

STRUCTURAL AND CHEMICAL EFFECTS ON THE Al K β X-RAY EMISSION BAND AMONG ALUMINUM CONTAINING SILICATES AND ALUMINUM OXIDES

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ABSTRACT

The Al K β peak, as measured on the spectrometer of a microprobe, shifts as much as 8×10^{-3} Å, as a function of Al coordination number and Al-O distance, but independent of O coordination number.

INTRODUCTION

In an earlier paper (White and Gibbs, 1967) data were reported for shifts in the Si K β emission band for a large number of silicates. Changes in the band position were correlated with systematic variations in mean Si-O distance—hence silicate structure type and average coordination number of the oxygen—and degree of substitution of cations for silicon in tetrahedral sites. Although it was observed that the band position also depends upon the kind of coordinating anion, the exact nature of this dependence was not determined. For the present study, changes in the Al K β emission band have been measured. Interpretation of wavelength shifts in this case becomes somewhat more complicated because the Al³⁺ cation plays a more variable role in silicate crystal chemistry than does Si⁴⁺. Commonly, the Al³⁺ cation is found in four-, five-, and six-fold coordination with oxygen whereas the Si⁴⁺ cation is almost invariably in four-fold coordination. The purpose of this paper is to interpret observed correlations in the Al K β shifts in terms of known crystal chemical parameters and to relate these, where possible, to the earlier findings for Si K β .

EXPERIMENTAL PROCEDURE

The Al K β bands were recorded using an ADP spectrometer of an Applied Research Laboratories model EMX electron microprobe. As in the earlier study of the Si K β emission band, positions were measured at 2/3 peak height. Measurements were made as changes in wavelength (Δ Al K β) taken with respect to the peak from α -Al₂O₃. This method circumvents difficulties in determining accurate wavelength values. Peak positions occur over a wavelength range of some 0.01 Å. The precision of individual shift measurements is on the order of ± 0.0008 Å. The data reported are the averages of four to five individual measurements. Additional details of the experiment are given in the earlier paper (White and Gibbs, 1967).

Results and discussion. The aluminum K-emission bands for three widely different materials are shown in Figure 1. The shape and width of the band of aluminum metal agree well with curves reported in the literature. The emission bands for α - Al_2O_3 and sanidine (KAlSi_3O_8) appear to represent the two extremes for the samples—excluding metallic aluminum. It appears that the band actually consists of two overlapping peaks whose relative intensities vary, giving an effective change in wavelength. This apparent doubling was not observed in the Si K-emission band but it is very well resolved for the Mg K-emission band (unpublished data). The measurement of band position at 2/3 peak height was an arbitrary choice and merely expedited comparison of results with the Si K-emission study.

All data from this study including the ideal compositions of the samples, mean Al-O distance where known and measured shifts are compiled in Table 1. The exact chemical analysis of a compound does not appear to be a critical parameter. For example, a wide variety of corundum specimens have been studied including: (1) single crystal corundum, (2) blue sapphire, (3) ruby containing some three percent Cr_2O_3 in solution, and (4) fine-grained α - Al_2O_3 powder used as a polishing agent. All

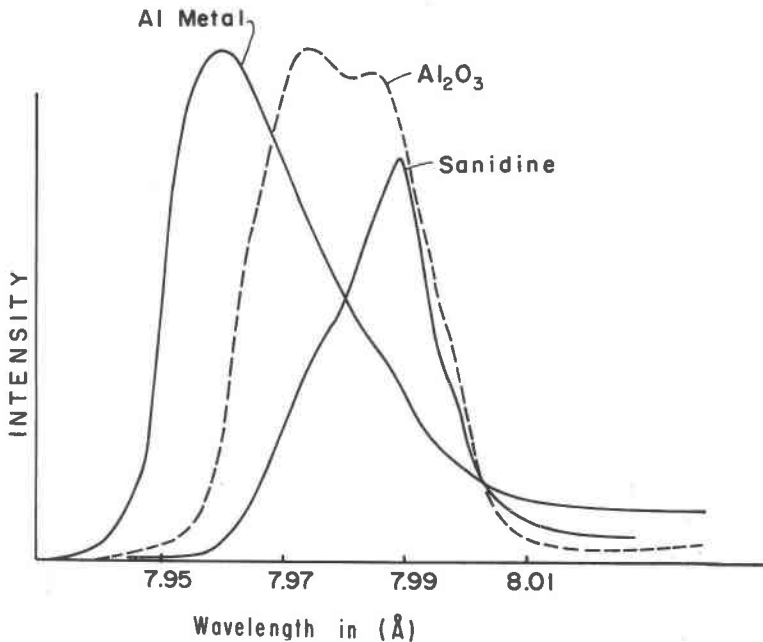


FIG. 1 The Al $K\beta$ emission bands for metallic aluminum, α - Al_2O_3 and sanidine.

TABLE 1. SUMMARY OF FORMULAS, Al K β SHIFTS AND MEAN Al-O BOND

Name	Ideal Composition	Δ Al K β ($\text{\AA} \times 10^{-3}$)	Mean C.N.	Mean Al-O(\AA)
Beryl	$\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$	22	6	1.902 (Gibbs, <i>et al.</i> , 1968)
Andesine	$\text{Ab}_{70}\text{An}_{30}$ to $\text{Ab}_{90}\text{An}_{10}$	50	4	—
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	45	4	1.749 (Kempster, <i>et al.</i> , 1962)
Leucite	KAlSi_3O_6	60	4	—
Haddam Cordierite	$\text{Mg}_2(\text{Be}, \text{Al}, \text{Si})_3\text{O}_{13}$	48	4	1.743 (Meagher, 1967)
Saguma Cordierite	$\text{Mg}_3(\text{Mg}, \text{Al}, \text{Si})_3\text{O}_{18}$	52	4	—
Synthetic Cordierite		33	4	—
Kragero Cordierite		44	4	—
Sanidine	KAlSi_3O_8	86	4	—
Microcline	KAlSi_3O_8	66	4	1.741 (Brown and Bailey, 1964)
Orthoclase	KAlSi_3O_8	58	4	—
Orthoclase	KAlSi_3O_8			
Spodumene	$\text{LiAlSi}_3\text{O}_6$	27	6	—
Tourmaline	$\text{NaMg}_3\text{B}_3\text{Al}_3\text{Si}_6\text{O}_{27}(\text{OH})_4$	0	6	—
Axinite	$\text{HCa}(\text{Mn}, \text{Fe})\text{Al}_2\text{B}(\text{SiO}_4)_4$	30	6	—
Almandite	$\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$	42	6	—
Pyrope	$\text{Mg}_2\text{Al}_2(\text{SiO}_4)_2$	47	6	1.886 (Gibbs and Smith, 1965)
Vesuvianite	$\text{Ca}_{10}\text{Al}_4(\text{Mg}, \text{Fe})_2\text{Si}_3\text{O}_{23}(\text{OH})_4$	8	6	—
Kyanite	Al_2SiO_5	6	6	1.906 (Burnham, 1963)
Topaz	$\text{Al}_2\text{SiO}_4(\text{F}, \text{OH})_2$	52	6	1.895 (Ribbe and Gibbs, 1969)
Andalusite	Al_2SiO_5	10	5.5	1.890 (Burnham and Buerger, 1961)
Sillimanite	Al_2SiO_5	18	5	1.855 (Burnham, 1962)
Ordered LiAl_3O_8	LiAl_3O_8	-4	6	—
Disordered LiAl_3O_8	LiAl_3O_8	-4	6	—
Spinel	MgAlO_4	-15	6	1.93 (Stefan Hafner, Univ. Chicago, pers. commun., 1967)
Aluminum	Al	-204	12	—
α - Al_2O_3	Al_2O_3	0	6	1.917 (Newnham and de Haan, 1962)

give identical emission bands at the level of resolution used in this study. The spectrometer used in the experiment has a resolution ($\lambda/\Delta\lambda$) of approximately 1,000.

Figure 2 is a plot of Δ Al $K\beta$ versus mean Al^{3+} coordination number. The Δ Al $K\beta$ values for all the compounds studied lie in a range of some 0.01 Å. Al^{3+} in four- (Al^{IV}) and six-fold (Al^{VI}) coordination fall in two slightly overlapping groups. As in the case of Si^{4+} (stishovite *versus* α -quartz), the four-fold compounds generally yield emission bands at larger wavelengths and are narrower than the bands for the octahedrally coordinated compounds. The large range of Δ Al $K\beta$ values ($<80 \times 10^{-4}$ Å) for the octahedrally coordinated compounds was unexpected at the outset. An explanation for this wide spread was sought in variations of the Al-O distances for these compounds. Figure 3 is a plot of Δ Al $K\beta$ versus the mean Al-O distance for the Al^{VI} compounds for which recent structural refinements have been reported. A strong correlation is observed but unfortunately precise structural data are not available for all the compounds used in the study. Tourmaline falls slightly off the

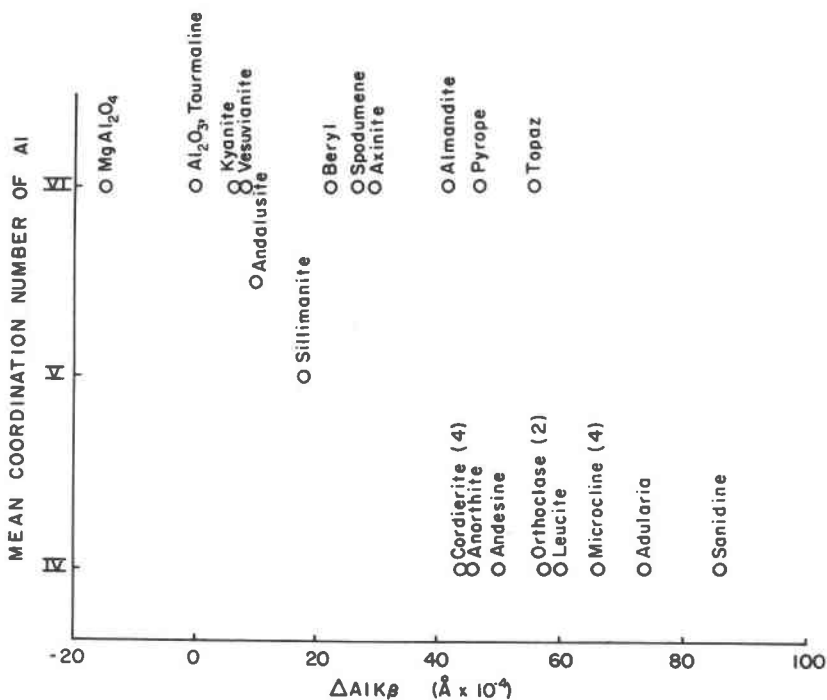


FIG. 2 The Al $K\beta$ peak shift versus Al^{3+} coordination number.

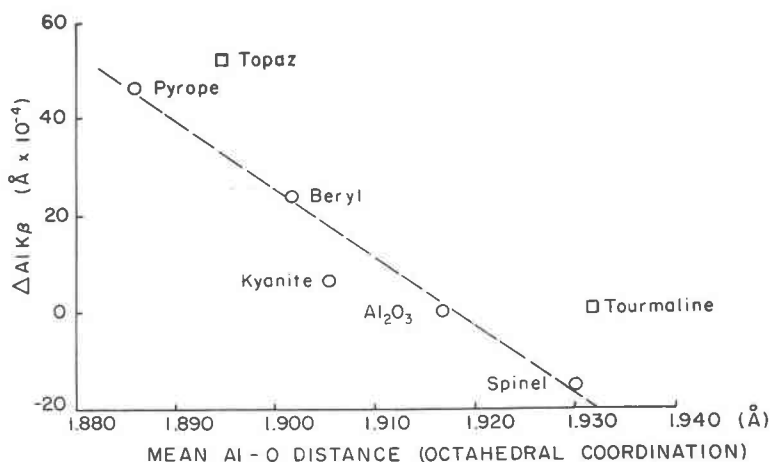


FIG. 3 Mean Al-O bond distance versus peak shift for compounds having Al^{3+} in octahedral coordination

straight line as might be expected because the Al^{3+} is coordinated by monovalent anions (F^- and OH^-) in addition to oxygen and, as determined for the Si $K\beta$ band, the anion species affects the shift parameter. It was not feasible to make a comparable plot for the Al^{IV} compounds due to lack of Al-O distance data. As the average coordination number of oxygen is three in both beryl and tourmaline and four in the other structures used to construct Figure 3, it appears that $\Delta Al K\beta$ is independent of the number of cations coordinated to the oxygen.

In summary, a correlation can be made between $\Delta Al K\beta$ and both the coordination number and the mean Al-O distance. Accordingly, when carefully applied, the Al $K\beta$ peak shifts can give an indication of the aluminum coordination number and Al-O distances in unknown materials regardless of degree of crystallinity.

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Manuscript received, January 24, 1969; accepted for publication, March 3, 1969.