

Table 1. Crystallographic data of some salts of malic acid

	K(C ₄ H ₅ O ₅) · H ₂ O	K ₂ (C ₄ H ₄ O ₅) · H ₂ O	Fe(C ₄ H ₅ O ₅) ₂ · 4H ₂ O
<i>a</i> (Å)	8·608 ± 0·004	7·339 ± 0·003	7·468 ± 0·003
<i>b</i>	13·049 ± 0·004	8·549 ± 0·003	7·673 ± 0·003
<i>c</i>	7·249 ± 0·003	7·026 ± 0·002	7·376 ± 0·003
α (°)	90	102·83 ± 0·03	99·10 ± 0·02
β	118·60 ± 0·03	109·54 ± 0·03	103·67 ± 0·02
γ	90	92·60 ± 0·03	63·54 ± 0·02
Reliability index, <i>M</i>	39	29	34
Possible space groups	C2/c or Cc	P $\bar{1}$ or P1	P $\bar{1}$ or P1
Number of formula units, <i>Z</i>	4	2	1
ρ _{cal} (g.cm ⁻³)	1·77	1·78	1·89
ρ _{exp}	1·77	1·77	1·86

values of *Q*. *M* > 10 means complete reliability. The values of *M* given in Table 1 were calculated before minimizing the discrepancies with the aid of a computer program. After this procedure the quantities *M* increased by a factor of about four.

For the malates (I), (II), and (III) the lattice constants and possible space groups given in Table 1 result. The experimental density and the calculated value with *Z* formula units within the cell are given for each of the three malates. The powder pattern of salt (IV) could not be indexed. We suppose that the crystals are unstable in air and that the sample contained a mixture of some compounds when we received it.

No further work on these substances is contemplated.

My thanks are due to Prof. K. Boll-Dornberger for valuable comments on the paper.

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Re-examination of the crystal structure of ferroelectric tetragonal bronze-type Ba₆Ti₂Nb₈O₃₀. By P. B. JAMIESON and S. C. ABRAHAMS, Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, U.S.A.

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Stephenson's visually estimated Ba₆Ti₂Nb₈O₃₀ room temperature structure factors have been corrected for absorption, and for anomalous dispersion as is appropriate for measurements on a polar crystal. Least-squares refinement of his original model, with the corrected data, results in physically reasonable temperature factors and in more meaningful estimates of error in the atomic positions, as compared with the previously published values. The random distribution of the Nb and Ti atoms over the 10 available sites was confirmed. In the closely related structure of Ba_{0.27}Sr_{0.75}Nb₂O_{5.8} the polar space group *P4bm* transforms to the antipolar space group *P4b2* at higher temperature. The homopolar Nb/Ti composite atom in Ba₆Ti₂Nb₈O₃₀ is calculated, by analogy, to be displaced by 0·18 ± 0·10 Å for a similar transformation.

In the course of studying a series of ferroelectric tungsten bronze-type crystal structures, such as Ba_{0.27}Sr_{0.75}Nb₂O_{5.8} (Jamieson, Abrahams & Bernstein, 1968), we became interested in the details of the study by Stephenson (1965) on the related material Ba₆Ti₂Nb₈O₃₀. Accurately determined atomic positions for this ferroelectric crystal would provide a valuable datum point in our recently discovered relationship between atomic displacements and both Curie temperature and spontaneous polarization (Abrahams, Kurtz & Jamieson, 1968). In the original work on tetragonal Ba₆Ti₂Nb₈O₃₀ (*a* = 12·54 ± 0·05, *c* = 4·01 ± 0·01 Å, space group *P4bm*) by Stephenson, neither absorption corrections nor allowance for the imaginary part of the atomic scattering factor dispersion were made. Neglect of these corrections in this polar crystal could introduce serious error into the resulting atomic coordinates.

Structure factors were calculated on the basis of Stephenson's final coordinates, using the scattering factors he quoted. The agreement between Stephenson's *F*_{obs} and *F*_{calc} values, as listed in his Table 2, corresponds to *R* = 0·217. Our *F*_{calc} values differed considerably [by a maximum of 67 electrons for *F*(140)] from his, and corresponded to *R* = 0·196. Our values were confirmed by an independent method of calculation. His coordinates were thereupon refined by the method of least squares, using Busing, Martin & Levy's (1962) *ORFLS* program. Each structure factor was assigned a weight given by $w(F_{\text{obs}}) = 1/(\sigma F_{\text{obs}})^2$, where

$$\sigma F_{\text{obs}} = 0.15 |F_{\text{obs}}| \text{ for } |F_{\text{obs}}| \geq 5 |F_{\text{min}}|,$$

$$\sigma F_{\text{obs}} = 0.75 |F_{\text{min}}| \text{ for } 4 |F_{\text{min}}| \leq |F_{\text{obs}}| < 5 |F_{\text{min}}|,$$

and

$$\sigma F_{\text{obs}} = 0.15\{9|F_{\text{min}}| - |F_{\text{obs}}|\} \text{ for } |F_{\text{obs}}| < 4|F_{\text{min}}|,$$

and F_{min} was the minimum observed structure factor. The z coordinate and temperature factor for most atoms changed considerably. The four independent metal atom isotropic temperature factors ranged from -0.02 to -0.95 \AA^2 , and those of the oxygen atoms had values between -1.0 and $+2.2 \text{ \AA}^2$. The agreement indices became $R=0.154$ and $wR=0.218$.

Stephenson's structure factors were now corrected for absorption, using Cu $K\alpha$ mass absorption coefficients and assuming that the needle-like crystal shape could be approximated by a cylinder of radius 0.025 mm (the average cross-section diameter was quoted as 0.07 mm). The radius used was based on the criterion that the metal atom isotropic temperature factors should have values close to 1 \AA^2 ; a radius of 0.035 mm corresponds to B values for these atoms ranging from 1.3 to 2.3 \AA^2 .

A ferroelectric crystal in the unpoled state consists of domains ordered both parallel and antiparallel to the ferroelectric axis. Stephenson's crystal was not, apparently, poled and his observation that the intensities of equivalent reflections with unlike signs of l appeared the same supports an assumption of an approximately equal distribution of domains. Accordingly, corrections were made for both the real and imaginary dispersion components by Patterson's (1963) method, using Bernstein's (1964) program.

There was no evidence of extinction, and it was hence not necessary to apply an extinction correction.

Least-squares refinement with the corrected structure factors resulted in physically realistic isotropic temperature factors for the metal atoms (Table 1). It was confirmed that Ti and Nb were randomly distributed over the $2(b)$ and $8(d)$ sites. The temperature factor of Ba in $4(c)$ was significantly higher than in $2(a)$: the possibility of nonstoichiometric composition was hence investigated by allowing the occupation factor of the $4(c)$ site to vary. The resulting occupancy factor was not significantly different from unity. A final series of least-squares calculations in which all shifts became less than one-tenth of a standard deviation, with anisotropic temperature factors for all atoms, gave the coordinates and standard deviations of Table 1. The corresponding agreement indices are $R=0.143$, $wR=0.178$ and $S=1.137$ (the standard deviation of an observation of unit weight).

An examination of the equal domain distribution assumption was made by comparison with models having a single sense of l , corresponding to a single domain crystal. In the ensuing calculations, the dispersion corrections were made to the F_{calc} magnitudes within the least-squares program. Refinement with l positive resulted in $wR=0.183$; with l negative in $wR=0.188$. The sets of atomic coordinates thus obtained differed from those given in Table 1 by a maximum of 3.2 standard deviations. The significantly lower value of wR corresponding to the equal domain model, together with the large oscillations in parameter shifts obtained after many refinement cycles (comparable in magnitude to one standard deviation), strongly supports the validity of the equal domain assumption.

The positional coordinates in Table 1 differ from those of Stephenson by less than three standard deviations: however, both the magnitudes of the temperature factors and the errors in the coordinates are now more realistic. In the xy plane, the standard deviations in atomic coordinates are generally less than 0.06 \AA , but in the z direction are as great as 0.16 \AA . The atomic positions are remarkably similar to those in $\text{Ba}_{0.27}\text{Sr}_{0.73}\text{Nb}_2\text{O}_{5.8}$, except that there appears to be no major disorder associated with any of the oxygen atoms. In barium strontium niobate, distribution of five barium and strontium atoms over six sites, together with composite Ba/Sr atoms at the $4(c)$ site, leads to considerable oxygen atom disorder.

Our relationship with Curie temperature requires well-determined atomic displacements along the polar direction. In this study these displacements are unfortunately of low accuracy. The displacement magnitude is calculated with respect to the mean position of the oxygen atom framework, for which the origin is $z=0.04 \pm 0.10 \text{ \AA}$. The space group transformation at the Curie temperature is assumed to be the same as for $\text{Ba}_{0.27}\text{Sr}_{0.73}\text{Nb}_2\text{O}_{5.8}$, *i.e.* from $P4bm$ to $P4b2$. The homopolar Nb/Ti composite atom in $2(b)$ is then displaced by $0.04 + 0.14 \text{ \AA} = 0.18 \pm 0.10 \text{ \AA}$, at room temperature, from the position with point symmetry 222 in the antipolar space group $P4b2$. Above the Curie temperature, the other Nb/Ti atom in $8(d)$ becomes distributed above and below the mean oxygen plane formed by $O(2)$, $O(4)$ and $O(5)$.

The Curie temperature of $\text{Ba}_6\text{Ti}_2\text{Nb}_8\text{O}_{30}$ has been determined by Brown (1967) as $505^\circ \pm 15^\circ \text{K}$. The atomic displacement predicted by the relationship

Table 1. Atomic position coordinates and temperature coefficients for $\text{Ba}_6\text{Ti}_2\text{Nb}_8\text{O}_{30}$ *

Point position	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B^\dagger
Ba $2(a)$	0	0	0	9 ± 2	9 ± 2	335 ± 55	0	0	0	$0.80 \pm 13 \text{ \AA}^2$
Ba $4(c)$	0.1720 ± 2	0.6720 ± 2	0.991 ± 4	30 ± 2	30 ± 2	377 ± 51	-14 ± 2	15 ± 21	15 ± 21	1.76 ± 15
Nb/Ti $2(b)$	0	$\frac{1}{2}$	0.465 ± 5	14 ± 3	14 ± 3	390 ± 130	0	0	0	1.09 ± 19
Nb/Ti $8(d)$	0.0748 ± 3	0.2155 ± 3	0.470 ± 4	12 ± 2	15 ± 3	193 ± 52	-3 ± 2	26 ± 12	-20 ± 13	0.80 ± 12
O(1) $2(b)$	0	$\frac{1}{2}$	0.020 ± 39	3 ± 3	3 ± 3	10 ± 67	0	0	0	1.61 ± 152
O(2)‡ $4(c)$	0.277 ± 3	0.777 ± 3	0.516 ± 31	4 ± 2	4 ± 2	39 ± 60	0	0	0	4.53 ± 186
O(3)‡ $8(d)$	0.063 ± 7	0.224 ± 4	-0.001 ± 31	15 ± 7	3 ± 3	47 ± 62	0	0	0	4.06 ± 130
O(4)§ $8(d)$	0.346 ± 2	0.012 ± 4	0.516 ± 18	-1 ± 2	9 ± 4	35 ± 37	-2 ± 2	-1 ± 8	25 ± 11	1.97 ± 71
O(5)§ $8(d)$	0.144 ± 3	0.071 ± 2	0.513 ± 16	2 ± 2	1 ± 2	56 ± 44	3 ± 1	26 ± 9	1 ± 9	0.64 ± 53

* Values of β in the expression $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$ are $\times 10^4$ for metal atoms and $\times 10^3$ for oxygen atoms. Error values without decimal point correspond to the least significant digit in the function.

† Values of B obtained from a least-squares refinement to completion with all atoms vibrating isotropically.

‡ The O(2) and O(3) cross terms (β_{ij}) were maintained at a fixed value of zero; in previous refinements, these terms oscillated about zero.

§ The temperature coefficients of O(4) and O(5) are slightly nonpositive definite: modification of β_{ij} by less than $2\sigma\beta_{ij}$ restores the condition to positive definite.

$$T_c = (2.00 \pm 0.09) \times 10^4 (\Delta z)^2 \text{K}$$

of Abrahams, Kurtz & Jamieson using this value of T_c is 0.16 Å, in accord with the value derived above.

It is a pleasure to thank J. L. Bernstein for applying his dispersion correction program to Stephenson's experimental data.

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Notes and News

Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. The notes (in duplicate) should be sent to the General Secretary of the International Union of Crystallography (G. Boom, Laboratorium voor Technische Natuurkunde der Rijksuniversiteit, Westersingel 34, Groningen, The Netherlands). Publication of an item in a particular issue cannot be guaranteed unless the draft is received 8 weeks before the date of publication.

Vladimir Vand 1911–1968

After an illness of one year and a half, Professor Vladimir Vand died in Bellefonte, Pennsylvania on 4 April 1968. Professor Vand was a crystallography professor at the Pennsylvania State University, U.S.A.

Congress on the Integration of Science Teaching 11–19 September 1968, Varna, Bulgaria

A Congress on the Integration of Science Teaching will be held on 11–19 September 1968 in Varna, Bulgaria. It is

organized by the Inter-Union Commission on Science Teaching (IUCST) of the International Council of Scientific Unions. The subject of the Congress will be the study of the feasibility of organizing scientific education at the secondary level (ages about 11 to 19, and parallel studies undertaken at a later age) into a coherent entity, avoiding artificial barriers and overlapping and providing improved training in scientific methods, while at the same time demonstrating the recent development of science and its role in human progress.

Those interested should contact the Congress Secretariat as soon as possible. The address is: Prof. P. Fleury, Secretary IUCST, 3, Boulevard Pasteur, PARIS 15e, France.

Book Review

Works intended for notice in this column should be sent direct to the Book-Review Editor (M.M. Woolfson, Physics Department, University of York, Heslington, York, England). As far as practicable books will be reviewed in a country different from that of publication.

Selected topics in structure chemistry. A collection of papers dedicated to Professor Odd Hassel on his 70th birthday, 17 May 1967. Edited by PER ANDERSEN, OTTO BASTIANSEN and SVEN FURBERG. Pp. 307. Oslo: Universitetsforlaget, 1967. Price N. kr. 68.00.

This *Festschrift* is dedicated to Professor Hassel, the eminent Norwegian chemist, by his scientific children and grandchildren. It contains fifteen original papers on various aspects of structural chemistry and a complete bibliography of 220 papers by Hassel, which commences with the publication of his graduation thesis of 1922.

P. Andersen and O. Bastiansen introduce the volume with a dedication *Odd Hassel*. E. W. Lund and C. Rømming in the chapter *Forty five years of achievement* vividly present the scientific career of Professor Hassel, his great contributions to many fields of chemistry over more than 45 years

and the influence he exerted on a large group of younger chemists in Norway.

The research papers reflect Professor Hassel's major interests in structural chemistry: Gas electron diffraction (six papers on the theory and on structural problems) and X-ray structure determination (five papers, again treating both experimental and theoretical problems). The last group of four papers is concerned with various methods and chemical problems.

Even though the publications in this volume are collected for a special occasion, their high level make the book stimulating reading for chemists, crystallographers and, of course, for every friend of Odd Hassel.

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