X-ray crystallographic data on the compound $Bi_{2-x}La_xWO_6$

Bi_2WO_6 is one of the family of bismuth oxide compounds with layered structures which are known as ferroelectrics which are widely used as solid state catalysts. Bi_2WO_6 is composed of a Bi_2O_2-layer and a WO_4-layer alternately stacked in the c-axis direction [1, 2]. The Bi atom is coordinated to four oxygen atoms arranged in a flat tetragonal pyramid in a Bi_2O_2-layer, whilst W is octahedrally coordinated to oxygen in a WO_4-layer.

Recently, a new compound of $Bi_{2-x}La_xWO_6$ ($0.4 \leqslant x \leqslant 1.0$) has been successfully synthesized from mixtures of Bi_2O_3, La_2O_3 and WO_3 powder [3]. This new compound is also considered as one of the layered bismuth oxide family. This layer structure may be composed of a $Bi_{2-x}La_xO_2$-layer and a WO_4-layer stacked alternately in such a way that Bi_2WO_6 is formed. This new compound could be formed by partial substitution of a La atom for a Bi atom in the Bi_2WO_6 structure.

The following is an attempt to interpret the crystallographic data obtained from the X-ray single crystal method and the powder diffraction method for a new compound, $Bi_{1.4}La_{0.6}WO_6$. The X-ray powder diffraction lines in the 2θ-range from 10° to 70° are given with their indices, their planar spacings, their 2θ-values and their relative intensity distribution. The space group of this crystal has been identified as $P2/a$ using single crystal diffraction techniques. The precise unit cell dimensions, obtained by a least-square computer program, are also given as $a = 16.704$ Å, $b = 7.683$ Å, $c = 8.280$ Å and $\beta = 102.18°$. The X-ray powder data for $Bi_{1.4}La_{0.6}WO_6$ are compared with those of the $Bi_{1.6}La_{0.4}WO_6$ and $Bi_{1.0}La_{1.0}WO_6$ compounds.

Bi_2O_3, La_2O_3 and WO_3 powders were mixed according to the composition of $Bi_{2-x}La_xWO_6$ ($0.4 \leqslant x \leqslant 1.0$) with ethyl alcohol and ground into powder. These mixtures were dried, put in a crucible and heated at 1000° C for 20 h in an electric furnace. The specimens thus obtained were crushed and powdered in order to determine their phase relations and structural changes by X-ray powder diffraction method.

On the other hand, the molten specimen of $Bi_{1.4}La_{0.6}WO_6$ composition was slowly cooled down from 1170° C to room temperature at an annealing rate of 5° C h^{-1} in a platinum crucible. In the annealing process, a lot of single crystals grew from the melt. The single crystals appeared transparent and light yellow in colour. The average size of the crystals was 1.0 mm diameter and 0.2 mm in depth.

A single crystal of suitable size was chosen for X-ray crystal determination. The unit cell dimensions and space group were identified with a Weissenberg camera using CuK_α-radiation. As a result, the approximate unit cell constants were $a = 16.4$ Å, $b = 7.68$ Å, $c = 8.28$ Å and $\beta = 102.25°$ in a monoclinic system. The $h0l$ reciprocal plane taken by precession camera with 40 kV × 30 mA Mo-radiation is shown in Fig. 1. The conditions limiting possible reflections are as follows

$$h0l : h = 2n$$

$$(h00 : h = 2n)$$

On the basis of systematic extinctions [4], the possible space group of this crystal is identified as $P2/a$.

X-ray powder diffraction profiles of $Bi_{1.4}La_{0.6}WO_6$ were taken by a Rigaku Geigerflex using Cu K_α-radiation with a Ni-filter and a scintillation counter detector scanning at 2θ-1° per minute. The X-ray powder reflections were collected in the range of 2θ from 10° to 70°; they were successfully indexed by taking account of

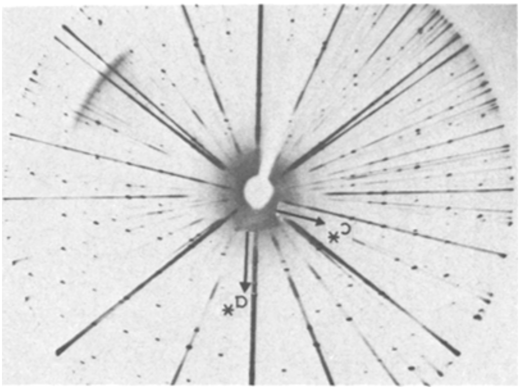

Figure 1 A precession photograph of $h0l$ reciprocal plane of $Bi_{1.4}La_{0.6}WO_6$ crystal using Mo-radiation. Twinning of this crystal caused a mirror symmetry perpendicular to a* direction.

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TABLE I The refined unit cell constant and cell volumes of Bi$_{2-x}$La$_x$WO$_6$ (x = 0.4, 0.6 and 1.0)

x	0.4	0.6	1.0
a	16.354(0.004)Å	16.407(0.003)Å	16.482(0.003)Å
b	7.674(0.002)Å	7.683(0.001)Å	7.716(0.001)Å
c	8.258(0.001)Å	8.280(0.001)Å	8.313(0.001)Å
β	102.08 (0.02)°	102.18 (0.01)°	102.23 (0.02)°
V	1013.4 (0.3) Å^3	1020.2 (0.2) Å^3	1033.1 (0.2) Å^3

TABLE II Powder X-ray data on Bi$_{1.6}$La$_{0.4}$WO$_6$. The indices, calculated planer spacings, calculated 2θ-values, observed 2θ-values and relative intensity distribution are indicated by hkl, d_{calc}, $2\theta_{\text{calc}}$, $2\theta_{\text{obs}}$ and I/I_0, respectively.

$h\,k\,l$	d_{calc} (Å)	$2\theta_{\text{calc}}$ (degrees)	$2\theta_{\text{obs}}$ (degrees)	I/I_0 (%)
0 0 1	8.075	10.847	10.98	8
2 0 0	7.996	11.056	11.07	8
$\bar{2}\,0\,1$	6.390	13.847	13.85	10
4 0 0	3.998	22.217	22.23	8
$\bar{4}\,0\,1$	3.924	22.638	22.65	5
2 0 2, 1 2 1	3.334	26.714	26.74	87
$4\,0\,\bar{2}$	3.195	27.901	27.93	71
3 2 0	3.114	28.641	28.66	100
$1\,2\,\bar{2}$, $\bar{5}\,0\,2$	2.809	31.824	31.85	81
0 0 3	2.692	33.256	33.29	10
6 0 0	2.665	33.596	33.63	50
4 0 2, $\bar{1}\,1\,3$	2.583	34.696	34.69	2
$\bar{4}\,0\,3$	2.487	36.083	36.10	5
$\bar{6}\,0\,2$	2.475	36.259	36.28	5
$\bar{5}\,2\,1$	2.463	36.443		
$\bar{5}\,2\,0$, $\bar{4}\,2\,2$	2.456	36.544	36.55	4
4 1 2	2.448	36.675		
$3\,2\,\bar{3}$, $\bar{1}\,3\,2$	2.172	41.539	41.54	4
$6\,0\,\bar{3}$, 1 2 3, 3 1 3	2.130	42.400	42.41	4
2 0 4, $\bar{1}\,0\,4$	2.063	43.857	43.85	13
0 0 4	2.019	44.859	44.85	3
5 2 2, $\bar{7}\,0\,3$	1.963	46.201	46.20	19
0 4 0, $\bar{4}\,1\,4$	1.918	47.343	47.33	26
$8\,0\,\bar{3}$, $\bar{3}\,2\,4$, 2 4 1	1.795	50.830	50.81	3
1 2 4, $\bar{1}\,4\,2$	1.740	52.539	52.53	10
4 4 1, $\bar{7}\,3\,1$	1.724	53.090	53.11	6
$5\,2\,\bar{4}$, $\bar{7}\,0\,4$	1,700	53.900	53.89	9
2 4 2, $\bar{7}\,1\,4$, 4 4 1	1.663	55.190	55.19	18
$4\,4\,\bar{2}$, $\bar{5}\,4\,0$, $\bar{3}\,0\,5$	1.645	55.850	55.84	10
$\bar{9}\,2\,2$, $\bar{1}0{\cdot}0\,2$, $\bar{3}\,1\,5$	1.606	57.314	57.30	13
6 4 0, $\bar{7}\,2\,4$	1.557	59.300	59.33	6
2 0 5, 8 2 2	1.522	60.790	60.78	4
10·0 1, 5 3 3, $\bar{1}\,2\,5$	1.510	61.359	61.34	4
$2\,4\,\bar{4}$, $\bar{1}0{\cdot}0\,4$, 10·2 1, $\bar{1}\,4\,4$	1.405	66.504	66.50	5
5 3 4, $6\,5\,\bar{1}$	1.335	70.466	70.62	2

TABLE III Powder X-ray data on $Bi_{1.4}La_{0.6}WO_6$. The indices, calculated planer spacings, calculated 2θ-values, observed 2θ-values and relative intensity distribution are indicated by hkl, d_{calc}, $2\theta_{calc}$, $2\theta_{obs}$ and I/I_o, respectively.

hkl	d_{calc} (Å)	$2\theta_{calc}$ (degrees)	$2\theta_{obs}$ (degrees)	I/I_o (%)
001	8.093	10.922	10.97	8
200	8.019	11.024		
201	6.413	13.798	13.80	10
400	4.010	22.151	22.15	8
$\bar{4}01$	3.938	22.557	22.55	5
202, 121	3.340	26.663	26.68	87
$40\bar{2}$	3.206	27.800	27.82	71
320	3.120	28.558	28.60	100
$12\bar{2}, \bar{5}02$	2.815	31.704	31.78	81
003	2.698	33.179	33.21	10
600	2.673	33.495	33.50	50
$402, \bar{1}13$	2.588	34.626	34.62	2
$\bar{4}03$	2.495	35.960	35.96	5
$\bar{6}02$	2.484	36.124	36.14	5
$\bar{5}21$	2.470	36.348	36.45	4
$\bar{5}20, \bar{4}22$	2.462	36.460		
412	2.453	36.603		
$32\bar{3}, \bar{1}32$	2.178	41.431	41.42	4
$60\bar{3}, 123, 313$	2.138	42.243	42.25	4
$204, \bar{1}04$	2.068	43.734	43.73	13
004	2.023	44.752	44.75	3
$522, \bar{7}03$	1.967	46.112	46.11	19
$040, \bar{4}14$	1.921	47.282	47.28	26
$80\bar{3}, \bar{3}24, 241$	1.801	50.634	50.63	3
$124, \bar{1}42$	1.744	52.431	52.42	10
$441, \bar{7}31$	1.726	52.994	52.98	5
$52\bar{4}, \bar{7}04$	1.704	53.733	53.73	9
$242, \bar{7}14, 441$	1.665	55.106	55.13	18
$44\bar{2}, \bar{5}40, \bar{3}05$	1.648	55.738	55.73	10
$\bar{9}22, \overline{10}\cdot 2, \bar{3}15$	1.611	57.120	57.10	13
$640, \bar{7}24$	1.560	59.181	59.20	6
205, 822	1.525	60.652	60.65	4
$10\cdot 01, 533, \bar{1}25$	1.514	61.183	61.17	4
$24\bar{4}, \overline{10}\cdot 04, 10\cdot 21, \bar{1}44$	1.407	66.363	66.35	5
$534, 65\bar{1}$	1.338	70.317	70.33	2

the primary unit cell dimensions obtained from the X-ray single crystal method.

For accurate determination of the unit cell dimensions, the X-ray powder diffraction profiles of $Bi_{2-x}La_xWO_6$ ($x = 0.4$, 0.6 and 1.0) were taken with a scanning rate of 2θ-1° per 4 min. Silicon powder was mixed in the $Bi_{2-x}La_xWO_6$ samples as a standard. The 22 reflections thus obtained, which showed clear intensity peaks and were not superimposed on other reflections, were selected for the least-square refinment calculation. The precise unit cell dimensions were calculated by the least-square computer program of Appleman and Evans [5]. The refined unit cell dimensions of each sample ($x = 0.4$, 0.6 and 1.0) are given in Table I. The values in parentheses indicate the standard deviations. On the other hand, the powder X-ray diffraction profiles of $Bi_{1.6}La_{0.4}WO_6$ and $Bi_{1.0}La_{1.0}WO_6$ in the range of 2θ from 10° to 70° were also successfully indexed. Their indices, the calculated planar spacings, the calculated and observed 2θ-values, and the relative intensity distributions I/I_o of the specimens ($x = 0.4$, 0.6 and 1.0) are given in Tables II, III and IV, respectively.

It has been found that a continuous solid solution of $Bi_{2-x}La_xWO_6$ exists in the range of

TABLE IV Powder X-ray data on $Bi_{1.0}La_{1.0}WO_6$. The indices, calculated planer spacings, calculated 2θ-values, observed 2θ-values and relative intensity distribution are indicated by hkl, d_{calc}, $2\theta_{calc}$, $2\theta_{obs}$ and I/I_0, respectively.

$h\,k\,l$	d_{calc} (Å)	$2\theta_{calc}$ (degrees)	$2\theta_{obs}$ (degrees)	I/I_0 (%)
0 0 1	8.124	10.881	10.83	8
2 0 0	8.058	10.976	10.89	8
$\bar{2}$ 0 1	6.443	13.733	13.74	10
4 0 0	4.027	22.055	22.05	8
$\bar{4}$ 0 1	3.957	22.449	22.45	5
2 0 2, 1 2 1	3.353	26.567	26.58	87
4 0 $\bar{2}$	3.221	27.667	27.69	71
3 2 0	3.133	28.465	28.47	100
1 2 $\bar{2}$, $\bar{5}$ 0 2	2.826	31.628	31.65	81
0 0 3	2.708	33.051	33.08	10
6 0 0	2.684	33.347	33.34	50
4 0 2, $\bar{1}$ 1 3	2.598	34.496	34.48	3
$\bar{4}$ 0 3	2.507	35.793	35.83	5
$\bar{6}$ 0 2	2.496	54.947		
$\bar{5}$ 2 1	2.481	36.176	36.29	4
$\bar{5}$ 2 0, $\bar{4}$ 2 2	2.473	36.299		
4 1 2	2.462	36.464		
3 2 $\bar{3}$, $\bar{1}$ 3 2	2.187	41.246	41.24	4
6 0 $\bar{3}$, 1 2 3, 3 1 3	2.148	42.036	42.03	4
2 0 4, $\bar{1}$ 0 4	2.076	43.549	43.55	13
0 0 4	2.031	44.575	44.57	3
5 2 2, $\bar{7}$ 0 3	1.974	45.926	45.90	19
0 4 0, $\bar{4}$ 1 4	1.929	47.072	47.07	26
8 0 $\bar{3}$, $\bar{3}$ 2 4, 2 4 1	1.810	50.377	50.36	3
1 2 4, $\bar{1}$ 4 2	1.750	52.218	52.21	10
4 4 1, $\bar{7}$ 3 1	1.734	52.749	52.76	5
5 2 4, $\bar{7}$ 0 4	1.712	53.477	53.48	9
2 4 2, $\bar{7}$ 1 4, 4 4 1	1.672	54.865	54.86	18
4 4 $\bar{2}$, $\bar{5}$ 4 0, $\bar{3}$ 0 5	1.655	55.478	55.45	10
$\bar{9}$ 2 2, $\bar{1}\bar{0}$·0 2, $\bar{3}$ 1 5	1.619	56.832	56.72	13
6 4 0, $\bar{7}$ 2 4	1.566	58.906	58.93	6
2 0 5, 8 2 2	1.531	60.410	60.41	4
10·0 1, 5 3 3, $\bar{1}$ 2 5	1.520	60.906	60.92	4
2 4 $\bar{4}$, $\bar{1}\bar{0}$·0 4, 1 0·2 1, $\bar{1}$ 4 4	1.413	66.054	66.01	5
5 3 4, 6 5 $\bar{1}$	1.343	69.993	69.96	2

$0.4 \leqslant x \leqslant 1.0$ [3]. The crystal structure does not change over this range of x-values, but the chemical composition and the crystal lattice constants very continuously with the change in x-value. The unit cell volume becomes larger as x increases. Among the compounds of $0.4 \leqslant x \leqslant 1.0$, the minimum cell volume is given by $a = 16.35$ Å, $b = 7.674$ Å, $c = 8.258$ Å, $\beta = 102.08°$ and therefore $V = 1013.4$ Å^3 when x is 0.4; the maximum is given by $a = 16.482$ Å, $b = 7.716$ Å, $c = 8.313$ Å, $\beta = 102.23°$ and $V = 1033.1$ Å^3 when $x = 1.0$. As is evident from Tables II, III and IV, the change in x-value causes a positional shift of the powder diffraction peaks, namely, the shift of the 2θ-diffraction angle. Therefore, if the precise unit cell dimensions of the $Bi_{2-x}La_xWO_6$ compound in the range of $0.4 \leqslant x \leqslant 1.0$ are known, the unknown x-value, which is peculiar to the lattice constant, can easily be evaluated from the correlation between the unit cell dimensions and the chemical composition [3]. The unit cell constants of the single crystal used for the determination of the space group were $a = 16.4$ Å, $b = 7.68$ Å, $c = 8.28$ Å and $\beta = 102.25°$. The chemical composition of this single crystal may consequently be judged to be $Bi_{1.4}La_{0.6}WO_6$.

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A note on the dissolution mechanism of MgO crystals in acids

According to the recent treatment of the dissolution of MgO crystals [1], the rates of surface dissolution, v_s, and selected etching, v_d, are given by

$$v_s = 1.1 \times 10^7 \alpha^{-0.9} c^{0.2} \mu^{-0.5} r_m^{-0.25} \exp\left[-E_s/kT\right] \quad (1)$$

and

$$v_d = 6.0 \times 10^8 \alpha^{-0.9} c^{0.2} \mu^{-0.5} r_m^{-0.25} \exp\left[-E_d/kT\right], \quad (2)$$

where μ is the reduced mass of an activated complex, E_s and E_d are the activation energy of dissolution at a surface and the activation energy of dissolution at a dislocation site, respectively, α is the degree of dissociation of an acid, c its concentration and r_m the ratio of the mass of an anion to that of an H^+ ion. It was, however, noted that in various acids containing light and heavy anions, $\mu^{0.5}$ and $r_m^{0.25}$ have values ranging from 8.7 to 15.2 and from 2.45 to 6.63, respectively. When explaining the concentration dependence of dissolution rates, it was assumed [1] that $\mu^{0.5} = 10$ and $r_m^{0.25} = 3$. In this article the hydration of acid

TABLE I Estimated radii of hydrated ions, number of water molecules and $r_{mh}^{0.25}$

Ion	Crystallographic radius R_c (Å)	Hydrated ion radius R (Å)	Number of associated water molecules n_h	Mass of hydrated ion m_h	$r_{mh}^{0.25}$
F^-	1.36	3.3	4.7	104	0.96
Cl^-	1.81	2.6	1.7	66	0.85
Br^-	1.95	2.6	1.3	103	0.95
I^-	2.16	2.6	1.0	145	1.03
NO_3^-	(2.5)*	2.7	0.7	74	0.86
HSO_4^-	(2.5)	2.6	0.3	103	0.96
HCO_2^-	(2.0)	3.3	4.0	121	1.00
$CH_3CO_2^-$	(2.5)	3.6	4.3	137	1.01
SO_4^{2-}	(2.5)	3.6	4.3	174	1.08
$C_2H_5CO_2^-$	(2.7)	3.8	4.0	145	1.03
$C_3H_7CO_2^-$	(3.0)	3.8	4.0	157	1.05
$(CO_2)_2^{2-}$	(2.5)	3.8	5.0	148	1.03
$H(CO_2)_2^-$	2.0	2.6	1.3	119	0.99
H^+	–	3.7	7.0	127	1.00

*Values in parenthesis are uncertain.

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