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The Crystal Structure of $BaNiO_3$

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The crystal structure of $BaNiO_3$ has been determined by single-crystal analysis. The space group is $P6_3/mmc$ and lattice constants are $a=5{\cdot}629$ (3) and $c=4{\cdot}811$ (3) Å with $Z=2$. The structure has been refined by the block-diagonal least-squares technique to a final R value of 0·049. The structure is characteristic with linear chains of nickel atoms having a Ni–Ni distance of 2·405 (2) Å; the NiO_6 octahedron is trigonally distorted.

Introduction

Lander (1951) first reported the synthesis of $BaNiO_3$ and determined its structure on the basis of powder work. In his study the structure was described in terms of hexagonal close-packing of BaO_3 layers and NiO_6 octahedra sharing a pair of opposite faces to form Ni chains parallel to the c axis with a Ni–Ni distance of 2·41 Å, which is shorter than that in Ni metal (2·49 Å).

Compounds denoted as ABX_3 (A, B and X represent a large cation, a small cation and an anion respectively) have been classified into several modifications by the stacking sequence (for example two-layer, three-layer, six-layer types, and so on) in the close-packing of the AX_3 layers (Katz & Ward, 1964). In the so-called perovskite structure with cubic close packing of the AX_3 layers, all BX_6 octahedra are linked through their corners. On the other hand, in $BaNiO_3$ with hexagonal close packing of BaO_3 layers, NiO_6 octahedra are stacked in columns sharing faces, as described above. Comparing these two structures, it is clear that the structure of $BaNiO_3$ is more unstable than that of perovskite, if only ionic bond natures are considered, because the short Ni–Ni distance induces large interionic repulsion between the Ni^{4+} ions. Longo & Kafalas (1968) pointed out that the large A cations (Ba, Cs, for example) stabilize the hexagonal close packing of the AX_3 layers. An increase in the interlayer distance of the AX_3 layers decreases the repulsive force between B ions and thereby stabilizes face-sharing of BX_6 octahedra. However, the fact that $SrNiO_3$ (Takeda, Hashino, Miyamoto, Kanamaru, Kume & Koizumi, 1972) has hexagonal stacking of SrO_3 suggests that the ionic size of an A ion does not necessarily determine the AX_3 layer sequence, but the bond nature between B and O ions plays an important role in stabilizing the face-shared structure of the octahedra.

In order to clarify the problem, an attempt was made to refine the crystal structure of $BaNiO_3$ using a single crystal.

Experimental

$BaNiO_3$ powders were prepared by heating a mixture of $BaCO_3$ and NiO or $NiCO_3$ at 1100°C for 48 h in air and then annealing at 600°C under high oxygen pressure (2000 bars). The X-ray powder diffraction lines of the product were indexed on the hexagonal cell with $a=5{\cdot}632$ (4) and $c=4{\cdot}809$ (3) Å. Crystals of $BaNiO_3$ were grown using $Ba(OH)_2.8H_2O$ as a flux. A mixture of powders of $BaNiO_3$ and $Ba(OH)_2.8H_2O$ in a mol ratio of 1:2 was charged in a gold-tube capsule with an open end and heated at 600°C and 2000 bars (P_{O_2}) for 48 h. When a thermal gradient of 10°C $(10\text{mm})^{-1}$ was imposed on a long axis of the reactor, gold-coloured crystals about 1 mm in diameter and 4 mm in length grew at the cooler end of the capsule. The details of the method have been reported by Shimada, Takeda, Taguchi, Kanamaru & Koizumi (1975). The chemical composition of the single crystal was determined to be $BaNiO_3$ by thermogravimetric analysis and electron probe microanalysis. The density was found to be 6·10 g cm^{-3} by a pycnometric method. The calculated density is 6·13 g cm^{-3} with $Z=2$. The crystal used for the structure determination was about $0{\cdot}1\times0{\cdot}1\times0{\cdot}3$ mm. Precession and Weissenberg photographs showed that $BaNiO_3$ crystallized in the hexagonal system with systematic absences for hhl, when $l=2n+1$. The Laue symmetry was found to be $6/mmm$. Although the possible space groups having such a systematic absence were $P\bar{6}2C$, $P6_3mc$, or $P6_3/mmc$, it was decided initially to refine the structure assuming the centrosymmetric space group $P6_3/mmc$.

All reflexions to $\sin\theta/\lambda=1{\cdot}0$ were measured with zirconium-filtered Mo $K\alpha$ radiation on a Rigaku automatic four-circle diffractometer with a scintillation counter and the θ–2θ scan technique. The hexagonal cell dimensions were determined to be $a=5{\cdot}629$ (3) and $c=4{\cdot}811$ (3) Å, by least-squares refinement using six well-centred reflexions measured with the four-circle diffractometer. After correction for

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background, intensities of symmetrically related reflexions were averaged to give 222 independent reflexion data. Neither absorption nor extinction corrections were made.

The three-dimensional Patterson map, which was calculated with *RSSFR*-5 in the UNICS program system (Sakurai, 1967), indicated that the Ni, Ba and O atoms occupy the positions 2(*a*), 2(*d*) and 6(*h*) with $x \simeq 0{\cdot}167$ in the space group $P6_3/mmc$. The atomic parameters proposed by Lander gave an agreement index of $R=0{\cdot}32$. A block-diagonal least-squares refinement was carried out with the use of the program *HBLS*-V (Ashida, 1973). In the refinement procedure, neutral atomic form factors were taken from *International Tables for X-ray Crystallography* (1962). The weight function assigned for reflexions is $w=(\sigma^2+a|F_o|+b|F_o|^2)^{-1}$, where σ is the standard deviation in intensity, $a=0{\cdot}1320$ and $b=0{\cdot}086$. After four cycles of least-squares refinement using isotropic temperature factors, R was reduced to 0·105. Refinement was continued with anisotropic temperature factors, until the maximum shift of each parameter became less than one twentieth of its e.s.d. The final conventional R value was 0·048, while $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$ was 0·090. In the absence of any stereochemical evidence which would show the choice to be incorrect, $P6_3/mmc$ is assumed to be the correct space group. The final positional and thermal parameters are listed in Table 1. Interatomic distances and bond angles are listed in Table 2.*

Table 1. *Positional and thermal parameters*

The form of the temperature factor is $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)]$. For oxygen, $B_{11}=B_{22}$, $B_{23}=B_{13}=0$; and for nickel and barium, $B_{11}=B_{22}=2B_{12}$, $B_{23}=B_{13}=0$.

	Ba	Ni	O
Position	2(*d*)	2(*a*)	6(*h*)
x	$\frac{1}{3}$	0	0·1462 (2)
y	$\frac{2}{3}$	0	−0·1462
z	$\frac{3}{4}$	0	$\frac{1}{4}$
B_{11}	0·0024 (2)	0·0027 (4)	0·0017 (24)
B_{33}	0·0112 (2)	0·0067 (5)	0·0098 (19)
B_{12}			−0·0005 (30)

Table 2. *Selected distances and angles*

Ni–O	1·864 (7) Å	O^{i}–Ni–O^{ii}	82·7 (2)°
O^{i}–O^{ii}	2·466 (10)	O^{i}–Ni–O^{iii}	97·1 (2)
O^{i}–O^{iv}	3·164 (10)	Ni^{i}–O^{i}–Ni^{ii}	80·4 (2)
O^{i}–O^{iii}	2·795 (10)		
Ni^{i}–Ni^{ii}	2·406 (2)		
Ba^{i}–O^{i}	2·822 (7)		
Ba^{i}–O^{iii}	3·020 (7)		

Symmetry code

Superscript	O	Ni	Ba
i	$x, 2x, \frac{1}{4}$	0,0,0	$\frac{2}{3},\frac{1}{3},\frac{1}{4}$
ii	$x, \bar{x}, \frac{1}{4}$	$0,0,\frac{1}{2}$	
iii	$2x, x, \frac{3}{4}$		
iv	$x, 1-x, \frac{1}{4}$		

Results and discussion

The crystal structure of $BaNiO_3$ deduced from the powder data by Lander (1951) is approximately correct, but the oxygen parameters obtained in the present research ($x=0{\cdot}146$, $y=-0{\cdot}146$ and $z=0{\cdot}250$) indicate that the NiO_6 octahedron is fairly distorted from the ideal. Figs. 1 and 2 show the hexagonal close packing of Ba and O ions and the linkage of NiO_6 octahedron in $BaNiO_3$ respectively. Within the BaO_3 layers, the O–O distance is either 2·466 or 3·164 Å, while the O–O distance between the layers is 2·759 Å. The Ba–O distance within the layers is 2·823 Å. In the ideally close-packed structure, all the Ba–O and O–O distances within the layers and between adjacent layers should be the same. However, the interatomic distance between the oxygen atoms on the shared face of the NiO_6 octahedron is much shorter than the other O–O distances, as mentioned above.

NiO_6 octahedra are stacked in columns along the c axis sharing faces formed with three oxygen anions. The Ni^{4+} ions in the columns directly face each other at a very short distance of 2·41 Å. Since tetravalent nickel ions are highly charged, large electrostatic repulsions would be produced between the Ni^{4+} ions. The following three factors seem to account for the reduction of such a repulsion to stabilize the face-shared structure: (1) The nickel ions form Ni–Ni bonds by directly overlapping the d orbitals of the ions. (2) Oxygen atoms, which form triangles with a short O–O distance of 2·455 Å, effectively shield the charge of the Ni ion along the c axis. (3) Covalency is increased in the oxygen–nickel bond, because the small Ni^{4+} ions (about 0·5 Å in radius) strongly attract the oxygen electron clouds.

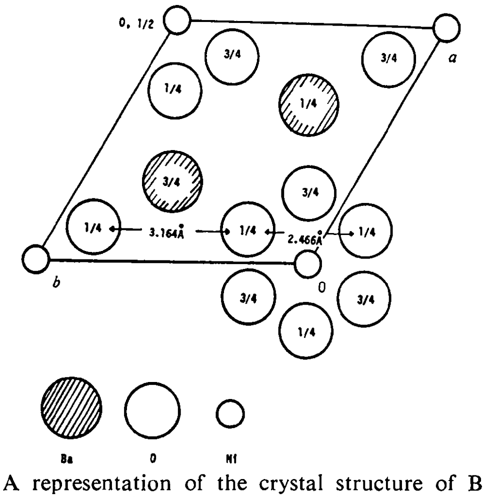

Fig. 1. A representation of the crystal structure of $BaNiO_3$ viewed along the c axis.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31767 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The fact that $BaNiO_3$ does not exhibit a metallic behaviour but does show very high electrical resistivity (Takeda, Shimada, Kanamaru, Koizumi & Yamamoto, 1974) indicates the absence of a bond between the Ni ions, even though the Ni–Ni distance in $BaNiO_3$ is shorter than that in Ni metal. On the other hand, the O–O distance in the face-sharing triangle is much shorter than that predicted from the ideal hexagonal close packing. Therefore it is reasonable to consider that the charge on the Ni^{4+} ion is sufficiently shielded by the surrounding oxygen ions and that the repulsion between Ni ions is weakened.

Goodenough & Kafalas (1973) have pointed out that face sharing of octahedra in ABO_3 compounds is favoured with an increase of covalency in the B–O bond. If the Ni–O bond has a strongly covalent character, the interatomic distance between Ni and O atoms is expected to be shorter than that predicted from a purely ionic model. Unfortunately, the Ni–O bond distance in $BaNiO_3$ cannot be properly discussed in comparison with that in other Ni^{4+} compounds, because there are few oxides involving Ni^{4+} ions other than $BaNiO_3$. But the Ni^{4+}–O distance, which was evaluated by extrapolating the curve of B–O bond distance *vs* valency of B (Fig. 3), is distinctly larger than the observed Ni–O distance in $BaNiO_3$.

In such a way the repulsive energy between the highly charged Ni^{4+} ions is counteracted by the increase of covalency in the Ni–O bond and by the strong shielding effect of the surrounding oxygens on the Ni^{4+} ions.

As seen in Fig. 1, $BaNiO_3$ does not have an ideal hexagonal close packing of Ba and O ions, but all oxygen ions are remarkably close to Ni ions. This indicates that $BaNiO_3$ is not a purely ionic crystal, but a polyacid salt type which consists of chains of NiO_3 groups held together by Ba ions.

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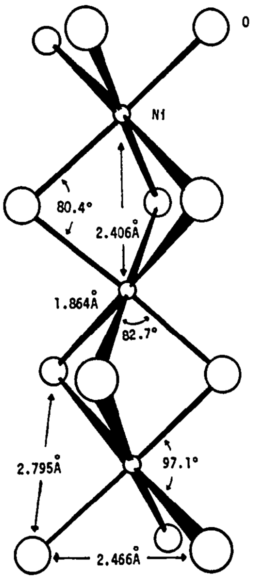

Fig. 2. A perspective view of the anionic chain in $BaNiO_3$.

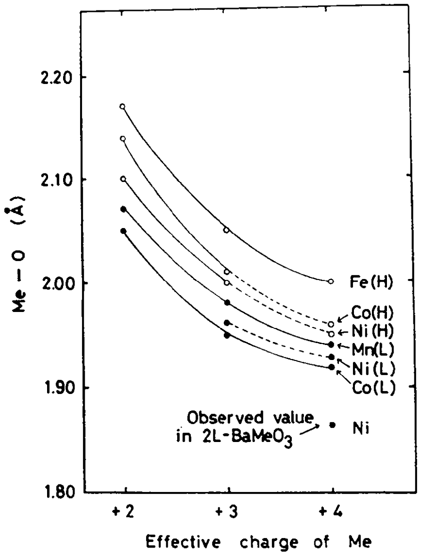

Fig. 3. Estimated metal–oxygen distances in the MO_6 octahedron for the metals of various valence states. The values on the solid lines are calculated from the ionic radii proposed by Shannon & Prewitt (1969); that of Co^{3+} (low spin)–O is taken from the data of Blasse (1965). The M–O values for the tetravalent nickel and cobalt are evaluated by extrapolation of the other M–O distances on solid lines.

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