

The Crystal Structure of  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>

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The crystal structure of monoclinic bismuth trioxide, space group  $P2_1/c$ , has been redetermined from single-crystal X-ray data. The unit cell contains four formula units and has the dimensions  $a=5.848$  Å,  $b=8.166$  Å,  $c=7.510$  Å,  $\beta=113.0^\circ$ .

The structure is built up of equidistant, 1.35 Å, layers parallel to the  $yz$  plane. Every second layer consists of bismuth atoms, the others of oxygen atoms. The coordination around bismuth is five- or six-fold, and both arrangements can be described starting from distorted octahedra. The distances Bi-O in the coordination polyhedra range from 2.08 to 2.80 Å. The polyhedra are linked together sharing corners and edges, thus forming a three-dimensional network. Tunnels run, however, through the structure parallel to the  $z$ -axis.

As part of an investigation on the polymorphy of bismuth trioxide, Sillén<sup>1</sup> in 1939 determined the crystal structure of  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> from  $hk0$ ,  $hk1$ ,  $0kl$ , and  $lkl$  reflexions. He determined the metal atom positions from Patterson analyses and gave possible oxygen positions from space considerations. Though these positions seemed reasonable it was decided to carry out a reinvestigation of the structure, in order to obtain more exact information on the structure, especially on the positions of the oxygen atoms and thereby on the coordination around the bismuth atoms. At this stage it is only fair to state that this investigation has confirmed the bismuth atom and two of the oxygen atom positions given in Table 1, while the third oxygen has moved considerably, cf. Figs. 1a and 1b.

## PREPARATION

Single crystals of  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> were prepared by treating commercial bismuth trioxide with a 40 % solution of KOH in a platinum crucible placed in an autoclave at 250°C for about one week. The crystals were irregularly shaped and light yellow. The powder pattern from the crystals prepared in this way was identical with that of commercial Bi<sub>2</sub>O<sub>3</sub>.

## SINGLE CRYSTAL WORK AND DATA REDUCTION

The linear absorption coefficient  $\mu$  for X-rays (MoK $\alpha$  radiation) of Bi<sub>2</sub>O<sub>3</sub> was calculated to be 1008 cm<sup>-1</sup>.<sup>2</sup> Due to this heavy absorption, and in order to facilitate the necessary calculations of the absorption corrections, it was advantageous to grind the crystals to spheres, which was done in an apparatus described by Buerger.<sup>3</sup> A well-formed sphere of radius  $r=0.00835$  cm, thus giving a  $\mu r$  value of 8.39, was picked out for the single crystal work. The 10 layer lines  $h0l-h9l$  were recorded by means of an integrating Weissenberg goniometer using Zr-filtered MoK $\alpha$  radiation. The multiple film technique (3 films) with thin (0.005 cm) steel foils between the films was used. The relative intensities of the reflexions were visually estimated by comparing the blackness of the spots with a calibrated scale. The collected intensities were corrected for absorption, using a method devised by van der Hende.<sup>4</sup> Corrections for Lorentz and polarization effects were performed in the usual way.

## STRUCTURE DETERMINATION

*Unit cell and space group.* Powder photographs were taken in a Guinier-Hägg focusing camera at 25°C with strictly monochromatized CuK $\alpha_1$  radiation and potassium chloride as internal standard ( $a_{\text{KCl}}=6.2929$  Å<sup>5</sup>). The powder pattern could be interpreted by means of a monoclinic unit cell. Refinement of the cell parameters was performed by the method of least squares. The following cell dimensions and estimated standard deviations\* were obtained:

$$\begin{aligned} a &= 5.8486 & (5) \text{ \AA} \\ b &= 8.1661 & (10) \text{ \AA} \\ c &= 7.5097 & (8) \text{ \AA} \\ \beta &= 113.00 & (1)^\circ \\ V &= 330.2 & (1) \text{ \AA}^3 \end{aligned}$$

The density of the crystals, 9.20 g cm<sup>-3</sup>, as given by Sillén, indicated a cell content of four formula units Bi<sub>2</sub>O<sub>3</sub>. The calculated density is 9.40 g cm<sup>-3</sup>.

The observed systematic extinctions in the Weissenberg photographs,  $h0l$  absent for  $l=2n+1$ , and  $0k0$  absent for  $k=2n+1$ , confirmed the space group  $P2_1/c$ ,  $b$  as unique axis, (No. 14 in the *International Tables*), as given by Sillén.

*The bismuth atoms.* The Patterson projection  $P(u,p,w)$  and the generalized projection  $P_1(u,w)$  were calculated. The following positional parameters of the bismuth atoms derived from these projections are in very good agreement with those given by Sillén (Table 1b):

$$\begin{aligned} 4 \text{ Bi}_1 &\text{ in } 4(e) \quad x=0.523, \quad y=0.184, \quad z=0.363 \\ 4 \text{ Bi}_2 &\text{ in } 4(e) \quad x=0.038, \quad y=0.038, \quad z=0.773. \end{aligned}$$

The coordinates of the bismuth atoms, their individual isotropic temperature factors, and 10 preliminary calculated scale factors, one for each layer, were then refined by means of the method of least squares. In all least-

\* Standard deviations in this paper refer to the last figure and are given within brackets.

squares refinements, reflexions with  $|F_o|/|F_c|$  less than 0.5 or greater than 2.0 were given zero weight. The discrepancy index  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  will be noted  $R_1$  when all 1656 reflexions are included and  $R_2(n)$  when only  $n$  reflexions with non-zero weight are considered. After five cycles of refinement  $R_1$  was 0.106 and  $R_2(1634)$  was 0.102.

*The oxygen atoms.* A preliminary Fourier projection  $\rho(x, p, z)$  based on  $F_o$ , and a difference projection  $\rho'(x, p, z)$  based on the observed structure factors with the contributions of the bismuth atoms subtracted, were calculated. No maxima corresponding to oxygen atoms could be detected, however. Therefore a three-dimensional Fourier difference synthesis  $\rho'(x, y, z)$  was computed, where sections were calculated from  $y=0.00$  to  $y=0.25$  in steps of 0.0125. The limits for  $x$  and  $z$  in each section were the unit cell. From these Fourier sections it was possible to solve the oxygen positions, *viz.*

- 4 O<sub>1</sub> in 4(e)  $x=0.775, y=0.306, z=0.700$
- 4 O<sub>2</sub> in 4(e)  $x=0.238, y=0.039, z=0.138$
- 4 O<sub>3</sub> in 4(e)  $x=0.275, y=0.025, z=0.513$ .

The corresponding parameters obtained by Sillén are given in Table 1b.

Most maxima in the Fourier sections could be interpreted by these oxygen coordinates. There remained some peaks, but none of them was higher than 85 % of the lowest oxygen peak. All extra peaks except the three smallest ones were located in the neighbourhood of the bismuth positions. It is plausible that they are due to errors inherent in the scale factors, which were calculated without including the contributions of the oxygen atoms.

*Refinement of the structure.* The positions of the bismuth and oxygen atoms given above, their individual temperature factors, and 10 inter-layer scale factors, together 30 parameters, were refined in a full matrix least-squares program. After five cycles of refinement, the discrepancy index  $R_1$  was 0.100 and  $R_2(1638)$  was 0.096. Anisotropic temperature factors were now introduced for the bismuth atoms. Simultaneously an overall scale factor was refined, obtained by fixing the inter-layer scale factors to the values found in the last cycle of the preceding refinement. Thus the number of parameters increased to 31. The least-squares refinements performed were based on  $F$  values, minimizing the function  $\sum w(|F_o| - |F_c|)^2$ . Cruickshank's weighting factor formula,  $w = 1/(a + |F_o| + c \cdot |F_o|^2 + d \cdot |F_o|^3)$ , was used, with  $a=85.0$ ,  $c=0.0025$ , and  $d=0.0005$ , which were found suitable for the final refinement. The atomic scattering factors used were those given by Cromer and Waber<sup>6</sup> for neutral bismuth, and those given by Hansen *et al.*<sup>7</sup> for neutral oxygen.

After three cycles of refinement the discrepancy indices obtained were  $R_1=0.090$  and  $R_2(1639)=0.087$ . The shifts in the parameters were then less than 1 % of their estimated standard deviations. An attempt to introduce anisotropic temperature factors for the oxygen atoms failed, probably due to errors inherent in the intensity material. At this point, a total Fourier difference synthesis  $\rho''(x, y, z)$ , was computed, but no peaks higher than 65 % of an oxygen peak could be detected.

The final atomic parameters with standard deviations are given in Table 1a, and in Table 2 the root-mean-square components of thermal vibration along the principal axes of the ellipsoids of the bismuth atoms. In Table 3

a weight analysis after the last cycle of refinement is given. It confirms that the weighting formula used applied acceptable weights to the reflexions. The observed and calculated structure factors are presented in Table 4.

Table 1a. Final fractional positional parameters and temperature factors and their estimated standard deviations. The expression used for the anisotropic temperature factors was  $\exp[-(h^2 \beta_{11} + k^2 \beta_{22} + l^2 \beta_{33} + hk \beta_{12} + hl \beta_{13} + kl \beta_{23})]$ .

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>		
Bi <sub>1</sub>	0.5240 (1)	0.1831 (2)	0.3613 (1)			
Bi <sub>2</sub>	0.0409 (2)	0.0425 (1)	0.7762 (1)			
O <sub>1</sub>	0.780 (4)	0.300 (3)	0.710 (3)	0.9 (2)		
O <sub>2</sub>	0.242 (5)	0.044 (4)	0.134 (4)	1.2 (3)		
O <sub>3</sub>	0.271 (4)	0.024 (3)	0.513 (3)	0.8 (2)		
	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Bi <sub>1</sub>	0.0042 (1)	0.0027 (2)	0.0031 (1)	0.0013 (2)	0.0024 (2)	-0.0003 (2)
Bi <sub>2</sub>	0.0045 (1)	0.0018 (2)	0.0040 (1)	-0.0004 (2)	0.0029 (2)	0.0003 (2)

Table 1b. Fractional positional parameters as found by Sillén. The unit cell is transformed to the one used in this paper. Some of the coordinates given in Ref. 1 are misprinted. Correct ones are given in Ref. 8.

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Bi <sub>1</sub>	0.520	0.188	0.365
Bi <sub>2</sub>	0.040	0.043	0.775
O <sub>1</sub>	0.773	0.278	0.684
O <sub>2</sub>	0.313	0.973	0.113
O <sub>3</sub>	0.254	0.084	0.540

Table 2. Root-mean-square components,  $R_i$  (Å), of thermal displacement along principal axes of the ellipsoids of vibration, calculated for the bismuth atoms from the  $\beta_{ij}$  values given in Table 1a. Estimated standard deviations are given within brackets.

Atom	$R_1$	$R_2$	$R_3$
Bi <sub>1</sub>	0.074 (3)	0.086 (2)	0.100 (3)
Bi <sub>2</sub>	0.075 (4)	0.082 (3)	0.102 (2)

Table 3. Analysis of the weight function used in the last cycle of the least-squares refinement.  $w$  is the weight applied to a reflexion.

$$\Delta = ||F_o| - |F_c||$$

Interval $F_o$	Number of reflexions	$w \Delta^2$	Interval $\sin \theta$	Number of reflexions	$w \Delta^2$
0-49	157	1.27	0.00-0.46	540	0.96
49-58	160	1.01	0.46-0.58	358	0.92
58-67	164	1.12	0.58-0.67	225	0.72
67-75	165	1.25	0.67-0.74	176	0.72
75-83	165	1.34	0.74-0.79	119	0.89
83-94	165	0.96	0.79-0.84	92	0.71
94-108	166	0.65	0.84-0.89	55	1.18
108-126	165	0.73	0.89-0.93	47	1.18
126-162	166	0.77	0.93-0.97	23	0.80
162-486	166	0.90	0.97-1.00	4	2.36











*Computer programs.* All calculations were performed on the CD 3600 computer in Uppsala, using the following programs.

1. PIRUM: Indexing of powder pattern and refinement of unit cell dimensions, written by P. E. Werner, Univ. of Stockholm, Stockholm.

2. DRF: Data reduction and Fourier calculations. Local modification of a program written by A. Zalkin, Berkeley, Calif.

3. DATACORR: Absorption correction, written by R. Liminga, Univ. of Uppsala, Uppsala.

4. LALS: Full matrix, least-squares calculations. Local modification of A. Zalkin's version of UCLALSI, originally written by P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Univ. of Calif., Los Angeles, Calif.

5. DISTAN: Calculation of distances and angles, written by A. Zalkin.

6. OR FFE: Crystallographic function and error program, written by W. R. Busing, K. O. Martin and H. A. Levy, Oak Ridge, Tenn.

7. OR TEP: A thermal-ellipsoid plot program for crystal structure illustrations, written by C. K. Johansson, Oak Ridge, Tenn.

### DESCRIPTION OF THE STRUCTURE

The structure of  $\alpha\text{-Bi}_2\text{O}_3$  consists of layers of oxygen atoms, parallel to the  $y$  and  $z$  axes at  $x \approx 0.25$  and  $x \approx 0.75$ . Between these are layers of bismuth atoms situated at  $x \approx 0.00$  and  $x \approx 0.50$  (Fig. 1a). The oxygen sheets, planar within  $\pm 0.13$  Å, are built up of pentagons and triangles, the corners of which are all connected with bismuth atoms (Fig. 2). The shortest O—O distance in the structure is 2.78 Å (*cf.* Fig. 2).

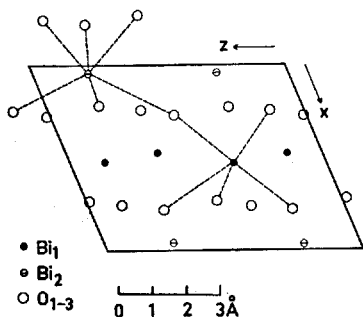


Fig. 1a. Projection of the structure on the  $xz$  plane.

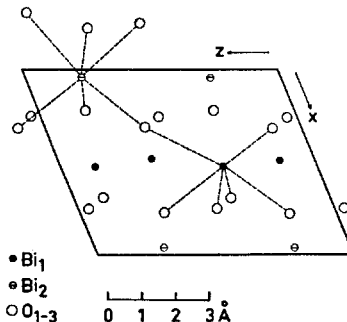


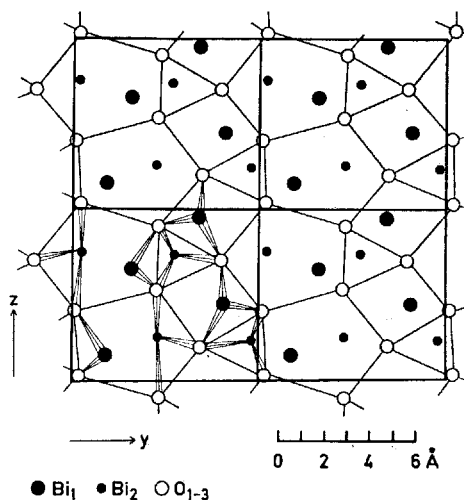
Fig. 1b. Projection of the structure, as given by Sillén, on the  $xz$  plane.

There are two types of oxygen coordination around the bismuth atoms, one five-fold around  $\text{Bi}_1$  and one six-fold around  $\text{Bi}_2$  (Fig. 1a). In the structure proposed by Sillén both bismuth atoms were six-coordinated by oxygen atoms, at distances ranging from 2.39 to 2.55 Å, in an irregular way (Fig. 1b). The Bi—O coordination distances in the structure presented in this paper may be classified in 2 distinct ranges, taking into account an estimated standard deviation in the Bi—O distances of 0.03 Å:

I. 2.08—2.29 Å,

II. 2.48—2.80 Å (Table 5).

Fig. 2. The oxygen layer at  $x=0.25$  projected along  $x^*$  on the  $yz$  plane of four unit cells. The bismuth atoms on each side of the layer are also plotted. The oxygen pattern is illustrated with single lines, while the Bi—O bonds have triple line design.



The oxygen polyhedron surrounding Bi<sub>1</sub> may be described as a distorted octahedron with one of its corners removed. The apical Bi—O bond is remarkably short, 2.08 Å. Of the four remaining bonds two fall in distance range I and two in range II (Fig. 3).

The coordination around Bi<sub>2</sub> has some resemblance to that around Bi<sub>1</sub>. The apical corner is at a distance of 2.14 Å from the central bismuth atom, which is somewhat longer than the corresponding Bi<sub>1</sub>—O bond. This difference,

Table 5. Interatomic distances  $D_1$  (Å) and their estimated standard deviations in the structure of  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>. The distances computed from the structure given by Sillén are listed under  $D_2$ .

Bond	Distance $D_1$	Distance $D_2$
Bi <sub>1</sub> —O <sub>3</sub>	2.08 (3)	2.54
—O <sub>2</sub>	2.17 (3)	2.52
—O <sub>1</sub>	2.21 (3)	2.39
—O <sub>3</sub>	2.54 (2)	2.54
—O <sub>1</sub>	2.63 (3)	2.39
—O <sub>2</sub>	3.25 (4)	2.51
Bi <sub>2</sub> —O <sub>2</sub>	2.14 (3)	2.52
—O <sub>1</sub>	2.22 (3)	2.39
—O <sub>3</sub>	2.29 (2)	2.54
—O <sub>2</sub>	2.48 (3)	2.48
—O <sub>1</sub>	2.54 (3)	2.40
—O <sub>3</sub>	2.80 (2)	2.55
remaining		
Bi—O	> 3.42 (3)	
Bi—Bi	> 3.465 (2)	> 3.42
O—O	> 2.78 (4)	> 2.63

which is not in fact significant on the 0.1 level, may be explained by the fact that a sixth oxygen atom is included in the arrangement. It is situated 2.80 Å from the  $\text{Bi}_2$  atom, thus including the remaining corner of a heavily distorted octahedron. The four remaining Bi—O bonds are distributed two and two in the distance ranges I and II, as in the  $\text{Bi}_1$  coordination. The coordination polyhedra are presented in Fig. 3.

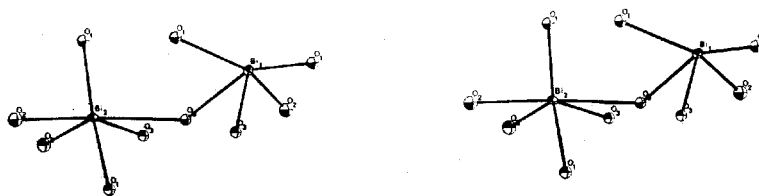


Fig. 3. Stereo view of the oxygen coordination around bismuth. The  $yz$ -plane is parallel to the paper.

The polyhedra are linked together sharing corners and edges, and in this way a three-dimensional network is built up (Fig. 4). As seen from this picture tunnels run through the structure parallel to the  $z$ -axis. These tunnels, having a minimum "diameter" of  $\sim 2.5$  Å (cf. Fig. 4), are bordered by the square

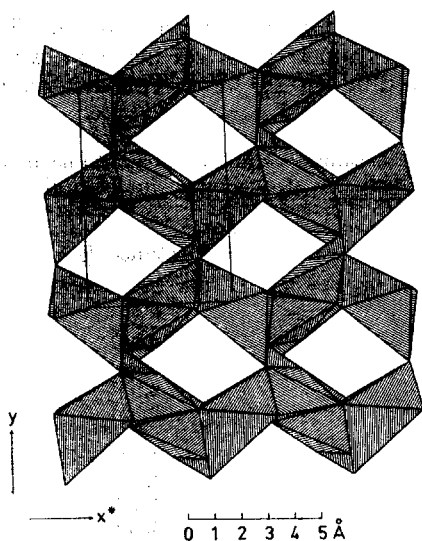


Fig. 4. Part of the structure projected along the  $z$ -axis, illustrating the polyhedra network and the tunnels parallel to the  $z$ -axis.

face of  $\text{Bi}_1$  polyhedra and by the largest triangular face of  $\text{Bi}_2$  octahedra. The smallest triangular face of  $\text{Bi}_2$  polyhedra, *viz.* the opposite face of the large one, also defines these tunnels. In place of a fourth bordering face there are ducts, thus connecting the parallel tunnels.

## DISCUSSION OF THE STRUCTURE

The coordination arrangement around Bi<sub>1</sub> is much like that in Bi<sub>12</sub>GeO<sub>20</sub>,<sup>9</sup> where bismuth is surrounded by seven oxygen atoms. Five of them constitute the incomplete octahedron having distances Bi—O ranging from 2.08 to 2.64 Å (Table 6a). The two remaining oxygen atoms are electrostatically coordinated

Table 6a. Interatomic distances Bi—O (Å) less than 3 Å in the structures of Bi<sub>12</sub>GeO<sub>20</sub>, according to Abrahams *et al.*,<sup>9</sup> and in Bi<sub>2</sub>Ti<sub>4</sub>O<sub>11</sub>, according to Jensen.<sup>10</sup>

Bi <sub>12</sub> GeO <sub>20</sub>	Bi <sub>2</sub> Ti <sub>4</sub> O <sub>11</sub>
2.08	2.14
2.22	2.23
2.23	2.26
2.62	2.60
2.64	2.72

Table 6b. Coordination distances Bi—O (Å) in the structures of Bi<sub>4</sub>Si<sub>3</sub>O<sub>12</sub> according to Segal *et al.*<sup>12</sup> and in Bi(OOCH)<sub>3</sub> according to Stålhandske.<sup>13</sup>

Bi <sub>4</sub> Si <sub>3</sub> O <sub>12</sub>		Bi(OOCH) <sub>3</sub>	
2.15	2.40	2.40	2.34
2.15	2.40	2.40	2.34
2.15	2.40	2.40	2.34
2.62	2.49	2.56	2.50
2.62	2.49	2.56	2.50
2.62	2.49	2.56	2.50

at  $\sim 3.1$  Å. The same type of one-sided five-fold coordination has also been found in the structure of Bi<sub>2</sub>Ti<sub>4</sub>O<sub>11</sub><sup>10</sup> (*cf.* Table 6a). In all these structures the point symmetry of the bismuth atoms is 1.

The electronic configuration of Bi<sup>3+</sup> consists of a closed fifth-shell followed by a pair of 6s electrons. Orgel<sup>11</sup> has pointed out that in the case of five-fold coordination, obtained from an octahedron distorted along a four-fold axis, the pair of inert electrons occupies an orbital pointing directly at the empty sixth corner. This is a reasonable explanation for oxygen arrangement around Bi<sub>1</sub> in  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>.

If an octahedron is distorted along a three-fold axis, the coordination will, according to Orgel,<sup>11</sup> still be six-fold, but three of the bonds will be remarkably shorter than the other three. This is the case in the coordination polyhedron around Bi<sub>2</sub> in the present structure, and has also been found in eulytite, Bi<sub>4</sub>Si<sub>3</sub>O<sub>12</sub><sup>12</sup> and in bismuth formate, Bi(OOCH)<sub>3</sub>.<sup>13</sup> A list of the Bi—O distances in these structures is given in Table 6b. However, in Bi<sub>2</sub>O<sub>3</sub> the bond lengths of the polyhedron surrounding Bi<sub>2</sub> include one short, 2.14 Å, and one rather long distance, 2.80 Å, thus giving the octahedron a more distorted shape than in the case of eulytite and bismuth formate. It should be noted that the point symmetry of the bismuth atom in these structures is 3 while it is 1 for Bi<sub>2</sub> in  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>. One explanation to the more irregular shape

of the oxygen polyhedron around  $\text{Bi}_2$  may be that it is an octahedron not only distorted along a three-fold axis, but also somewhat along a four-fold one, which also seems reasonable with respect to the low point symmetry for  $\text{Bi}_2$ .

For these reasons it seems plausible that the inert pair of electrons, belonging to the  $\text{Bi}_2$  atom, points out from the largest face of the octahedron. As mentioned earlier, that face and the square face of the  $\text{Bi}_1$  coordination arrangement define the tunnels running through the structure, thus indicating that all orbitals occupied by the inert pair of electrons are projecting into these tunnels.

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