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Morphology of rutile and brookite nanocrystallites obtained by X-ray diffraction and Rietveld refinements

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ABSTRACT

Titanium oxide was prepared under hydrothermal conditions from a very acidic solution, with titanium butoxide as titanium precursor and hydrochloric acid as the source of protons; the pH was regulated adding water to this solution. The H_2O/HCl molar ratio was varied from 10 to 50; this ratio, together with the synthesis temperature, which varied between 90 °C and 200 °C, determined the phase concentrations. Samples contained mainly the titania polymorphs rutile and brookite; the highest concentration of this last phase was obtained for the ratio of 20 and the synthesis temperature of 120 °C. The synthesized powder was analyzed with X-ray powder diffraction, refinement of the crystalline structures and transmission electron microscopy. The refinement provided information not only about the average crystallites dimensions but also about their morphologies, which were similar to those observed by transmission electron microscopy. The refinement also shows that the lattice parameters of rutile changed with H_2O/HCl molar ratio and synthesis temperature, while those of brookite were almost constant.

1. Introduction

In the last years, titania has been studied extensively, because of its diversity of applications in high technology [1–5]. Titania more stable polymorphs, rutile, anatase and brookite have been synthesized at low temperatures [6–8]. Recently, some authors have pointed out the potential technological applications of brookite [5,9,10], but until now, it is difficult to synthesize samples with only this titania polymorph; in most of the brookite-rich samples, anatase or rutile are also present [11].

Many efforts have been made to obtain titania samples of pure brookite in order to know better the physical and chemical properties of this titania phase [12–17]. Some authors claim to have samples that contain only brookite, which were prepared by thermolysis of strong acidic solution [8], or hydrothermal synthesis using basic solutions [11]. In both cases, the authors used $TiCl_4$ as the titanium precursor. They, however, did not demonstrate that their samples contained only brookite; for example, by refining the crystalline structure.

In the present work, we synthesized titania samples rich in brookite, which coexisted with rutile. The synthesis was performed under hydrothermal conditions from an acidic solution of titanium butoxide, at different temperatures. The samples were characterized with X-ray powder diffraction and refinement of the crystalline structures using the Rietveld method as well as with transmission electron microscopy.

2. Experimental

2.1. Sample preparation

Titania synthesis was made using titanium butoxide (Aldrich, 97%), hydrochloric acid (J.T. Baker, 38%) and de-ionized H_2O, with a constant butoxide to hydrochloric acid molar ratio of 1:9.2. The amount of water was varied to get a water to acid molar ratio of 10, 20, 30, 40 and 50. At room temperature, the titanium butoxide was added to the HCl, stirring strongly. Then, the de-ionized water was added drop by drop. The respective solution was treated under hydrothermal conditions for 15 h, at temperatures of 90, 120, 160 and 200 °C.

2.2. Characterization

2.2.1. X-ray powder diffraction

The X-ray powder diffraction patterns of the samples packed in a glass holder were recorded at room temperature with Cu Kα radiation in a Bruker Advance D-8 diffractometer that had a θ–θ configuration and a graphite monochromator in the secondary beam. Diffraction intensity was measured between 15° and 135°, with a 2θ step of 0.02° for 6.0 s per point. Crystalline structures were refined with the Rietveld technique by using FULLPROF98 code [18]; peak profiles were modeled with pseudo-Voigt functions [19] that contained information about the average crystallite size and the microstrain [20]. The effect of the microstrain was included in the Gaussian part of the function, while the corresponding effect of the size was included in the Lorentzian one. The standard deviations of the refined parameters, modified by taking into account serial correlations, are not estimates of the probable error in the analysis as a whole, but

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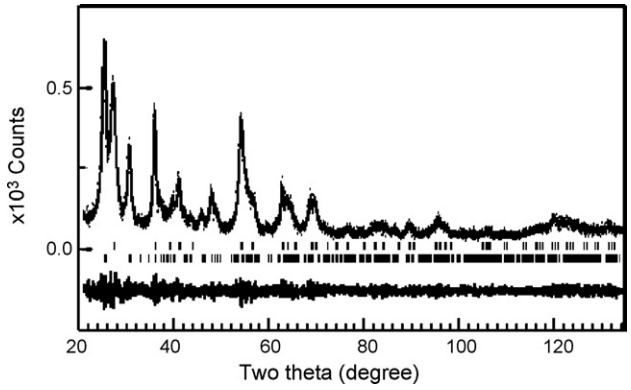

Fig. 1. Typical refinement plot. Upper marks correspond to rutile and lower ones to brookite. The experimental diffraction pattern is described by symbols and the refined one with a continuous line. The quality of the refinement is shown by the difference between both patterns, which correspond to the curve at the bottom of the figure.

only of the minimum possible probable errors based on their normal distribution [21].

The maximum number of refined parameters was 52; when anatase phase was not in the sample this number reduced to 44. For brookite, these variables included the scale factor, all atom fractional coordinates, isotropic atomic displacements, atom occupancies, lattice parameters, and anisotropic crystallite size; for anatase, similar parameters were refined. For rutile, the refined variables included scale factor, the *x* and *y* atom fractional coordinates of oxygen atom, isotropic atomic displacements, atom occupancies, lattice parameters and the anisotropic crystallite size.

2.2.2. Transmission electron microscopy (TEM)

Samples were analyzed with transmission electron microscopy in a JEOL JEM-2010F microscope. The sample powder was dispersed in ethanol, before placing it in the copper grid with formvar.

3. Results and discussion

Depending on the H_2O/HCl molar ratio and synthesis temperature, samples contained the three titania polymorphs: rutile, brookite and anatase; most of the samples, however, contained only rutile and brookite. The initial model for the refinements included only these phases. For the samples synthesized with the H_2O/HCl molar ratios of 40 and 50 the fitting was improved by including anatase in the model.

Table 1
Phase concentration as a function of the H_2O/HCl molar ratio and the hydrothermal synthesis temperature for all samples.

Molar ratio H_2O/HCl	Temperature (°C)	Rutile (wt%)	Brookite (wt%)	Anatase (wt%)
10	90	100 (3)		
	120	74 (4)	26 (3)	
	160	94 (2)	6 (1)	
	200	98 (2)	2.2(1)	
20	90	100 (2)		
	120	55(3)	45 (3)	
	160	62 (2)	38(1)	
	200	72 (2)	28 (1)	
30	90	100 (2)		
	120	76 (2)	24.4 (7)	
	160	80 (2)	20 (1)	
	200	89 (2)	10.8 (9)	
40	90	46 (2)	38 (2)	16 (1)
	120	78 (2)	21.9 (7)	
	160	76 (2)	24 (2)	
	200	96 (2)	3.9 (7)	
50	90	99 (2)		1.3 (2)
	120	59 (2)	25 (2)	16.5(6)
	160	69 (2)	31 (2)	
	200	84 (2)	16 (1)	

In order to perform the refinement, the crystalline structure of brookite was modeled with an orthorhombic unit cell that had the symmetry given by the space group *Pbca*; the initial atom positions were taken from the literature [22]. The crystalline structure of anatase was modeled with a tetragonal unit cell having the symmetry described by the space group $I4_1/amd$ and the atom positions reported elsewhere [6]. The structure of rutile was modeled with a tetragonal unit cell whose symmetry is given by the space group $P4_2/mnm$ and the atom positions described elsewhere [6].

Fig. 1 shows a typical Rietveld refinement plot; it corresponds to the sample synthesized with the H_2O/HCl molar ratio of 20 and the synthesis temperature of 120 °C. This pattern was modeled

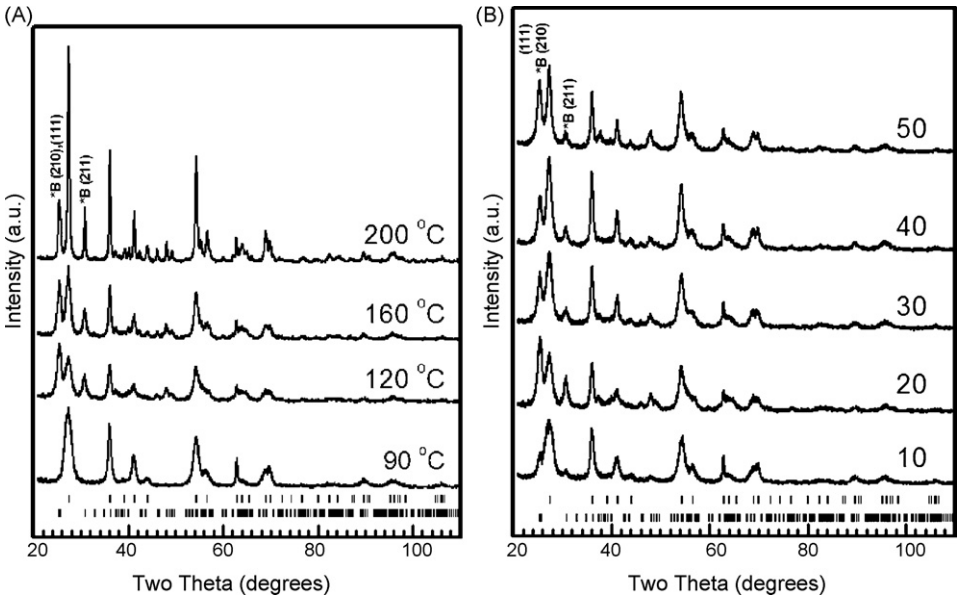

Fig. 2. (A) Diffraction pattern of the samples prepared with the H_2O/HCl molar ratio of 20 at different synthesis temperatures. Upper marks correspond to rutile; the lower ones to brookite. Main reflections of brookite are also starred and labeled by Miller indices. (B) Diffraction pattern of the samples synthesized at 120 °C and different molar ratios (MR). Upper marks correspond to rutile; the lower ones to brookite. Main reflections of brookite are also starred and labeled by Miller indices.

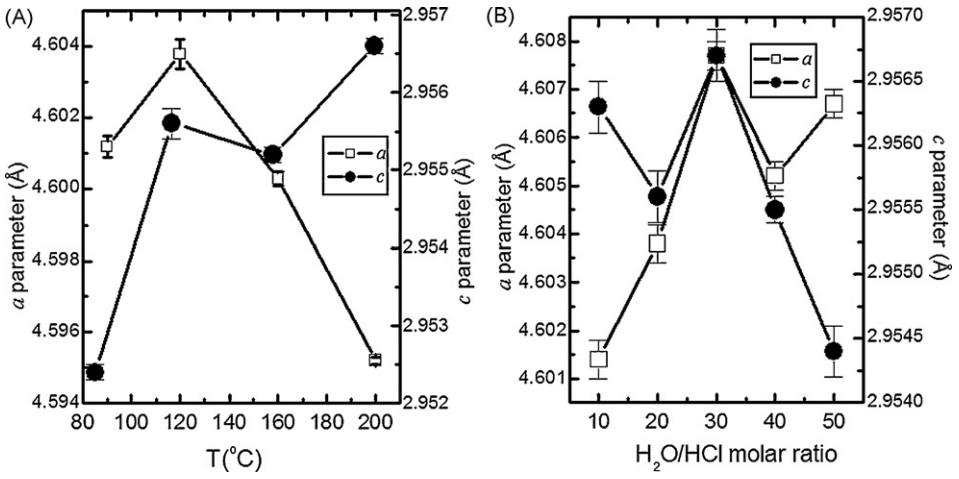

Fig. 3. (A) Lattice parameters of rutile as a function of synthesis temperature at the H_2O/HCl molar ratio of 20. (B) Lattice parameters of rutile for different H_2O/HCl molar ratios at a constant synthesis temperature of 120 °C.

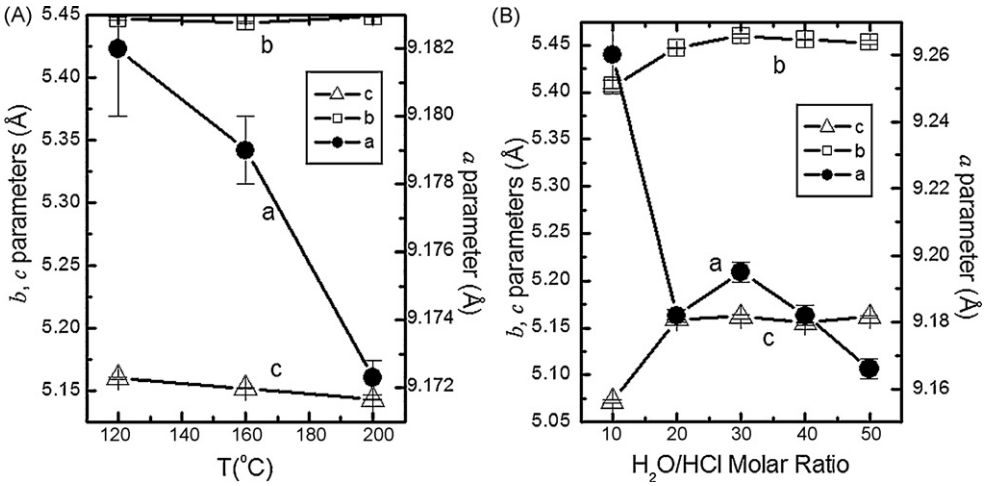

Fig. 4. (A) Lattice parameters of brookite as a function of synthesis temperature, at the constant H_2O/HCl molar ratio of 20. (B) Lattice parameters of brookite for different H_2O/HCl molar ratios at a constant synthesis temperature of 120 °C.

Table 2
Minimal (*d*) and maximal (*L*) lengths (with their directions) in the crystallites, also the average size, of the rutile phase as a function of the molar ratio H_2O/HCl and the temperature, for all samples.

Molar ratio H_2O/HCl	Temperature (°C)	*d* (nm)-(Dir)	*L* (nm)-(Dir)	Av. size (sda) (nm)	*L*/*d*
10	90	3.72-(200)	34.35-(002)	6(5)	9.23
	120	3.05-(200)	23.45-(002)	6(4)	7.68
	160	5.49-(200)	45.58-(002)	10(7)	8.30
	200	16.18-(200)	89.88-(002)	29(17)	5.55
20	90	3.67-(200)	26.98-(002)	7(4)	7.35
	120	3.11-(200)	41.25-(002)	7(6)	13.26
	160	5.46-(200)	23.45-(002)	9(5)	5.80
	200	13.78-(200)	35.92-(002)	20(6)	2.60
30	90	4.63-(200)	39.42-(002)	8(7)	8.51
	120	3.72-(200)	31.03-(002)	8(5)	8.31
	160	5.49-(200)	39.78-(002)	11(7)	6.94
	200	13.35-(200)	41.12-(002)	20(7)	3.08
40	90	4.71-(210)	22.45-(002)	8(4)	4.66
	120	4.63-(200)	30.69-(002)	9(5)	6.62
	160	6.61-(200)	33.83-(002)	11(6)	5.11
	200	12.54-(200)	37.14-(002)	19(6)	2.96
50	90	5.23-(200)	17.76-(002)	8(3)	3.40
	120	5.92-(200)	25.78-(002)	9(5)	4.35
	160	6.13-(200)	36.58-(002)	12(6)	5.96
	200	13.34-(200)	30.37-(002)	19(5)	2.27

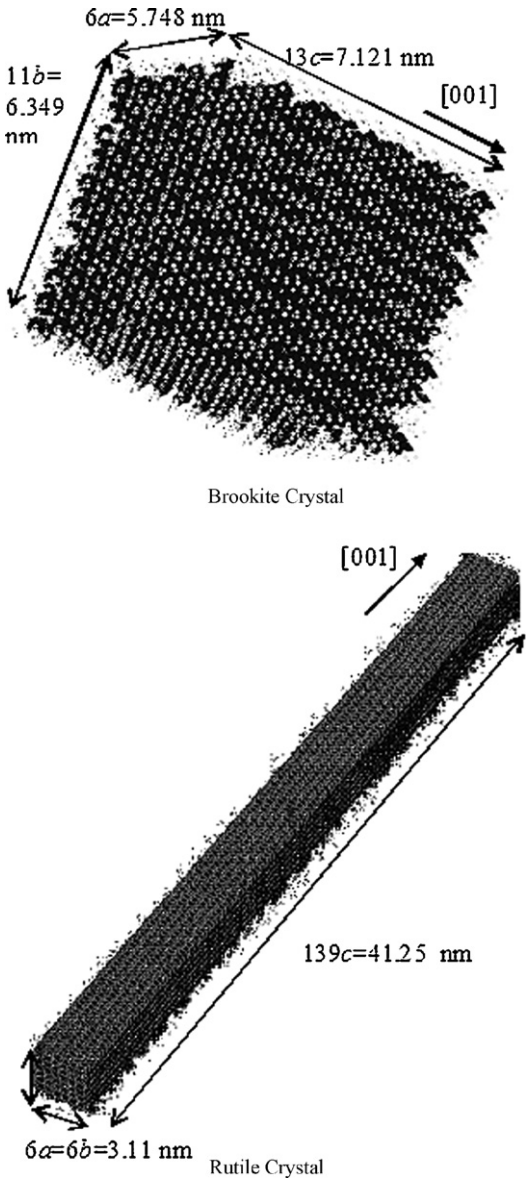

Fig. 5. Models of the brookite and rutile average crystallites generated by using the data obtained from the X-ray powder diffraction and the Rietveld refinement.

assuming that the sample contained only brookite and rutile. For all samples the residua Rp and Rwp were lower than 0.11 and 0.15, respectively.

When the synthesis temperature was 90 °C, the samples contained only rutile (Fig. 2A and Table 1). For the synthesis with the H_2O/HCl molar ratios of 40 and 50, the three polymorphs coexisted with an important contribution of brookite (Fig. 2B and Table 1); the presence of anatase reveals that this synthesis conditions were not favorable to stabilize brookite. In the synthesis at 120 °C, samples contained both, brookite and rutile (Table 1). At this synthesis temperature, the H_2O/HCl molar ratio 20 appeared as the most favorable to synthesize brookite (Fig. 2A and B and Table 1).

The samples synthesized at 160 °C contained a lower brookite concentration than those synthesized at 120 °C (Fig. 2A and Table 1). At this temperature, the H_2O/HCl molar ratio of 20 appeared as the most favorable ratio for the synthesis of brookite. When samples were synthesized at 200 °C, the brookite concentration decreased notably in favor of rutile (Fig. 2A and Table 1). At this temperature, also the H_2O/HCl molar ratio of 20 was the most appropriated to get brookite.

As consequence of the above results, for the aim of this work, we see that the synthesis temperature of 120 °C and the H_2O/HCl molar ratio of 20 were the most favorable synthesis conditions to get a high concentration of brookite, coexisting with rutile. Therefore, most of the following analysis will be concentrated on the samples synthesized at this molar ratio and at this temperature.

For the H_2O/HCl molar ratio of 20, the lattice parameter *a* of rutile decreased as the synthesis temperature increased, while the lattice parameter *c* increased (Fig. 3A). When this analysis was done as a function of H_2O/HCl molar ratio, for the temperature of 120 °C (Fig. 3B), we observed that the lattice parameter *a* increased when the molar ratio increased, while the lattice parameter *c* decreased.

For the case of brookite, when the H_2O/HCl molar ratio was 20, the lattice parameter *a* decreased as the synthesis temperature increased; the lattices parameters *b* and *c* stayed almost constant (Fig. 4A). For the synthesis temperature of 120 °C the lattice parameter *a* changed drastically when the H_2O/HCl molar ratio changed from 10 to 20 (Fig. 4B). The lattice parameters *b* and *c* were almost independent of this molar ratio.

The crystallites of brookite and rutile had anisotropic form (Fig. 5): brookite crystallites were platelets while those of rutile were needles. The dimensions of both crystallites increased with the synthesis temperature (Table 2). The anisotropy of rutile crystallites decreased with the sintering temperature (Table 2); this is clearly observed when the ratio of the crystallite dimension

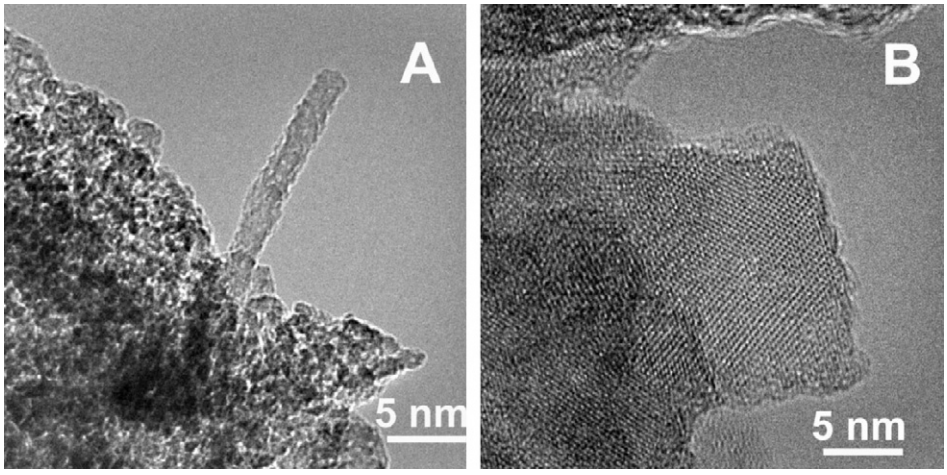

Fig. 6. TEM micrographs of (A) a rutile crystallite and (B) a brookite crystallite.

perpendicular to the (200) and (002) was calculated (Table 2). The anisotropy of the brookite crystallites, however, was almost independent of synthesis temperature.

The models of the average crystallites of rutile and brookite (Fig. 5) constructed using the data obtained from the Rietveld refinement were similar to those observed by transmission electron microscopy (Fig. 6A and B).

The good correspondence between the crystallite images observed with transmission electron microscopy and those generated using the data obtained X-ray diffraction patterns and the Rietveld refinement shows that this last technique can also be used to obtain crystallite dimensions and morphology.

4. Conclusions

Titanium oxide was prepared under hydrothermal conditions from a very acidic solution, with titanium butoxide as titanium precursor and hydrochloric acid as the source of protons; the pH was regulated adding water to this solution. The H_2O/HCl molar ratio (with a fixed alkoxide to acid molar ratio) determined the brookite concentration, which was maximal for a ratio of 20 and the temperature of 120 °C; when this ratio was 40, anatase was formed even at 90 °C. The synthesis temperature also determined the brookite concentration, as well as the crystallite size of both, rutile and brookite. The analysis of the samples with X-ray powder diffraction and the refinement of the crystalline structures provided information not only of the average crystallites dimensions but also about their morphologies. The dimensions of the average crystallites increased with the synthesis temperature; this temperature affected the anisotropy of the form of rutile crystallites but not the one of brookite crystallites. The morphologies of rutile and brookite crystallites were similar to those observed by transmission electron microscopy. This analysis also shows that the lattice parameters of rutile changed with the H_2O/HCl molar ratio and the synthesis temperature, while those of brookite were almost independent of them.

References

[1] G. Phani, G. Tulloch, D. Vittorio, I. Skryabin, Renew. Ener. 22 (2001) 303–309.
[2] M. Najbar, J. Camra, Sol. State Ionics 101–103 (1997) 707–711.
[3] S. Ono, Y. Nishi, S. Hirano, J. Am. Ceram. Soc. 84 (2001) 3054–3056.
[4] A. Stoch, G. Brozek, J. Kmita, W. Stoch, A. Jastrzebski, Rakowska, J. Mol. Struct. 596 (2001) 191–200.
[5] H. Kominami, Y. Ishii, M. Cono, S. Konishi, Y. Kera, B. Ohtani, Catal. Lett. 91 (2003) 41–47.
[6] X. Bokhimi, A. Morales, M. Aguilar, J.A. Toledo-Antonio, F. Pedraza, Int. J. Hydrog. Ener. 26 (2001) 1279–1287.
[7] H. Kominami, M. Kohno, Y. Kera, J. Mater. Chem. 10 (2000) 1151–1156.
[8] A. Pottier, C. Chanéac, E. Tronc, L. Mazerolles, J.-P. Jolivet, J. Mater. Chem. 11 (2001) 1116–1121.
[9] J.-G. Li, C. Tang, D. Li, H. Haneda, T. Ishigaki, J. Am. Ceram. Soc. 87 (2004) 1358–1361.
[10] M. Koelsch, S.C. Cassaignon, J.F. Guillemoles, J.P. Jolivet, Thin Solid Films 403–404 (2002) 312–319.
[11] Y. Zheng, E. Shi, S. Cui, W. Li, X. Hu, J. Am. Ceram. Soc. 83 (2000) 2634–2636.
[12] N. Kuznetsova, V. Blaskov, I. Stambolova, L. Znaidi, A. Kanaev, Mater. Lett. 59 (2005) 3820–3823.
[13] B.I. Lee, X. Wang, R. Bhave, M. Hu, Mater. Lett. 60 (2006) 1179–1183.
[14] S. Cassaignon, M. Koelsch, J.-P. Jolivet, J. Mater. Sci. 42 (2007) 6689–6695.
[15] M. Iwasaki, Ch-W. Lee, T.-H. Kim, W.-K. Park, J. Ceram. Soc. Jpn. 116 (2008) 153–157.
[16] S.-C. Liu, K-Le. Lu, K.-J. Ding, H.-M. Tang, X.-F. Li, Imag. Sci. Photochem. 26 (2008) 138–147.
[17] D. Reyes-Coronado, G. Rodriguez-Gattorno, M.E. Espinosa-Pesqueira, C. Cab, R. de Coss, G. Oskam, Nanotechnology 19 (2008) 145605.
[18] J. Rodríguez-Carbajal, Laboratoire Leon Brillouin (CEA-CNRS) (France, Tel: +33 1 6908 3343, fax: +33 1 6908 8261, e-mail: juan@llb.saclay.cea.fr).
[19] P. Thompson, D.E. Cox, J.B. Hastings, J. Appl. Crystallogr. 20 (1987) 79–83.
[20] R.A. Young, P. Desai, Arch. Nauki Mater. 10 (1989) 71–90.
[21] E. Prince, J. Appl. Crystallogr. 14 (1981) 157–159.
[22] M. Pauling, J.H. Sturdivant, Zeitsch, K., K., K., K. 68 (1928) 239–256.