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PREPARATION AND MAGNETIC PROPERTY OF $BaNiO_3$ SINGLE CRYSTALS

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Single crystals of $BaNiO_3$(2H) were prepared under oxygen pressure of 2000 bars. They have a hexagonal unit cell with dimensions a=5.63±0.01, c=4.81±0.01Å. The space group is $P\bar{6}2C$, $P6_3mc$ or $P6_3/mmc$. Its magnetic susceptibility is almost temperature-independent down to 4.2K, showing $BaNiO_3$ to be diamagnetic.

In the course of a systematic study on perovskite-type oxides containing first row transition metals in higher valence state, such as Fe^{4+}, Co^{4+} and Ni^{4+} ions, Takeda et al. (1,2) have succeeded to prepare some new oxides which have perovskite structure and are stable only at high oxygen pressure. Recently, we have attempted to prepare large single crystals of these oxides at 2000-3000 bars of oxygen pressure to do further studies on crystallographic and physical properties of these compounds.

Among these oxides, phase system of Ba-Ni-O was already studied by Lander and Wooten (3), Lander (4,5) and Krischner et al. (6). The crystal structure of $BaNiO_3$ was investigated by Lander (5) based on X-ray powder photographs. According to Lander, $BaNiO_3$ has a hexagonal close-packed structure consisting of BaO_3 layer, with Ni ions filling the O_6 octahedra. Each NiO_6 octahedron shares faces with the adjacent octahedra to form columns parallel to the c-axis. It seems very interesting to examine the physical properties as a result of the strong interaction between transition metal ions located at the octahedral sites. Few results have so far been reported, however, because little examples of oxides having such a structure is known.

In our present study, powdered specimen of $Ba_2Ni_2O_5$ was first prepared by calcining an mixture of $BaCO_3$ and NiO powders at 1100°C for 48 hours in air. This reaction mixture was charged in a gold tube capsule with an open end which was placed in a test-tube type reactor. Finally the specimen was oxidized at 600°C and 2000 bars (Po_2) for 48 hours. The X-ray powder diffraction patterns of the product were completely indexed as 2-layer hexagonal perovskite structure proposed by Lander (5). The calculated lattice constants are a=5.632±0.004Å and c=4.809±0.003Å. In preparing the single crystals, powders of $BaNiO_3$ were added to flux, reagent-grade

$Ba(OH)_2 \cdot 8H_2O$, in a molar ratio 1:2. The material was treated in the same way mentioned above. When a thermal gradient was given along the long axis of the reactor, several gold-colored single crystals of about 1mm in diameter and 4mm long grew at the cooler end of the gold tube. Precession and Weissenberg photographs were taken with MoKα radiation, which showed that $BaNiO_3$ crystallized in hexagonal system with systematic absences of hhl, $l \neq 2n$. Since the Laue group of $BaNiO_3$ is 6/mmm, the possible space group is D_{3h}^4-P$\bar{6}$2C, C_{6v}^4-P6_3mc or D_{6h}^4-P6_3/mmc and cell dimensions are $a=5.63 \pm 0.01$Å and $c=4.81 \pm 0.01$Å. The crystal data from the powder diffraction by Lander (5) were confirmed by our single crystal study. The chemical composition of the single crystal under investigation was determined to be $BaNiO_3$ by an electron probe microanalysis and a thermogravimetric analysis.

Temperature dependency of magnetic susceptibility of the single crystal was measured down to 4.2K. The crystal showed a weak and temperature-independent paramagnetic susceptibility as shown in Table 1. A measurement of electric conductivity revealed that the specific resistivity for $BaNiO_3$ at room temperature was larger than $10^8 \Omega$cm, though $BaNiO_3$ had been expected to have a good conductivity along the c-axis, because of shorter Ni-Ni distance (2.41Å) along the direction than that in Ni metal (2.49Å).

Table 1. Magnetic susceptibility of $BaNiO_3$

Temperature (K)	4.2	77	295
$\chi g \times 10^7$	2.0	2.2	2.1

The constant susceptibility of $BaNiO_3$ shows that Ni ion has no magnetic moment. This result suggests that the Ni ion is tetravalent and in low spin state of $(3d)^6$ configuration. The present result is consistent with the EPR result reported by Krischner et al. (6). The expense of this study was defrayed by a Grant in Aid for Special Research Project from the Ministry of Education.

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