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Neutron-diffraction study of $Bi_4Si_3O_{12}$

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Auszug

Die Lage der Sauerstoff- und Siliciumatome im Mineral Eulytin wurde mittels Neutronbeugung bestimmt. Die verfeinerte Struktur entspricht einem der zwei von Menzer vorgeschlagenen Modelle, in welchem irregularkoordinierte Wismutionen sich an isolierte SiO_4 Tetraeder binden.

Abstract

Oxygen and silicon positions in the mineral eulytite have been determined by neutron-diffraction analysis. The refined structure corresponds to one of the two models proposed by Menzer, in which irregularly coordinated bismuth ions link discrete SiO_4 tetrahedra.

Eulytite, $Bi_4Si_3O_{12}$, is a rare mineral found in association with elemental bismuth and quartz. A number of lead and bismuth compounds[1] are isotypic with the mineral. Two possible structures for bismuth orthosilicate were proposed by Menzer[2] in 1931. The cubic unit cell ($a = 10.300$ Å) contains four molecules in the following positions of space group $I\,\bar{4}3d$: Bi in 16*c* *uuu*, Si in 12*a* $\frac{3}{8}0\frac{1}{4}$, and O in 48*e* *xyz*. From x-ray intensities, the bismuth coordinate was measured as $u = 0.083 \pm .005$. Silicon and oxygen do not contribute appreciably to the x-ray intensities and their coordinates were inferred from crystallochemical arguments. The oxygen coordinates for the two structures deduced by Menzer are

Model 1: $x = -.035 \pm .015$, $y = .125 \pm .005$, $z = .284 \pm .005$

Model 2: $x = \quad .055 \pm .03$, $\quad y = .11 \quad \pm .02$, $\quad z = .284 \pm .005$.

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[1] A. Durif, Sur quelques composés isomorphes de l'eulytine. Compt. Rend. 244 (1957) 2815—2817.

[2] G. Menzer, Die Kristallstruktur von Eulytin. Z. Kristallogr. 78 (1931) 136—163.

Since the neutron-scattering lengths of Si (0.42) and O (0.577) are comparable to that of Bi (0.864), their positions can be obtained from neutron-diffraction measurements. Figure 1 shows the room-temperature powder pattern of eulytite taken with unpolarized monochromatic (1.2 Å) neutrons. The data were collected at angular intervals of $3'$ in 2θ using a cylindrical aluminum specimen holder. Polycrystalline $Bi_4Si_3O_{12}$ was synthesized from finely divided silica and bismuth sesquioxide, reacted in air at 800 °C.

Table 1. *Comparison of observed intensities with values calculated from the two* MENZER *models (1 and 2) and from the refined coordinates (3)*

$h\ k\ l$	d	$I_c(1)$	$I_c(2)$	$I_c(3)$	I_o
2 1 1	4.21 Å	15	159	190	187
2 2 0	3.64	81	57	45	47
3 1 0	3.26	260	398	366	360
3 2 1	2.75	365	143	190	190
4 0 0	2.58	4	22	50	51
4 2 0	2.30	210	81	79	80
3 3 2	2.20	77	110	230	241
4 2 2	2.10	223	189	230	256
5 1 0	2.02	20	297	315	310
4 3 1	2.02	589	67	19	
5 2 1	1.88	5	91	67	65
4 4 0	1.82	24	11	6	5
5 3 0	1.77	40	243	272	272
6 1 1	1.67	200	181	28	281
5 3 2	1.67	69	169	245	
6 2 0	1.63	117	61	35	35
5 4 1	1.59	69	240	145	148
6 3 1	1.52	90	29	75	73
4 4 4	1.49	119	103	22	20
7 1 0	1.46	32	9	8	80
5 4 3	1.46	92	44	83	

In Table 1, the observed integrated intensities are compared with three calculated values, two based on the structures proposed by MENZER, and the third on a set of refined coordinates:

Model 3: $u = .0857 \pm .002$, $x = .0607 \pm .002$, $y = .1335 \pm .004$, $z = .2875 \pm .002$. The latter were obtained by minimizing the disagreement index R; models 1, 2 and 3 give R factors of .67, .30 and .04 respectively. Multiplicity and Lorentz factors were included in the calculation, and absorption and thermal vibration corrections proved negligible. Within their respective limits of uncertainty, models 2 and

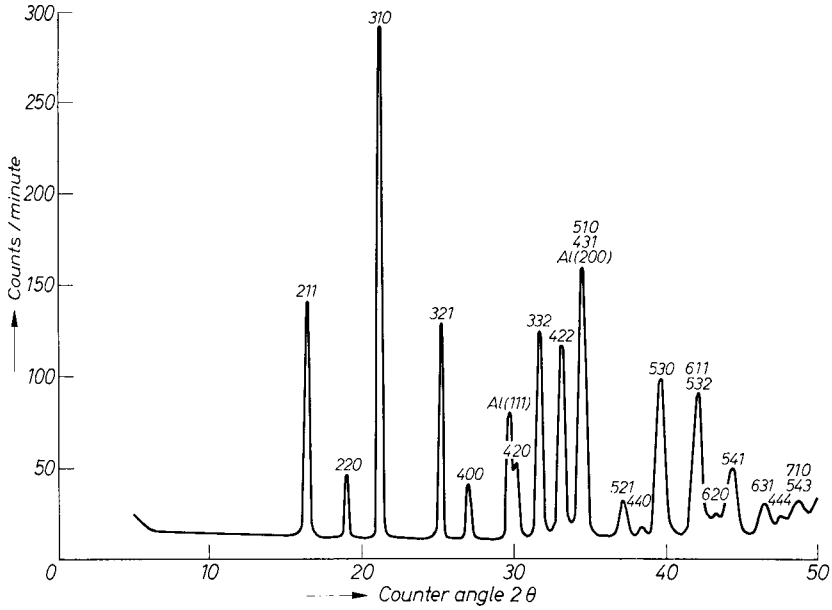

Fig. 1. Neutron-diffraction pattern of polycrystalline $Bi_4Si_3O_{12}$

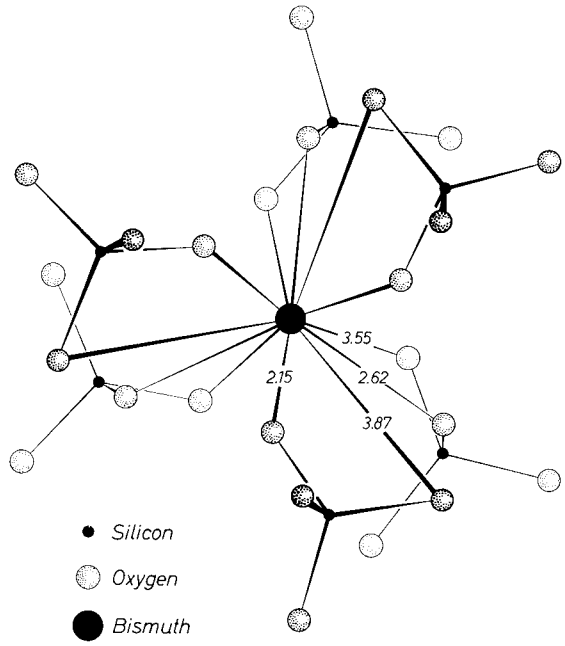

Fig. 2. Crystal structure of eulytite viewed along [111]. Bi, Si and O are represented by large and small solid circles, and by open circles, respectively

3 agree. It is unfortunate that model 1, the least-correct structure, is the only one quoted in reference works[3].

The refined coordinates give an Si—O distance of 1.63 Å, in agreement with the values found in other orthosilicates[4]. Each bismuth ion is coordinated to a distorted octahedron of oxygen atoms: three close neighbors at 2.15 Å and three more at 2.62 Å. The next-nearest oxygen atoms are at 3.55 Å. Every oxygen atom is surrounded by eight other oxygen atoms, with O—O distances ranging between 2.62 and 3.15 Å. The structure is illustrated in Fig. 2.

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[3] R. W. G. WYCKOFF, Crystal structures. (Interscience Inc., New York, 1953.) Vol. III, Chapter XII.

[4] J. V. SMITH and S. W. BAILEY, Second review of Al—O and Si—O tetrahedral distances. Acta Crystallogr. **16** (1963) 801—811.