin, Grenoble, France, 2003.
- [12] A.J.C. Wilson, *International Tables for Crystallography*, vol. C, Kluwer Academic Publishers, Dordrecht, 1992.
- [13] X.L. Chen, J.K. Liang, C. Wang, *Acta Phys. Sin.* 4 (1995) 259 (overseas edition).
- [14] I.D. Brown, D. Altermatt, *Acta Crystallogr.* B41 (1985) 244.
- [15] J.S. Browder, S.S. Ballard, *Appl. Opt.* 8 (1969) 793.
- [16] N. Khosrovani, A.W. Sleight, *Int. J. Inorg. Mater.* 1 (1999) 3.
- [17] M.J. Hardie, A. Martin, A.A. Pinkerton, E.A. Zhurova, *Acta Cryst. B57* (2001) 113.
- [18] H.D. Megav, *Acta Cryst. A26* (1970) 235.