XPS study of the major minerals in bauxite: Gibbsite, bayerite and (pseudo-)boehmite

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Abstract

Synthetic corundum (Al_2O_3), gibbsite ($Al(OH)_3$), bayerite ($Al(OH)_3$), boehmite ($AlO(OH)$) and pseudoboehmite ($AlO(OH)$) have been studied by high resolution XPS. The chemical compositions based on the XPS survey scans were in good agreement with the expected composition. High resolution $Al2p$ scans showed no significant changes in binding energy, with all values between 73.9 and 74.4 eV. Only bayerite showed two transitions, associated with the presence of amorphous material in the sample. More information about the chemical and crystallographic environment was obtained from the $O1s$ high resolution spectra. Here a clear distinction could be made between oxygen in the crystal structure, hydroxyl groups and adsorbed water. Oxygen in the crystal structure was characterised by a binding energy of about 530.6 eV in all minerals. Hydroxyl groups, present either in the crystal structure or on the surface, exhibited binding energies around 531.9 eV, while water on the surface showed binding energies around 533.0 eV. A distinction could be made between boehmite and pseudoboehmite based on the slightly lower ratio of oxygen to hydroxyl groups and water in pseudoboehmite.
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1. Introduction

Bauxite forms a major resource of aluminum in Australia and especially in Queensland. For that reason research on the mineralogy of these bauxites is of importance to the mining industry. The major aluminum phases recognised in bauxites and laterites are gibbsite also known as hydrargillite (γ-$Al(OH)_3$), and boehmite (γ-$AlO(OH)$).

Gibbsite is the main mineral in bauxites formed in areas characterized by a tropical climate with alternating rainy and dry periods (monsoon). Bauxites with primarily boehmite appear to be more constrained to the subtropical areas (Mediterranean type bauxite). Thermal action or low-grade metamorphism mostly favors diaspore formation. Furthermore, diaspore is formed as a minor constituent in many types of bauxite in addition to gibbsite and boehmite [1–3]. For comparative reasons

bayerite (β-$Al(OH)_3$) and corundum (Al_2O_3) have been incorporated in this study. The thermal behaviour and spectroscopy of these bauxite minerals has been reported in earlier work by our group [4–11].

X-ray photoelectron spectroscopy (XPS) is widely used for determining the surface composition of solid materials, including aluminum and aluminum phases [12–14]. Rotole and Sherwood have published a series of short papers reporting the XPS spectra of a variety of aluminium phases, but did not report any curve fitting or an interpretation of their results [12,15–21]. Although XPS has become a powerful tool to identify different phases, it has been so far less successful in determining subtle changes in aluminum oxide/hydroxide minerals. Although the binding energies of the core lines (i.e. $Al2p$, $Al2s$, $O1s$, $O2s$) are easily measured, the differences in binding energy of Al among the aluminum oxides, hydroxides and oxyhydroxides are very small, generally in the order of 0–0.5 eV, which is in the same order of magnitude as the experimental precision of XPS [22–25]. Some limited work has been done on the use of valence band XPS to distinguish these minerals

[26,27]. The oxygen core lines may however be more sensitive to changes in the crystal chemistry. This paper therefore reports on the possible use of high resolution XPS for the identification of the major aluminum oxide/hydroxide/oxyhydroxide minerals.

2. Structure of the aluminum (oxo)hydroxides

2.1. Gibbsite Al(OH)₃

Gibbsite is monoclinic ($P2_1/n$, $a = 8.684$ Å, $b = 5.078$ Å, $c = 9.736$ Å, $\beta = 94.54°$) with mostly a tabular pseudohexagonal habit. The structure can be visualized as sheets of hcp layers with open packing between successive sheets. In the lateral extension of the hexagonal closed packed sheets each Al cation is octahedrally coordinated by 6 OH groups and each hydroxyl group is coordinated by two Al cations with one octahedral site vacant [28,29]. This can also be visualized as double layers of OH groups with Al cations occupying two thirds of the interstices within the layers. Each double layer is positioned in such a way that the upper and lower neighboring layers have their hydroxyl groups directly opposite to each other and not in the position of the closest packing. This type of layer structure explains the perfect cleavage of gibbsite parallel to the basal plane (001).

2.2. Bayerite Al(OH)₃

Bayerite is monoclinic ($P2_1/a$, $a = 5.0626$ Å, $b = 8.6719$ Å, $c = 9.4254$ Å, $\beta = 90.26°$) forming mostly very fine fibers in radiating hemispherical aggregates and sometimes flaky to tabular crystals to about 0.1 mm. The crystal lattice of bayerite is composed of layers of hydroxyl groups similar to those in gibbsite. These layers, however, are arranged in an AB–AB–AB sequence; in other words, the hydroxyl groups of the third layer lie in the depressions between the hydroxyl positions of the second layer.

2.3. Boehmite AlO(OH)

Boehmite has the same structure as lepidocrocite (γ-FeO-(OH)). The structure of boehmite consists of double layers of oxygen octahedra partially filled with Al cations [30]. Boehmite is orthorhombic with space group *Amam* ($a = 3.6936$ Å, $b = 12.214$ Å, $c = 2.8679$ Å) [29,31]. The stacking arrangement of the three oxygen layers is such that the double octahedral layer is in cubic closed packing. Within the double layer one can discriminate between two different types of oxygen. Each oxygen atom in the middle of the double layer is shared by four other octahedra, while the oxygen atoms on the outside are only shared by two octahedra. These outer oxygen atoms are hydrogen-bonded to two other similarly coordinated oxygen atoms in the neighboring double layers above and below. The stacking of the layers is such that the hydroxyl groups of one layer are located over the depression between the hydroxyl groups in the adjacent layer.

3. Experimental

3.1. Mineral samples

The aluminum phases used in this study are synthetic gibbsite produced in our laboratory, synthetic gibbsite (γ-alumina) produced by Baikowski International Corporation (Charlotte, NC), pseudoboehmite synthesized by P. Buining [32], boehmite synthesized by Ray Frost, synthetic bayerite synthesized by Comelco. The samples were analysed for phase purity by X-ray diffraction prior to the XPS analysis. X-ray diffraction has shown that the gibbsites, bayerite and the boehmites are pure. For comparative reasons synthetic corundum produced by Baikowski International Corporation (Charlott, NC) was used.

3.2. XPS analysis

The minerals were analysed in freshly powdered form in order to prevent surface oxidation changes. Prior to the analysis the samples were outgassed under vacuum for 72 h. The XPS analyses were performed on a Kratos AXIS Ultra with a monochromatic Al X-ray source at 150 W. Each analysis started with a survey scan from 0 to 1200 eV with a dwell time of 100 ms, pass energy of 160 eV at steps of 1 eV with 1 sweep. For the high resolution analysis the number of sweeps was increased, the pass energy was lowered to 20 eV at steps of 100 meV and the dwell time was changed to 250 ms.

Band component analysis was undertaken using the Jandel 'Peakfit' software package, which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz–Gauss cross-product function with the minimum number of component bands used for the fitting process. The Gaussian–Lorentzian ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with correlations of r^2 greater than 0.995.

4. Results and discussion

For all minerals XPS survey spectra and high resolution core line spectra (O1s and Al2p) were obtained. Table 1 gives an overview of the chemical composition of the minerals analysed based on the XPS survey scans. In addition to the elements

Table 1
Chemical compositions (atom%) of the alumina phases based on the high resolution XPS analyses

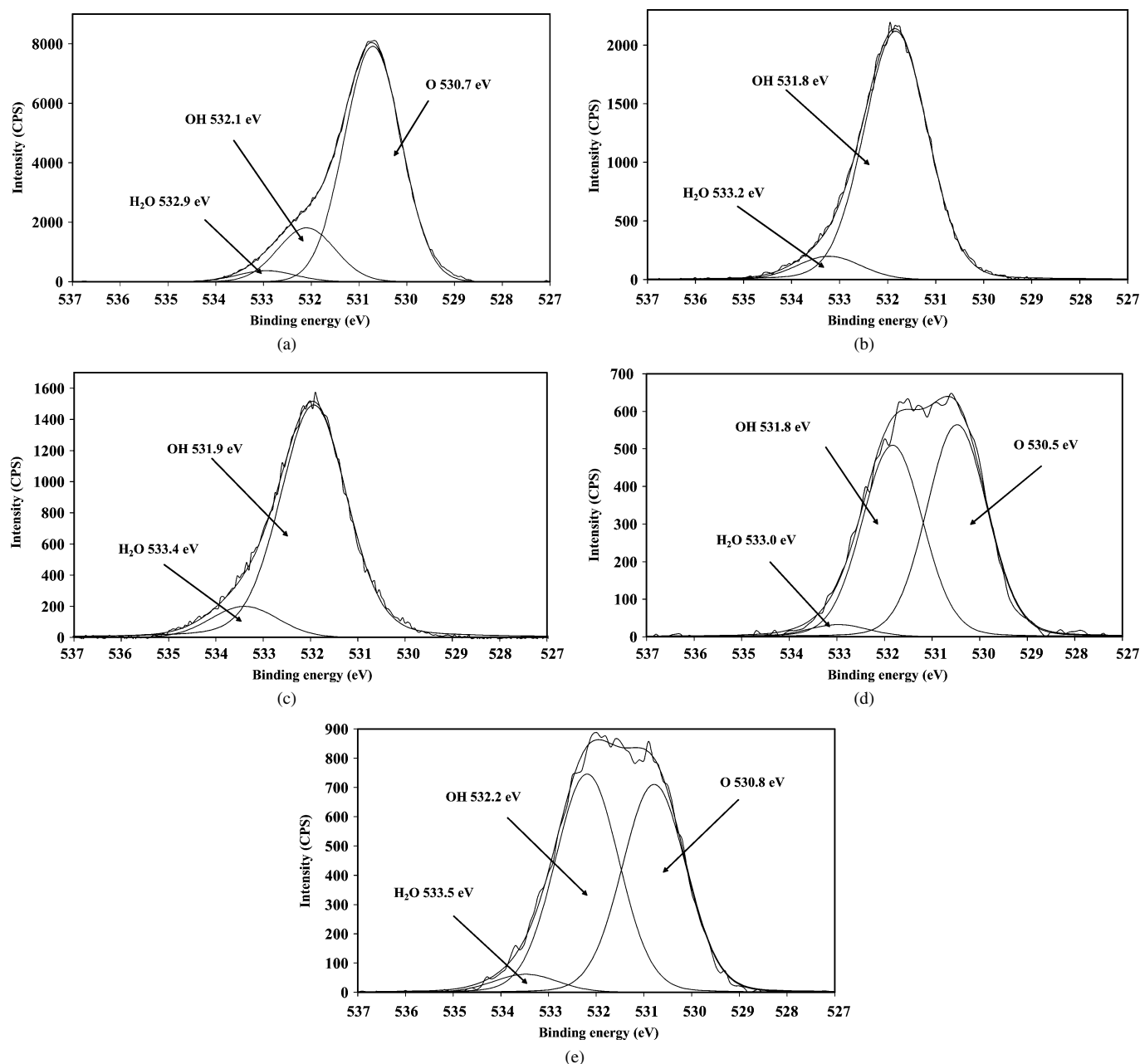|	Corundum Al₂O₃	Gibbsite Al(OH)₃	Bayerite Al(OH)₃	Boehmite Al(OOH)	Pseudoboehmite Al(OOH)
O	61.62	72.89	68.78	67.55	62.54
Al	38.38	24.41	23.94	32.45	27.29
Na[a]	bd	2.69	4.83	bd[b]	bd
N[a]	bd	bd	1.78	bd	bd
Cl[a]	bd	bd	0.66	bd	1.35
Al/O molar ratio	0.63	0.33	0.34	0.48	0.43

[a] Impurities.
[b] bd—below detection limit.

Fig. 1. (a) O1*s* corundum, (b) O1*s* gibbsite, (c) O1*s* bayerite, (d) O1*s* boehmite, (e) O1*s* pseudoboehmite.

belonging to the mineral one always observes the presence of carbon, the so-called advantageous or rubbish carbon. The C1*s* transition of this carbon is used to correct for charging, which results in a shift of all other transitions. The ratio of oxygen to aluminum for corundum is slightly higher than expected based on the composition of Al_2O_3. The reason for this becomes apparent from Fig. 1 where the O1*s* spectrum shows the presence of three different oxygen species. In addition to the bulk oxygen with a binding energy of 530.7 eV from the crystal structure, the surface of corundum contains hydroxyl groups with an O1*s* binding energy of 532.1 eV and a minor amount of adsorbed water with an O1*s* binding energy of 532.9 eV. All three signals have similar FWHM of about 1.4 eV. Only one Al2*p* transition is observed at 74.1 eV (Fig. 2).

For gibbsite and bayerite the ratio O to Al should be equal to 3 to 1 based on a compositon of $Al(OH)_3$, which is exactly what is observed for gibbsite. For the bayerite, however, the ratio is slightly lower than expected but within experimental error. For gibbsite and bayerite only two O1*s* transitions are observed at 531.8 and 533.2 eV and at 531.9 and 533.4 eV, respectively, associated with the hydroxyl groups in the crystal structure (Al–O–H) and absorbed water on the surface (H–O–H). Gibbsite and bayerite both show one major Al2*p* transition at 74.3 and 74.4 eV respectively. In addition, bayerite shows a second transition at 75 eV. XRD showed that this bayerite sample had a very low crystallinity and possibly some amorphous content. It might well be that this second transition is associated with this amorphous phase.
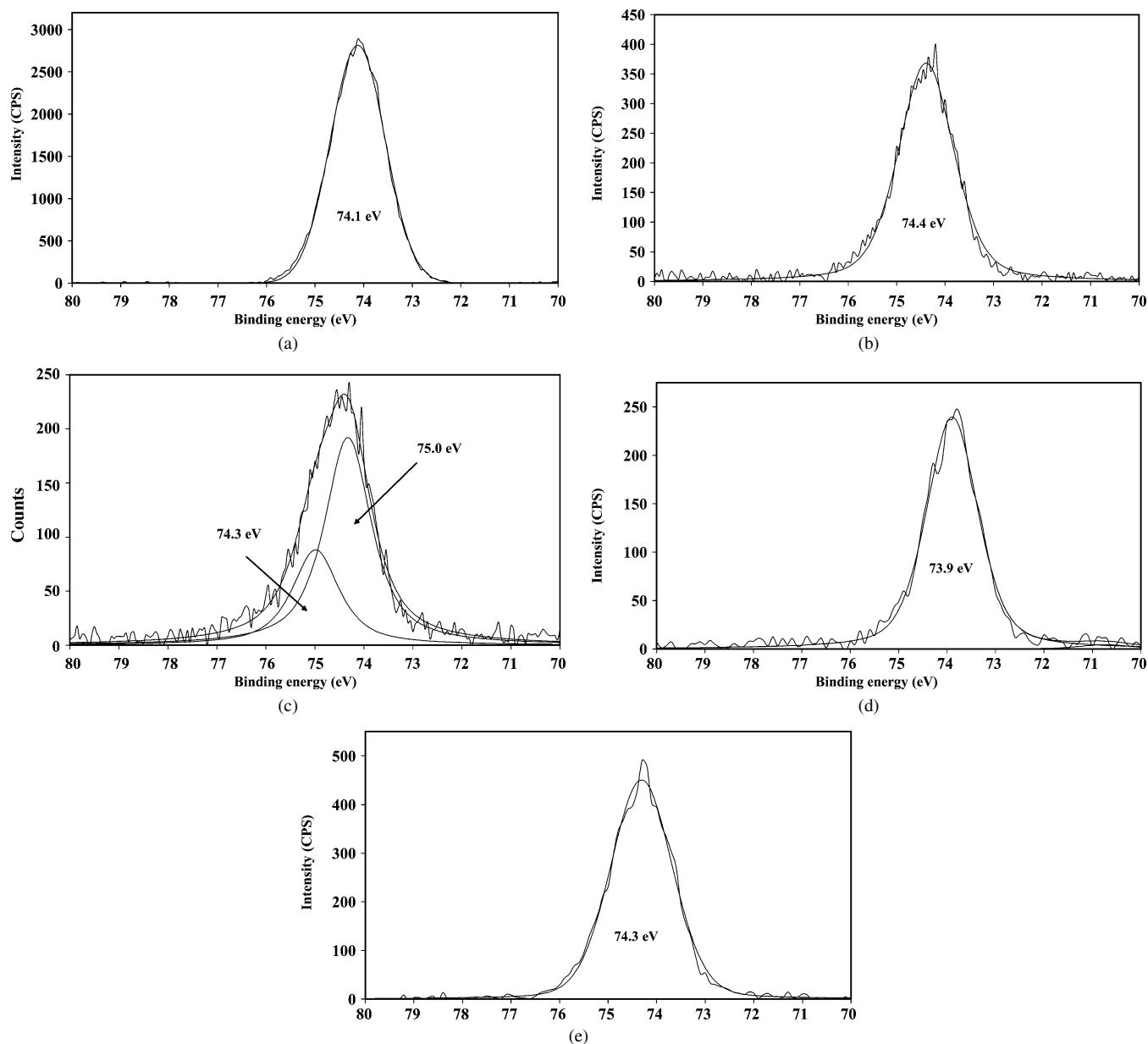
Fig. 2. (a) Al2*p* corundum, (b) Al2*p* gibbsite, (c) Al2*p* bayerite, (d) Al2*p* boehmite, (e) Al2*p* pseudoboehmite.

The difference between boehmite and pseudoboehmite has been a matter of discussion for a long time. In general there is some consensus that the unit cell of pseudoboehmite is slightly larger than that of boehmite. It has been indicated in the literature that this would be due to the incorporation of water in the crystal structure. In this study two boehmite samples were analysed, one of which was thought to be pseudoboehmite based on the slightly different XRD pattern with much broader reflections [33]. The chemical analyses clearly show a difference in composition. Boehmite in its purest form has a chemical formula of AlOOH and therefore an O to Al ratio from 2 to 1 has to be expected. The boehmite sample has significantly less oxygen than expected whereas the pseudoboehmite has more oxygen than expected plus a trace amount of chlorine. The Al2*p* transitions are slightly different, although still within the experimental error. The same is the case for the O1*s* transi-

tions, but again the values for the pseudoboehmite are slightly higher than for boehmite. The high resolution O1*s* spectrum of boehmite shows a nearly 1:1 ratio of oxygen (Al–O–Al) and hydroxyl groups (Al–O–H) as expected in boehmite. The amount of water in this sample is minimal. In the pseudoboehmite the amount of hydroxyl groups and water are both slightly higher than in boehmite. This may explain the slightly larger unit cell, where a small amount of the oxygen atoms has been replaced by hydroxyl groups and maybe even water molecules.

It is well known, and this study confirms this, that it is very difficult to unambiguously determine any chemical shifts in the Al2*p* binding energies among the oxides, hydroxides and oxohydroxides, as these shifts are generally in the order of 0.2 to 0.5 eV, which is not much more than the typical precision of the XPS instrument [22–25]. In general a chemical shift is caused by changes in the electrostatic potential field experienced by

the core electrons. Oxidation number, ligand type and coordination (e.g., tetrahedral vs octahedral) can all change the chemical shift of the Al2p line. This work shows that the differences in these parameters are very small for aluminum in the bauxite minerals in accordance with earlier published work [13].

The O1s peaks show a slightly larger chemical shifts (up to 0.6 eV) than the Al2p peaks. In addition, the O1s peak allows one to distinguish between oxygen, hydroxyl groups and water in the crystal structure and can therefore be used as a technique to identify within the different bauxite minerals the difference between gibbsite and bayerite on the one hand and boehmite and diaspore on the other. However, due to the very small chemical shifts no distinction can be made between minerals with the same chemical composition such gibbsite and bayerite.

References

[1] R. Schoen, C.E. Roberson, Am. Mineral. 55 (1970) 43.

[2] A.C.D. Newman, Chemistry of Clay and Clay Minerals, vol. 6, Longman Scientific & Technical, Harlow, UK, 1987.

[3] H.W. van der Marel, H. Beutelspacher, Atlas of Infrared Spectroscopy of Clay Minerals and Their Admixtures, Elsevier, Amsterdam, 1974.

[4] H.D. Ruan, R.L. Frost, J.T. Kloprogge, J. Raman Spectrosc. 32 (2001) 745.

[5] H.D. Ruan, R.L. Frost, J.T. Kloprogge, Appl. Spectrosc. 55 (2001) 190.

[6] H.D. Ruan, R.L. Frost, J.T. Kloprogge, L. Duong, Spectrochim. Acta A 58 (2002) 265.

[7] J.T. Kloprogge, H.D. Ruan, R.L. Frost, J. Mater. Sci. 37 (2002) 1121.

[8] R.L. Frost, J.T. Kloprogge, S.C. Russell, J. Szetu, Appl. Spectrosc. 53 (1999) 572.

[9] R.L. Frost, J.T. Kloprogge, S.C. Russell, J. Szetu, Appl. Spectrosc. 53 (1999) 829.

[10] R.L. Frost, J.T. Kloprogge, S.C. Russell, J.L. Szetu, Appl. Spectrosc. 53 (1999) 423.

[11] R.L. Frost, J.T. Kloprogge, S.C. Russell, J.L. Szetu, Appl. Spectrosc. 53 (1999) 423.

[12] J.A. Rotole, P.M.A. Sherwood, Surf. Sci. Spectra 5 (1998) 4.

[13] M.R. Alexander, G.E. Thompson, G. Beamson, Surf. Interface Anal. 29 (2000) 468.

[14] J. van den Brand, P.C. Snijders, W.G. Sloof, H. Terryn, J.H.W. de Wit, J. Phys. Chem. B 108 (2004) 6017.

[15] J.A. Rotole, P.M.A. Sherwood, Surf. Sci. Spectra 5 (1998) 53.

[16] J.A. Rotole, P.M.A. Sherwood, Surf. Sci. Spectra 5 (1998) 11.

[17] J.A. Rotole, P.M.A. Sherwood, Surf. Sci. Spectra 5 (1998) 18.

[18] J.A. Rotole, P.M.A. Sherwood, Surf. Sci. Spectra 5 (1998) 25.

[19] J.A. Rotole, P.M.A. Sherwood, Surf. Sci. Spectra 5 (1998) 32.

[20] J.A. Rotole, P.M.A. Sherwood, Surf. Sci. Spectra 5 (1998) 39.

[21] J.A. Rotole, P.M.A. Sherwood, Surf. Sci. Spectra 5 (1998) 46.

[22] A. Strahlin, T. Hjertberg, Appl. Surf. Sci. 74 (1994) 263.

[23] T. Tsuchida, T. Takahashi, J. Mater. Res. 9 (1994) 29219.

[24] A. Nylund, I. Olefjord, Surf. Interface Anal. 21 (1994) 283.

[25] B.R. Strohmeier, Surf. Interface Anal. 15 (1990) 51.

[26] S. Thomas, P.M.A. Sherwood, J. Chem. Soc., Faraday Trans. 89 (1993) 263.

[27] S. Thomas, P.M.A. Sherwood, Anal. Chem. 64 (1992) 2488.

[28] H.D. Megaw, Z. Kristallogr. 87A (1934) 185.

[29] A. Ramos-Gallardo, A. Vegas, Z. Kristallogr. 211 (1996) 299.

[30] W.O. Milligan, J.L. McAtee, J. Phys. Chem. 60 (1956) 273.

[31] G.G. Christoph, C.E. Corbato, A. Hofmann, R.T. Tettenhorst, Clays Clay Miner. 27 (1979) 81.

[32] P.A. Buining, C. Pathmamanoharan, J.B.H. Jansen, H.N.W. Lekkerkerker, J. Amer. Ceram. Soc. 74 (1991) 1303.

[33] D. Papée, R. Tertian, R. Biais, Bull. Soc. Chem. Fr. (1953) 1301.