& Kokotailo, 1969). In Pb(EP)₂, two oxygen atoms of different molecules are also relatively close to the lead atom; the Pb··O distances are 3·00(1) and 3·04(2) Å. The Pb···S and Pb···O contacts mentioned above are indicated in Figs. 1 and 2.

The numerical calculations were performed on the HITAC5020E computer of the computer center of the University of Tokyo and on the FACOM270-30 computer of this Institute, with a universal crystallographic computation program system, UNICS (Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967).

Fig. 3. (a) Interatomic distances (in Å) and (b) bond angles (in degrees) in lead diethyldithiophosphate.

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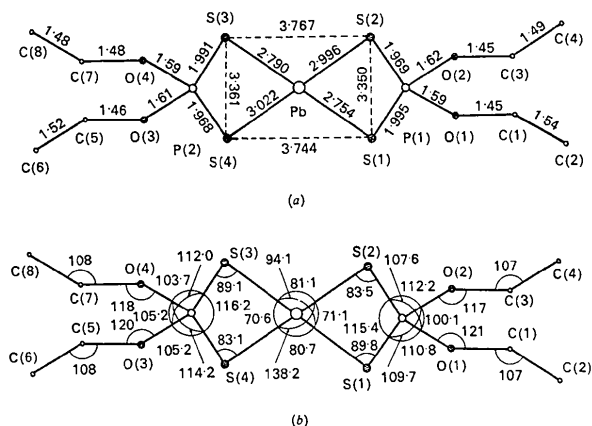SAKURAI, T., ITO, T., IWASAKI, H., WATANABE, Y. & FUKUHARA, M. (1967). Rep. Inst. Phys. Chem. Res. **43**, 62.

Structure Studies on Al₂TiO₅ at Room Temperature and at 600°C*

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The room-temperature structure of Al₂TiO₅ has been re-examined and is compared with the 600°C structure. This material is isomorphous with pseudobrookite, crystallizing in space group Bbmm with cell dimensions $a_0 = 9·429$, $b_0 = 9·636$, and $c_0 = 3·591$ Å at room temperature and $a_0 = 9·481$, $b_0 = 9·738$, and $c_0 = 3·583$ Å at 600°C. Our results, as well as refinement of previously published data, indicate that there is complete disorder in the metal sites for this compound. Provided that allowances are made concerning electrostatic interactions, the differences in the structure at the two temperatures appear to support the suggestion that the coordination polyhedra about the metal ions tend towards more regular configurations with increasing temperatures. The importance of cleavage planes, resulting from edge-shared octahedra in the hysteresis of the thermal expansion of the ceramic, is pointed out.

Introduction

As part of a program in which the relationship between the degree of anisotropy of crystal structures and their thermal expansion behavior is being studied, several oxide materials have been examined (Morosin & Lynch, 1971). Of particular interest are materials which, when heated, contract along at least one crystal-

lographic direction. Cartz (1968) and Li & Peacor (1969) suggested that the critical feature of crystalline anisotropy, leading to thermal expansion anisotropy, is the degree of distortion of the atomic coordination polyhedra. By 'distortion' it is implied that the bond lengths and angles vary markedly about the cations.

Aluminum titanate (tielite), Al₂TiO₅, is such a material. As a ceramic body, it exhibits a very low bulk thermal expansion coefficient, primarily because of a complex system of internal stresses and fractures. These stresses and fractures are developed upon

cooling from the required high sintering temperature, and are the result of the anisotropic structural properties of the individual grains which form the ceramic body.

Early structure studies (Austin & Schwartz, 1953) established that Al_2TiO_5 is isomorphous with the mineral pseudobrookite, Fe_2TiO_5 (Pauling, 1930), with only small differences in atomic positions. Later, a more complete structure study on these two materials was reported by Hamelin (1957). The rather large discrepancies in Hamelin's list of observed and calculated structure factors led us, initially, to re-examine the crystal structure at room temperature. Upon confirmation of the distorted polyhedra about the metal ions, the crystal structure was refined with data collected at 600°C. Our single-crystal structural results, together with their implication on the thermal expansion, are given in this paper.

Experimental

Aluminum titanate is one of several materials which crystallize in the so-called pseudobrookite structure. In general, these are of composition $M_2^{3+}Ti^{4+}O_5$ (in which M^{3+} may be Fe, Ti, Ga, or Al) or $M^{2+}Ti_2^{4+}O_5$ (in which M^{2+} may be Mg, Ti, Fe, or Co). These materials crystallize in space group $Bbmm$, with lattice constants similar to those for Al_2TiO_5; the latter are $a_0=9\cdot429\,(2)$, $b_0=9\cdot636\,(2)$, and $c_0=3\cdot591\,(1)$ Å as determined on our diffractometer.

The thermal expansion coefficients for several of these materials have been measured by powder methods (Al_2TiO_5 by Buessem, Thielke & Sarakauskas, 1952; $MgTi_2O_5$ by Bush & Hummel, 1959; Fe_2TiO_5 and Al_2TiO_5 by Cartz, 1968). Using a recently developed single-crystal high-temperature furnace (Lynch & Morosin, 1971), our results on Al_2TiO_5 are found to be in good agreement with these values. At room temperature, the expansion coefficients are $9\cdot8\times10^{-6}$, $20\cdot6\times10^{-6}$, and $-1\cdot4\times10^{-6}°C^{-1}$ along the a, b, and c axes, respectively. The measured reduced lattice constants, as a function of temperature, are shown in Fig. 1 (at 600°C, $a_0=9\cdot481$, $b_0=9\cdot738$, and $c_0=3\cdot583$ Å).

Single-crystal precession and Weissenberg photographs were taken to verify the quality of the specimens used and to verify the space group. Absences of $h+l$ odd for hkl, and k odd for $0kl$, together with the lack of a piezoelectric response, indicate the previously assigned space group, $Bbmm$, is correct. Four molecules per cell would be contained in such an orthorhombic unit; previous workers have assigned the metal atoms on fourfold sites at $\pm(x,\frac{1}{4},0)$ and $\pm(x+\frac{1}{2},\frac{1}{4},\frac{1}{2})$, on eightfold sites at $\pm(x,y,0)$, $\pm(x,\frac{1}{2}-y,0)$, $\pm(x+\frac{1}{2}, y,\frac{1}{2})$, and $\pm(x+\frac{1}{2},\frac{1}{2}-y,\frac{1}{2})$, and the oxygen atoms on similar symmetry sites (one fourfold and two different eightfold sites).

Room-temperature Mo $K\alpha$ intensity data were collected on two different crystal specimens obtained from two ceramic bodies prepared at different times. These are designated 1 and 2. Analysis of the ceramic body from which crystal 1 was obtained indicated $\sim0\cdot2\%$ each of Zr and Fe, $\sim0\cdot1\%$ of Mg, $0\cdot05\%$ Ca, and $\sim0\cdot01\%$ each of Ni and Cu. The second ceramic body was not subjected to analysis; however, constituent oxides used were analyzed and they contained 10 ppm Si and 3 ppm Fe, with other impurities less than 1 ppm. Intensity data were measured with a scintillation counter, employing pulse-height discrimination, using the θ–2θ scan technique (scan speed $\frac{1}{2}°\,min^{-1}$; width from $(2\theta_{\lambda1}-1\cdot25)°$ to $(2\theta_{\lambda2}+1\cdot25)°$; background 20-sec counts each at beginning and end of scan). Of these data, those which measured less than 3σ, [with $\sigma=(N_{SC}+K^2\cdot N_B)^{1/2}$ where N_{SC}, K, and N_B are the total scan count, ratio of the scan-to-background times, background counts, respectively)* were assigned a value equal to 3σ and were considered to be unobserved in subsequent least-squares refinement. (The number of reflections is summarized with other parameters in Table 1.) A set of intensity data was also collected at 600°C in a high-temperature furnace using the above mentioned procedure; a correction for scattering due to the thermocouple, upon which the crystal was mounted, was included. With $\mu=32\cdot2\,cm^{-1}$ for Mo $K\alpha$ radiation, and the crystal of maximum dimension near 0·3 mm (crystal 1: 0·18, 0·20, 0·31 mm; crystal 2: 0·073, 0·091, 0·292 mm, both mounted on maximum dimension which is [001]), no absorption corrections were considered necessary. Scattering factors for Al^{3+}, Ti^{4+}, and O^{2-} for use in calculating the structure were obtained or extrapolated from *International Tables for X-ray Crystallography*, (1962).

Table 1. *Positional and isotropic thermal parameters for Al_2TiO_5 (room-temperature data)*

		Hamelin (1957)	Crystal 1	Crystal 2	Crystal 2 (disordered)
Ti	x	0·1863 (9)	0·1852 (2)	0·1855 (4)	0·1858 (6)
	B	1·7 (2)	0·84 (6)	1·11 (9)	0·35 (8)
Al	x	0·1351 (7)	0·1346 (1)	0·1350 (3)	0·1355 (3)
	y	0·5613 (6)	0·5616 (1)	0·5617 (3)	0·5614 (3)
	B	0·1 (1)	−·01 (2)	−·24 (5)	0·49 (7)
O(1)	x	0·759 (2)	0·7575 (5)	0·7567 (12)	0·7581 (7)
	B	0·9 (4)	0·39 (4)	0·41 (13)	0·51 (11)
O(2)	x	0·048 (2)	0·0484 (9)	0·0491 (8)	0·0489 (5)
	y	0·118 (2)	0·1170 (4)	0·1176 (8)	0·1166 (5)
	B	0·6 (2)	0·47 (5)	0·48 (10)	0·56 (8)
O(3)	x	0·317 (2)	0·3133 (4)	0·3137 (8)	0·3128 (5)
	y	0·075 (2)	0·0719 (4)	0·734 (8)	0·723 (5)
	B	0·9 (3)	0·46 (4)	0·41 (9)	0·53 (8)
No. observed		125	1143	339	339
No. less than		56	377	82	82
R		0·174	0·098	0·098	0·062

* It has kindly been pointed out to us that the correct expression should contain K^2 rather than K which we employed. Also, we have made no allowances for instability or other errors which could be a function of intensity.

Table 2. *Positional and anisotropic thermal parameters for* Al$_2$TiO$_5$ (*crystal* 1 *at room temperature*)

Thermal parameters are of the form: exp $(-2\pi^2 \sum\sum U_{ij}h_ih_ja_i{}^*a_j{}^*)$.

	x	y	U_{11}	U_{22}	U_{33}	U_{12}	$(\times 10^{-2})$
M(1)	0·1854 (1)		0·54 (2)	0·52 (2)	0·36 (2)	0·05 (2)	
M(2)	0·13478 (8)	0·56150 (8)	0·38 (3)	0·24 (2)	0·26 (2)		
O(1)	0·7577 (3)		0·49 (7)	0·49 (7)	0·47 (7)		
O(2)	0·0485 (2)	0·1167 (2)	0·39 (5)	0·36 (5)	0·95 (6)	−0·06 (4)	
O(3)	0·3125 (2)	0·0721 (2)	0·50 (5)	0·79 (6)	0·38 (5)	0·07 (4)	

Refinement

Initially, Hamelin's (1957) data were subjected to a least-squares refinement. In such a full-matrix refinement, the function $\sum w(F_o - F_c)^2$, in which weights were set equal to 1·0 for observed reflections and zero for unobserved reflections, was minimized. With isotropic thermal parameters, an R value $(R = \sum||F_o| - |F_c||/ \sum|F_o|)$ equal to 0·174 was obtained with our parameters in excellent agreement with those published. This large value for R led us to collect our own intensity data on crystal 1; as seen in Table 1, the positional parameters obtained from this data set (crystal 1) are in good agreement with those we obtained on refinement of Hamelin's data. Note, however, in both refinements that the temperature parameter for Ti is rather large while that for Al is correspondingly low. Initially, the purity of our material was suspect; however, the chemical analysis obtained could not account for the anomalous values for the temperature factors. The assumption of disorder between the two metal sites was then investigated, resulting in a reduction in R from about 0·10 to 0·06 (with the assumption of disorder, the value of R on Hamelin's data reduces from 0·174 to 0·134). The procedure employed was a series of least-squares refinements using different ratios of Al and Ti at the metal sites, taking care to maintain proper stoichiometry. A minimum R was consistent with complete disorder of the metals. The presence of slight chemical impurities in our first sample (as mentioned above) together with the inauspicious loss of crystal 1, before the high-temperature data were collected, resulted in our second data set (crystal 2) to be collected and refined. These results are also included in Table 1. Refinement employing anisotropic thermal parameters on the larger data set (crystal 1) with complete disorder of the metal sites yields the parameters in Table 2. The value of R for this refinement is 0·058. (An R value of 0·050 is obtained with anisotropic thermal parameters using the data on crystal 2 with complete disorder.) Care should be used in interpreting the thermal ellipsoids as actual anisotropic thermal motion, since in such an 'alloy' (with complete disorder of the metal sites) part of the displacements may result from small static displacement of the slightly different sized Al and Ti ions and the resulting different metal–oxygen bond distances. Positional and isotropic thermal parameters obtained by refinement of the 600 °C data are listed in Table 3. Other than the thermal parameters, the only significant change from

the room-temperature results involves the $M(1)$ positional parameter which has shifted to a slightly smaller value [O(1) also has a smaller value; however, the difference cannot be considered significant at the usual 3σ confidence level]. In an anisotropic refinement of this high-temperature data, values for the thermal parameters were found to scale in proportion to the values shown in Table 2. Table 4 lists the observed and calculated structure factors for crystal 1 (left-hand side), crystal 2 at room temperature (right-hand upper side), and crystal 2 at 600 °C (lower right side).

Table 3. *Positional and isotropic thermal parameters for* Al$_2$TiO$_5$ *at* 600 °C (*crystal* 2)

	x	y	B
M(1)	0·1826 (4)		0·89 (6)
M(2)	0·1348 (3)	0·5614 (3)	1·13 (5)
O(1)	0·7556 (11)		1·49 (17)
O(2)	0·0484 (8)	0·1173 (8)	1·17 (11)
O(3)	0·3124 (8)	0·0717 (8)	1·10 (11)

Number observed 329, unobserved 105

Discussion

The most important contribution of this study is that disorder in the two metal sites has been established.
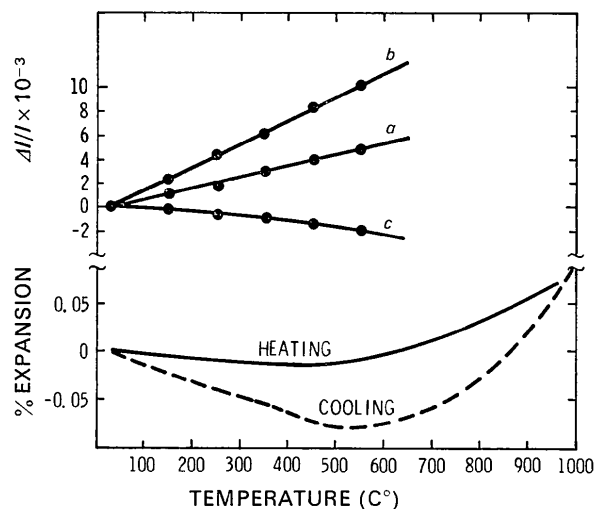

Fig. 1. Reduced single-crystal thermal expansivities of Al$_2$TiO$_5$ are shown for temperatures between room and 600° C. The c axis experiences a slight contraction in this temperature interval. Single-crystal behavior is compared with the contraction and marked hysteresis which ceramic bodies exhibit. An explanation of this hysteresis is given in the text.

Table 4. *Observed and calculated structure factors for* Al$_2$TiO$_5$

Room-temperature values ($\times 10$) for crystal 1 (left) and crystal 2 (upper right) as well as 600°C for 2 (lower right).

Since the ceramic is white and most trivalent titanium compounds are green or violet, all the titanium must be present as the tetravalent state. Such an ion has a radius near 0·69 Å compared with the 0·61 Å six-coordinated radius of aluminum (Shannon & Prewitt, 1969) and apparently the 12% difference is insufficient to produce order at the high temperatures required to form the compound. This is particularly interesting since it is known that slow cooling, rather than a rapid quench, decomposes the compound into its starting materials (implying rapid diffusion at temperatures in excess of 1000°C). Also, Mössbauer measurements on the compounds FeTi$_2$O$_5$ and Fe$_2$TiO$_5$ (pseudo-brookite) (Shirane, Cox & Ruby, 1962), in which the iron and titanium radii are more similar than those of aluminum and titanium, suggest the majority of the iron prefers the $M(2)$ site. In Fe$_2$TiO$_5$, however, the spread (1·91–1·95 Å) in the metal–oxygen separations for the $M(1)$ site is much smaller than that in Al$_2$TiO$_5$ (1·82–2·09 Å; Table 5). This suggests that the trivalent iron (with d electrons) prefers the more irregular $M(2)$ site than does quadrivalent titanium (with no d elec-

trons); in compounds having no d electrons such as is the case for Al$_2$TiO$_5$, no site preference can be established. (This hypothesis could be corroborated by a more detailed study of MgTi$_2$O$_5$ and Ga$_2$TiO$_5$.)

Table 5 lists the interatomic separations for distances less than the c-axis length and the corresponding angles determined in this study. There are two symmetry-related separations for each of the $M(1)$–oxygen and for $M(2)$–O(3) yielding six separations about each metal site. Both metal sites can be considered to be distorted octahedral. Even though the spread in values for the $M(2)$–oxygen separations is larger than for $M(1)$, it is difficult to conclude any preference for tetrahedral symmetry for site $M(2)$. Note that at 600°C the spread for values involving the $M(1)$ metal site has increased to be quite similar to that for the $M(2)$ site; the angles, on the other hand, are quite similar at both temperatures.

An examination of values listed in Table 5 should test Cartz's (1968) hypothesis (concerning the anomalous thermal expansion behavior of this material), namely, that with increasing temperature, the atomic coordination polyhedra become more regular. Such is the case with lead titanate, PbTiO$_3$, which is a typical member of the perovskite structure type isomorphous with tetragonal BaTiO$_3$. In PbTiO$_3$, which has $c/a > 1·0$, the c axis contracts (while the a axis expands) with increasing temperature, resulting in an overall slightly negative bulk thermal expansivity. At room temperature, the distorted coordination about the lead ion consists of twelve oxygen atoms at distances varying from 2·53 to 3·20 Å, while that about the titanium ion consists of six oxygen atoms at distances varying from 1·78 to 2·38 Å. In the cubic phase, stable above 490°C these polyhedra become regular with Ti–O separations of 1·98 Å and Pb–O separations of 2·80 Å. Based on the 'ordered' structure suggested by previous studies and the distortion of the metal sites at room temperature, Cartz found it attractive to suggest a parallel hypothesis in which chains of Ti–O octahedra (joined at an apex and running parallel to the c axis) separated by 'more highly distorted' Al–O octahedra would possibly 'twist' with increasing temperature, leading to a large anisotropy in the thermal expansion behavior.

Actually, the metal–metal separations (Table 5) suggest that the structure is more three-dimensional in nature. This does not exclude, however, a hypothesis similar to that advanced for PbTiO$_3$ for either an ordered or disordered structure. In such a three-dimensional structure, the distortions from more regular configuration about the metal ions at room temperature can be understood, provided electrostatic considerations are also included. As is usually found, edges of polyhedra that are shared tend to be shorter than unshared edges; this conditions arises from the electrostatic repulsion between the positive metal ions and the resulting displacement of the more polarizable oxygen ions so as to partially shield the positive charges. Fig. 2 outlines the octahedra that form the struc-

Table 5. *Interatomic separations and angles in* Al$_2$TiO$_5$

		Room Temperature (Å)	600°C (Å)
	$M(1)$–O(2)	1·823 (4)	1·814 (8)
	$M(1)$–O(1)	1·920 (2)	1·921 (5)
	$M(1)$–O(3)	2·087 (4)	2·128 (8)
	$M(2)$–O(2)	1·814 (4)	1·820 (8)
	$M(2)$–O(3)	1·864 (1)	1·863 (2)
	$M(2)$–O(2)	1·900 (4)	1·921 (7)
	$M(2)$–O(1)	2·076 (3)	2·110 (7)
	$M(2)$–O(3)	2·114 (4)	2·126 (8)
	$M(2')$–$M(2'')$	2·814 (2)	2·821 (4)
	$M(1)$–$M(2)$	3·040 (2)	3·095 (3)
	$M(2)$–$M(2')$	3·051 (2)	3·068 (3)
	$M(1)$–$M(2')$	3·060 (2)	3·066 (3)
	$M(1')$–$M(2')$	3·530 (2)	3·525 (4)
A	O(2)—O(2')	2·426 (6)	2·459 (10)
B	O(2)—O(3)	2·525 (6)	2·542 (10)
C	O(1)—O(3)	2·533 (3)	2·552 (6)
D	O(3)—O(3')	2·565 (4)	2·563 (8)
E	O(2)—O(2')	2·573 (6)	2·589 (10)
F	O(3)—O(2)	2·872 (5)	2·886 (8)
G	O(3)—O(2)	2·891 (5)	2·900 (8)
H	O(1)—O(2)	2·961 (5)	2·957 (10)
J	O(1)—O(2)	3·030 (7)	3·063 (13)
K	O(1)—O(3)	3·179 (5)	3·199 (8)
L	O(3)—O(3')	3·419 (6)	3·472 (11)
	O(3)–$M(1)$–O(1)	78·3 (1)	78·0 (2)
	O(2)–$M(1)$–O(3)	80·1 (2)	79·9 (3)
	O(2)–$M(1)$–O(2')	89·8 (2)	91·0 (4)
	O(2)–$M(1)$–O(1)	104·5 (1)	104·6 (2)
	O(3)–$M(1)$–O(3')	110·0 (2)	109·3 (3)
	O(1)–$M(1)$–O(1')	138·6 (3)	137·7 (5)
	O(2)–$M(2)$–O(3)	77·7 (2)	77·6 (3)
	O(3)–$M(2)$–O(3)	79·8 (2)	79·7 (2)
	O(1)–$M(2)$–O(3)	79·8 (2)	79·7 (3)
	O(2)–$M(2)$–O(2')	81·5 (2)	82·1 (3)
	O(1)–$M(2)$–O(3)	98·7 (2)	98·1 (4)
	O(2)–$M(2)$–O(3)	99·4 (2)	99·4 (3)
	O(1)–$M(2)$–O(2)	102·1 (2)	102·2 (4)
	O(2)–$M(2)$–O(3)	103·6 (2)	103·9 (2)

ture of Al_2TiO_5; shared edges are indicated by parallel lines (dashed lines are used for octahedra about metal sites located at $z=0.5$; solid lines indicate octahedra at $z=0$). Note that three polyhedra connected by apex-sharing form a unit (one such unit is shown by shading); these units stack along the c direction forming chains in a manner similar to the Ti–O octahedra chains originally proposed by Cartz (1968). With increasing temperature, the weaker, less favorable, interactions (those across shared edges of octahedra) might be expected to expand a bit more than the stronger inter-actions. Although few of the differences in the values of the interatomic separations between room temper-ature and 600 °C taken alone can be considered signi-ficant, the overall set of values indicates a tendency towards a more symmetric configuration at the higher temperature, provided electrostatic perturbations are taken into account. For example, separations C and D (see Fig. 2 and Table 5) as well as G and F tend towards similar values in the higher temperature structure, while the increase in C compared with H is much greater. These changes are accomplished with very small, if any, changes in the bond angles of the struc-ture. Thus, it appears that there is a tendency towards more symmetric configurations about the metal ions with increasing temperature for Al_2TiO_5 as postulated by Cartz.

The fact that the Al_2TiO_5 crystal is composed of tri-octahedral units forming infinite chains along c, which are weakly bonded together by edge sharing in the ab plane, is consistent with the complex thermal expansion behavior of the ceramic. The ceramic exhibits a marked thermal expansion hysteresis (shown in Fig. 1) which was first explained in full by Bush & Hummel (1959). These authors suggested that if the thermal expansion tensor of a material is highly anisotropic then, as a ceramic specimen cools from the sintering temperature, the contractions of the individual grains are incompatible causing a complex system of internal stresses to develop until, at some point, the tensile strength of the material is exceeded. With further cooling, fractures occur; these are generally oriented normal to directions of high expansion, be-cause tensile stresses develop where grains are bonded in directions of high expansion (actually contraction during cooling), and compressive stresses develop where grains are bonded in directions of low expansion. Thus, when heated from room temperature, the expan-sion of the ceramic initially follows the c-axis curve rather than following the average value $(\alpha_a+\alpha_b+\alpha_c)/3$ since expansion along the a and b axes merely goes to fill fractures. Our structure results are entirely con-sistent with the above description. For example, shared edges D, C, and D (Fig. 2) extend in a sheet perpendic-ular to the a axis, while shared edges D, B, A, B, and D extend in a rather crooked surface perpendicular to the b axis; cleavage could probably occur across such weak interactions. (Also note that when rupture occurs perpendicular to the a axis, the remaining metal ions near the cleavage surface are left in a distorted tetra-hedral configuration, acceptable to either aluminum or titanium, which are known to exhibit both configura-tions.) Bush & Hummel (1959) argued that the expan-sion behavior of the ceramic above 550 °C is directly related to chemical recombination of the fractured surfaces, i.e. the expansion represents the following net effect: (1) that part of the ceramic which has re-combined expands at the single-crystal average rate, (2) that part of the ceramic recombining in any dif-ferential temperature range suffers an elastic contrac-tion, and (3) that part of the ceramic which has not recombined expands at the c-axis rate. This argument was supported by the fact that the strength of the ceramic increases sharply at temperatures above 550 °C. We propose that the chemical recombination above 550 °C is accomplished by tetrahedral-to-octahedral interaction of surface metal ions on opposite sides of a given microfracture. Indeed, the ease with which such interactions accomplish recombination accounts for the rather remarkable ability for Al_2TiO_5 ceramics to sustain repeated temperature cycling without degrada-tion of the fracture-recombination mechanism.
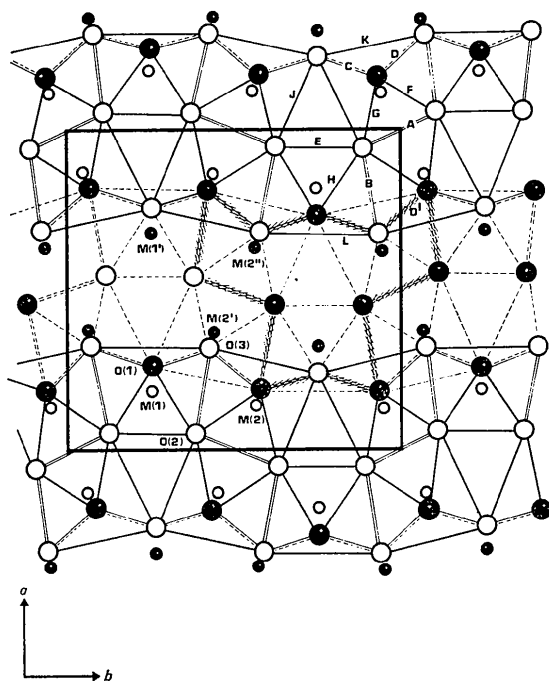

Fig. 2. Crystal structure of Al_2TiO_5 showing the oxygen octahedra about the metal sites. Note that the octahedra are edge-shared as indicated by double lines (dashed lines are used for octahedra centered about metal sites located at $z=\frac{1}{2}$, filled atoms lie at $z=\frac{1}{2}$). Cleavage presumably occurs across these weaker shared edges (edges of the type C and D). Such a cleavage plane can be seen to lie perpen-dicular to the a axis, while that perpendicular to the b axis takes a rather crooked path (using A, B, and D edges). Thermal expansion along chains of such tri-octahedral groups (strongly bonded by apex-sharing along the c axis) is very small and negative, while that perpendicular is along directions of weaker bonding and, thus, much larger.

In summary, our structure results show that the metal ions are completely disordered in Al_2TiO_5. The differences between our room temperature and 600 °C structures explain the anisotropic thermal expansion behavior of the single crystal. Furthermore, the importance of cleavage planes resulting from edge-shared octahedra in the hysteresis of the thermal expansion of the ceramic is pointed out.

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The Molecular Structure of 3',5,5',6-Tetramethoxyflavone, C₁₉H₁₈O₆*

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Sayre's relations were used to determine the structure of 3',5,5',6-tetramethoxyflavone. The flavone was extracted from the fruit of *Sargentia greggii*, a citrus plant found in Mexico. The space group is $P2_1/c$ and the cell dimensions are $a = 7\cdot335\,(5)$, $b = 11\cdot304\,(5)$, $c = 20\cdot249\,(6)$ Å and $\beta = 104\cdot5\,(4)°$. 2511 independent reflections were collected by counter methods. The observed density is 1·42 g.cm⁻³ which is consistent with four molecules per unit cell, $d_c = 1\cdot40$ g.cm⁻³. The model was refined by least-squares techniques to a conventional R value of 0·086 for 1249 of the largest intensities. The heterocyclic ring, which is fused to the benzene ring to form the γ-benzopyrone portion of the molecule, is slightly puckered and planes fitted to the two rings make an angle of 4°. The phenyl ring is planar and makes an angle of 28° with the γ-benzopyrone portion of the molecule. Three of the methoxyl groups are essentially coplanar with the benzene rings while the fourth is forced from the plane due to intramolecular crowding.

Introduction

A white crystalline compound was extracted from the fruit of *Sargentia greggii*. The citrus plant is known locally in Mexico as limoncello, chapote amarillo or naranjillo. The compound was identified as a flavone and was characterized by nuclear magnetic resonance and mass spectrometry. The highest mass peak (342) along with elemental analyses established the formula as $C_{19}H_{18}O_6$. Zeisel tests indicated the molecule contained four methoxyl groups. The positions of the three phenyl ring hydrogen atoms were established from the

n.m.r., and this established the positions of two of the methoxyl groups. The assignment of the hydrogen atoms associated with γ-benzopyrone portion of the molecule was not unequivocal; however, the molecule tentatively was assumed to be 3',5,5',8-tetramethoxyisoflavone. A few crystals of the flavone were submitted to the FASTBIOS Laboratory by Dr Xorge Domínguez.

Experimental

A large crystal was ground into an ellipsoid with axes of 0·46 mm, 0·48 mm and 1·0 mm. The crystal was mounted with the *a* axis (major axis of the ellipsoid) coincident with the rotation axis. The unit cell was found to be monoclinic and the room temperature cell