

# Influence of chemical bonding on X-ray spectra of different aluminium compounds

Rita Bonetto<sup>a,c</sup>, Jorge Trincavelli<sup>b,c,\*</sup>, Marcos Vasconcellos<sup>d</sup>

<sup>a</sup> Centro de Investigación y Desarrollo en Ciencias Aplicadas Dr. Jorge Ronco, Calle 47 No. 257, CC 59, 1900 La Plata, Argentina

<sup>b</sup> Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000, Córdoba, Argentina

<sup>c</sup> Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina

<sup>d</sup> Instituto de Física, Universidade Federal de Rio Grande do Sul, Campus do Vale, Av. Bento Gonçalves 9500, CEP: 91501-970, Porto Alegre, Brazil

Received 15 June 2005; accepted 27 September 2005

Available online 18 October 2005

## Abstract

Five minerals containing aluminium in different crystal configurations are studied. The different kinds of chemical bonding between aluminium and oxygen originate molecular orbitals with energy levels and transition probabilities varying from one compound to another. This effect appears as shifts and changes in relative intensities of  $K\alpha$  emission lines and as modifications of the  $K\beta$  characteristic spectrum. In the present work, the aluminium K characteristic spectra obtained by means of an electron microprobe with a wavelength dispersive system are compared for topaz, albite, spodumene, biotite and corundum.

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**Keywords:** Chemical bonding; X-ray spectrum; Aluminium; Molecular orbitals

## 1. Introduction

Electron probe microanalysis (EPMA) is a non-destructive analytical technique conventionally used for elemental quantification. Nevertheless, this technique has also been used for the characterisation of chemical bonds in compounds [1–6]. This last application is mainly based on peak energy shifts, variations in intensity ratios of characteristic lines and on the presence of satellite lines. These changes are due to the distortion of atomic energy levels when the atom of interest (main atom) is chemically bonded to others (ligands). These distorted orbitals are well described by the molecular orbital theory [7,8]. The corresponding energy levels as well as the mean life of each state may vary, even according to the crystal structure. These variations produce shifts in certain character-

istic lines of the X-ray emission spectrum and modifications of their relative intensity.

In the elements belonging to the third period, the  $K\alpha$  spectrum results from decays from L shell to K shell whereas the  $K\beta$  spectrum is caused by decays from M shell, where the valence electrons are placed, to K shell. Regarding the  $K\alpha$  spectrum, it was stated [9] that an adequate description of the  $K\alpha_{3,4}$  line group can be given in terms of transitions from a double ionised state, with a vacancy in K shell and the other one in L shell, to a state with two vacancies in L shell. In addition, it has been shown that these satellite lines are much more sensitive to chemical bonding than the main lines  $K\alpha_{1,2}$ . On the other hand, the main difference between the  $K\beta$  spectrum of a pure element and the spectrum corresponding to its compounds is the presence of a satellite line  $K\beta'$ , whose energy, slightly lower than the energy of the main line  $K\beta_{1,3}$ , is directly related to the ligand atom [7,10–12].

In the present work, EPMA spectra corresponding to five compounds of an element of the third period, aluminium, were measured and studied. The aim is to show that it is possible to identify different minerals which contain aluminium compounds, as well as to investigate the nature of the ligand

\* Corresponding author. Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000, Córdoba, Argentina. Tel.: +54 351 4334051; fax: +54 351 4334054.

E-mail addresses: bonetto@quimica.unlp.edu.ar (R. Bonetto), jorge@quechua.fis.uncor.edu (J. Trincavelli), marcos@ifufrgs.br (M. Vasconcellos).

(oxygen or fluorine in our case) not detectable by conventional systems.

## 2. Experimental

Spectra from five different compounds containing aluminium: corundum, topaz, spodumene, albite, and biotite were measured with a CAMECA microprobe at 15 keV and 50 nA. A wavelength dispersive (WD) spectrometer was used in order to achieve a good resolution. For each spectral region 100 measurements were performed at 20 s/step. The crystals employed were TAP[100], with an interplanar spacing  $2d=25.745$  Å, for aluminium and PET[002], with  $2d=8.74$  Å, for silicon spectra. In order to obtain values for the ratio between aluminium and oxygen concentrations, energy dispersive (ED) spectra were measured for some samples in a Philips SEM 505 electron microscope equipped with an EDAX system, at 15 keV. ED spectra were processed by AXIL [13] and the quantification process was carried out by means of MULTI [14]. This package allows the quantification of elements like H, Li and O, non-detectable through the detector used, by means of the stoichiometric relationship. The uncertainties assigned to these particular cases resulted from error propagation. The concentrations obtained, shown in Table 1, were employed to calculate the number of oxygen atoms per each aluminium atom used below.

## 3. Results and discussion

Two regions were considered for each spectra: one of them corresponding to the  $K\alpha$  group and the other around the  $K\beta$  group of lines. Background was removed visually from the measured spectra for each region. After this step, spectral regions were processed mathematically to deconvolute the different peaks. For this purpose, a Voigt function was used to fit  $K\alpha$  peaks. The Lorentzian component of the wider  $K\beta$  peaks, caused by the emission process, was negligible as

Table 1

Mass concentrations for the five studied minerals calculated from ED determinations

Element	Corundum <sup>a</sup> (%)	Topaz <sup>b</sup> (%)	Spodumene (%)	Albite (%)	Biotite (%)
H					0.21±0.07
Li			3.9±0.1		
O	58.15	44±3	52.0±0.1	48.2±0.1	40.5±0.1
F		10.4±0.3			
Na				5.96±0.04	
Mg					4.85±0.03
Al	41.85	29.5±0.2	15.06±0.06	12.24±0.05	9.78±0.05
Si		16±3	29.99±0.09	29.61±0.07	16.79±0.06
K				0.52±0.02	8.16±0.05
Ca				3.4±0.1	
Ti					1.27±0.02
Fe					17.5±0.1
Mn					0.83±0.08

<sup>a</sup> Nominal values were used.

<sup>b</sup> In this case,  $K\beta$  WD spectra were used for quantification. The uncertainty intervals correspond to 1 standard deviation.

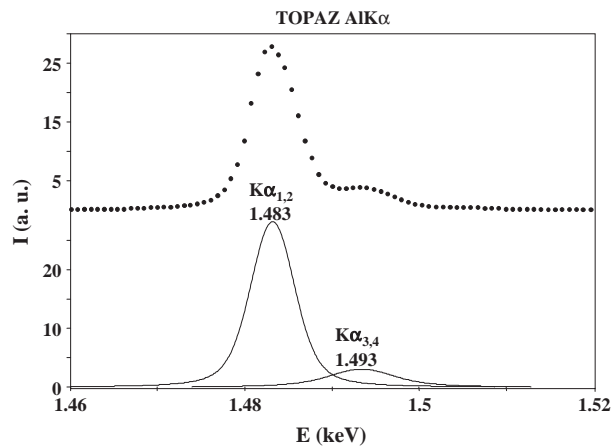


Fig. 1. Al  $K\alpha$  spectrum for topaz after background subtraction. Experimental data (●) are shown in the upper plot together with the obtained fit (—). In the lower plot, the contribution of each peak can be observed separately.

compared to their Gaussian component, due to detection and electronic processing. For this reason, a Gaussian function was enough to fit  $K\beta$  peaks. A unique FWHM value for all the peaks involved in each of these two groups was considered, since the involved energies were very close. Examples of the fitted spectra can be seen in Figs. 1 and 2, where Al  $K\alpha$  and Al  $K\beta$  spectra for topaz are respectively shown. In Fig. 1, the  $K\alpha_{3,4}$  group of lines can be observed to the right of the main  $K\alpha_{1,2}$  group. In Fig. 2, two groups of lines:  $K\beta_{1,3}$ ,  $K\beta_{2,5}$  and two  $K\beta'$  lines can be seen. The overlapped  $K\beta'$  lines are due to the presence of oxygen  $K\beta'(O)$  and fluorine  $K\beta'(F)$ . The structure of topaz includes octahedra surrounding aluminium atoms and tetrahedra surrounding silicon atoms. Two of the six corners in the octahedra contain fluorine atoms (or hydroxyl ions), whereas the other four have oxygen atoms. This feature explains the presence of the two  $K\beta'$  lines. The energy difference  $\Delta E$  between  $K\beta_{1,3}$  line and each  $K\beta'$  line should be close to the energy difference between the  $2p$  and  $2s$  orbitals of the ligand:  $\Delta E=15$  eV for oxygen and  $\Delta E=20$  eV for fluorine [15], since the ligand  $2p$  orbital is involved in the origin of  $K\beta_{1,3}$  lines and the ligand  $2s$  orbital is related to the

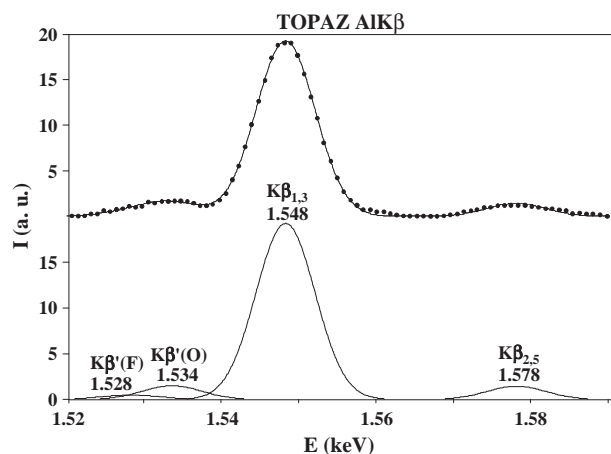


Fig. 2. Al  $K\beta$  spectrum for topaz after background subtraction. Experimental data (●) are shown in the upper plot together with the obtained fit (—). In the lower plot, the contribution of each peak can be observed separately.

Table 2  
Energy differences between  $K\beta'(O)$  and  $K\beta_{1,3}$  lines

Sample compound	Ref. [1]	This work
Topaz		$14.7 \pm 0.2$
Albite		$14.7 \pm 0.2$
Spodumene	$14.3 \pm 0.3$	$15.1 \pm 0.2$
Biotite	$14.3 \pm 0.3$	$14.8 \pm 0.2$
Corundum	$15.2 \pm 0.3$	$15.5 \pm 0.2$
Mean value		$15.0 \pm 0.3$

The uncertainty intervals correspond to 1 standard deviation.

generation of  $K\beta'$  line. Due to the low intensity of  $K\beta'(F)$  line, and the consequent high uncertainty, its energy was fixed at a value of 20 eV lower than the main peak energy to perform the fitting, as suggested by the theory. Instead, the energy corresponding to  $K\beta'(O)$  line was allowed to vary as a free parameter. The fit achieved by this strategy was better than that obtained without including the  $K\beta'(F)$  line. An additional analysis can be performed by observing the intensities of  $K\beta'(O)$  and  $K\beta'(F)$  lines: the area fitted for  $K\beta'(O)$  was about three times larger than the area fitted for

$K\beta'(F)$  ( $4.6 \pm 1.2$ ). Even when experimental errors were very important for  $K\beta'(F)$  line, it may be stated that the obtained result was in agreement with topaz structure, since some fluorine atoms are substituted by OH groups. For instance, by assuming that there is a substitution of 25% in each octahedron, the aluminium atom should be bonded to 4.5 atoms of oxygen and 1.5 atoms of fluorine, on average; i.e., there is a ratio 3:1 between the atoms that originate  $K\beta'(O)$  and  $K\beta'(F)$  lines.

In Table 2, the values obtained for the energy differences  $\Delta E$  between  $K\beta_{1,3}$  and  $K\beta'(O)$  lines are presented. An almost constant value is observed for all the compounds; the corresponding mean value  $\langle \Delta E \rangle = (15.0 \pm 0.3)$  eV exhibits a standard deviation of only 2% and coincides with the difference between  $2p$  and  $2s$  oxygen orbitals in agreement with theory. The results obtained in this work were compared with measurements performed by Lauser [1]. As it can be seen, taking into account the uncertainties, there is an agreement for biotite and corundum, whereas a slightly higher value is presented here for spodumene. The uncertainty intervals associated to Lauser's results were estimated from the propagation of errors. These were related to the process used

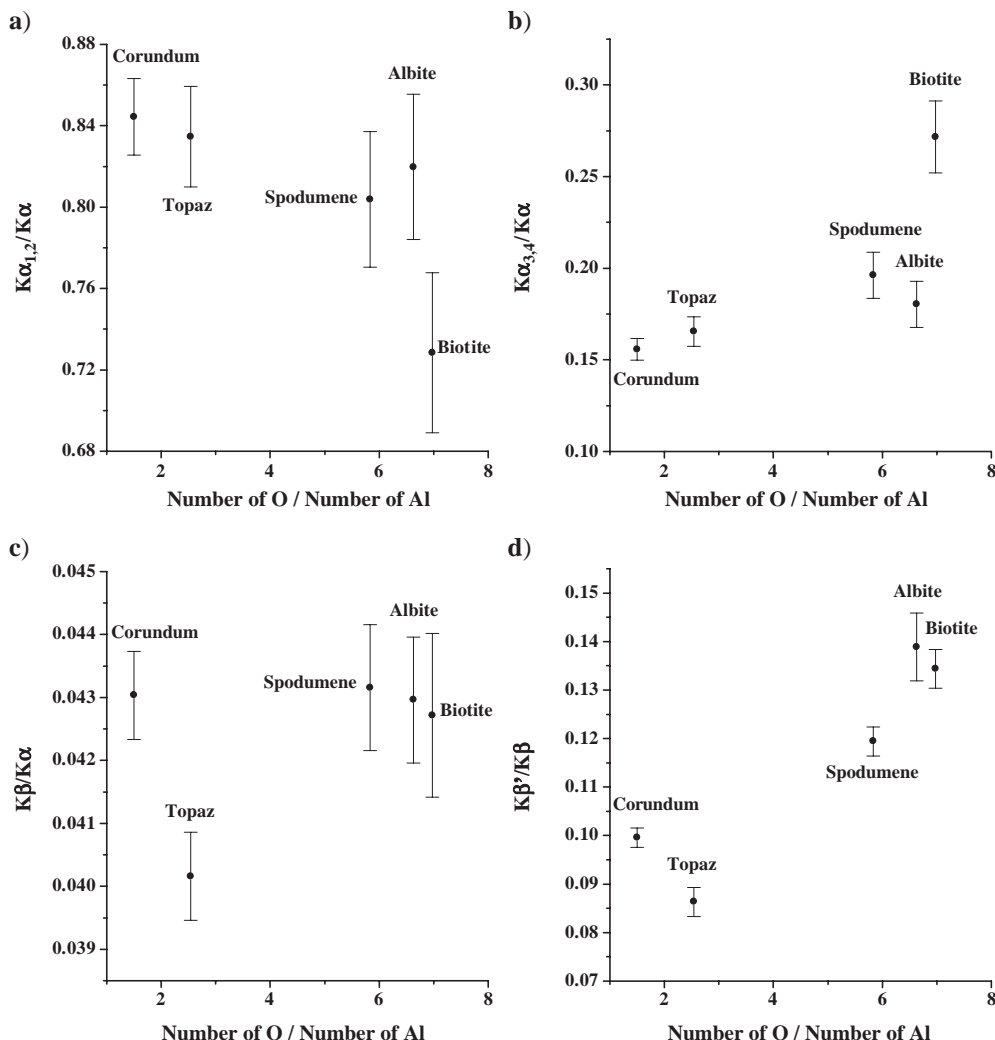


Fig. 3. Intensity ratios measured for different aluminium spectral lines in corundum, topaz, spodumene, albite and biotite: (a)  $K\alpha_{1,2}/K\alpha$ ; (b)  $K\alpha_{3,4}/K\alpha$ ; (c)  $K\beta/K\alpha$ ; (d)  $K\beta'/K\beta$ . The error bars correspond to 1 standard deviation.

to obtain the values tabulated here from the plots published by this author.

Different intensity ratios are plotted in Fig. 3 as a function of the quotient between the number of oxygen atoms and the number of aluminium atoms, according to the obtained quantification. This particular choice for the abscissa is somewhat arbitrary, since the spectrum variations, due to chemical bonding, may not correspond directly to a change in that variable. In fact, only the oxygen atoms directly bonded to aluminium should be taken into account. Besides that, it should be considered the way these oxygen atoms are shared with other elements, the distance between the main atom and each one of the ligand atoms, the covalence degree of the bonds, etc. Nevertheless, the variable chosen as abscissa allows to consider, in a first approximation, the magnitude of the effects due to chemical bonding, since when the number of anions bond to each main atom is great, there is, in principle, a high influence of the former on the spectra emitted by the latter.

Fig. 3a and b show that bonding effects in  $K\alpha$  spectrum are much more noticeable in  $K\alpha_{3,4}$  lines, due to double ionisation (with a relative variation above 50% for the  $K\alpha_{3,4}/K\alpha$  ratio) than in the main  $K\alpha_{1,2}$  lines (with a relative variation of 15% for the  $K\alpha_{1,2}/K\alpha$  ratio), corroborating the results obtained by other authors [7]. Fig. 3c shows, instead, that  $K\beta/K\alpha$  ratios do not almost vary from compound to compound ( $K\beta = K\beta_{1,3} + K\beta'$  and  $K\alpha = K\alpha_{1,2} + K\alpha_{3,4}$ ). Finally, by observing Fig. 3d, it can be stated that  $K\beta'/K\beta$  ratio is a clear indicator of the kind of compound, with a relative variation of about 50% as in the case of the  $K\alpha_{3,4}/K\alpha$  ratio.

#### 4. Conclusion

The results obtained in the present work corroborate that  $K\beta$  and  $K\alpha$  emission spectroscopy is a useful tool to identify different minerals which contain aluminium compounds. Particularly,  $K\alpha_{3,4}/K\alpha$  and  $K\beta'/K\beta$  intensity ratios are parameters sensitive to chemical bonding, whereas  $K\beta/K\alpha$  ratio does not depend appreciably on the compound, at least for the samples studied in this work. Although the number of bonded atoms for each main atom does not take into account all the present bonding effects, this variable is enough to show an increasing tendency in the most sensitive ratios. According to the results obtained here, the more the number of oxygen atoms per aluminium atom, the higher the relative intensity of  $K\beta'$ . The limiting case corresponds to zero oxygen atoms, i.e. pure aluminium, where  $K\beta'$  line is absent. The sensitivity of the mentioned intensity ratios with the kind of compound could allow to develop strategies for quantification of rocks with phases involving different minerals of aluminium.

Finally, it is important to emphasise the good agreement between the  $\Delta E$  values obtained for  $K\beta'$  and  $K\beta_{1,3}$  lines and the corresponding values predicted by the theory. This fact together with the detection of different  $K\beta'$  lines according to the nature of the ligand, may be used to investigate the presence of light elements like fluorine, boron, carbon, etc.,

not detectable by detectors with beryllium window or by WD systems equipped with conventional crystals. In addition, the presence of  $K\beta'$  lines allows to determine whether these light elements are chemically bonded to a specific element or not.

#### Acknowledgements

The authors wish to thank Dr. J.A. Riveros for his invaluable help in the revision of the manuscript. They also acknowledge the assistance of Lic. María del Rosario Torres Deluigi and Lic. María Elena Canafoglia in performing measurements of spectra. This work was partially supported by the Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina, the Agencia Córdoba Ciencia and the Secretaría de Ciencia y Técnica de la Universidad Nacional de Córdoba, Argentina.

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