# A Powder X-Ray Diffraction Survey of the Effects of Substituting Strontium for Barium in a Barium Nickel Oxide

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The effect of substituting strontium for barium in two-layer barium nickel oxide has been studied. Samples were prepared from appropriate mixtures of $BaO_2$, $SrO_2$, and $NiO$ at 700°C under a wet oxygen atmosphere. Under these conditions the two-layer structure does not persist across the composition range. Among the various ways in which the X-ray powder patterns could be indexed, the most plausible calls for two more phases, one which may have a nine-layer structure, the other a compressed two-layer structure analogous to "$Ba_3Ni_3O_8$."

## Introduction

The structures of many ternary oxides containing a large cation $A$ and a smaller cation $M$ may be correlated on the basis of cubic and hexagonal close-stacking of $AO_3$ layers with $M$ cations in the octahedral interstices among the oxide ions (*1*). If all the octahedral sites are occupied, the formula is $AMO_3$. Hexagonal close packing leads to face sharing of the oxygen octahedra. The structure of $BaNiO_3$ is described as one in which there are continuous chains of face-sharing $NiO_6$ octahedra (*2*). Although Pauling has pointed out that generally corner sharing is more stable than edge sharing, which in turn is more stable than face sharing (*3*), this extreme example of face sharing occurs not only in $BaNiO_3$ but also in $BaCoO_{3-x}$ (*4*) and in $BaMnO_3$ (*5*). In some cases where face sharing occurs, it has been shown that the extent of face sharing is reduced (replaced by corner sharing) by the reduction of the interlayer spacing, either by pressure (*5, 6*) or by substitution of a smaller $A$ cation, like Sr, for Ba (*7*). The present investigation was undertaken to test the persistence of face sharing of the $NiO_6$ octahedra when Sr is substituted for Ba. The 100% Ba end of the composition range has been studied by a number of investigators (*8–10*) in addition to Lander (*2*); the 100% Sr end has been the subject of a paper by Takeda et al. (*11*). Since the series is probably nonstoichiometric (*4, 12*), the system formula may be written $Ba_{1-x}Sr_xNiO_{3-y}$.

## Experimental

$BaNiO_3$ was prepared by pelletizing a 1:1 molar ratio of $BaO_2$ and $NiO$ and heating in a nickel boat at 700°C for 3 days under a wet oxygen atmosphere. The powder pattern was the same as that reported by Lander (*2*). The cation compositions $Ba_{1-x}Sr_xNi$ were sought by mixing appropriate ratios of $BaO_2$ and $SrO_2$ with a constant amount of $NiO$. The composition parameter $x$ was varied in steps of 0.1, and the mixtures were treated in the same way as for $BaNiO_3$. The samples were then ground and reheated for another 3 days

in an effort to promote completeness of reaction.

Powder patterns were obtained with a GE XRD-5 diffractometer with Ni-filtered Cu radiation. A 0.05° detector slit and a scan rate of 0.2°/min were used to obtain reasonable resolution, but the patterns were sharp and well resolved only for the barium-rich compositions.

## Interpretation of the Patterns

The pattern obtained for $BaNiO_3$ was the same as that obtained by Lander (2) and could be indexed on the basis of a hexagonal cell with $a \simeq 5.59$ Å, $c \simeq 4.85$ Å (Table I). As was the experience of Negas and Roth (8), a small amount of NiO was also present. We did not detect the extra lines they observed which required increasing the $a$ axis by a factor of $3^{1/2}$, although it is possible that the intensities of these lines were below our detection limits. In either case the $c$ axis is consistent with a two-layer structure which would place Ni atoms in vertical columns.

The patterns for $x = 0.1$ and $x = 0.2$ are

only slightly different from the $x = 0$ pattern (for $x = 0.2$, $a \simeq 5.58$ Å, $c \simeq 4.83$ Å) but by $x = 0.3$ there is the clear presence of a new line at $d = 3.18$ Å. Since there is only one new line to account for, a number of possible explanations could be offered: The $a$ axis should be increased by a factor of $3^{1/2}$, so that this new line would be indexable as 210; the $c$ axis should be doubled, which would be consistent with a four-layer structure, and the new line would be indexable as 003; or the new line marks the beginning of a new phase at about $x = 0.25$. Since at higher values of $x$ this new line becomes very strong, whereas the very strong 101 and 221 lines of the two-layer phase eventually disappear, the data are more convincingly explained on the basis of two phases than distortions in the unit cell of a single phase. In addition, the intensities which are later observed do not match those of a four-layer structure. However, it is also observed that the progressive shift in $d$ values, which is halted from $x \simeq 0.2$ to $x \simeq 0.5$, is resumed well before the pattern for the two-layer phase disappears at $x \simeq 0.75$. The two-phase explanation would require the hypothesis that true equilibrium had not been attained. Anyone who has prepared several

TABLE I

POWDER PATTERN FOR $BaNiO_3{}^a$

($a = 5.59$ Å, $c = 4.85$ Å)

| $d_{obs}$ | $d_{calc}$ | $h k l$ | $I_{obs}$ |
|---|---|---|---|
| 3.42 | 3.42 | 1 0 1 | S+ |
| 2.79 | 2.79 | 1 1 0 | S |
| 2.42[b] | 2.42 | 2 0 0, 0 0 2 | M- |
| 2.164 | 2.164 | 2 0 1, 1 0 2 | S |
| 1.829 | 1.828 | 1 1 2 | W |
| 1.711 | 1.711 | 2 1 1, 2 0 2 | M |
| 1.614 | 1.612 | 3 0 0 | W |
| 1.530 | 1.530 | 1 0 3, 3 0 1 | W- |
| 1.459 | 1.460 | 2 1 2 | W |
| 1.397 | 1.396 | 2 2 0 | W |
| 1.342 | 1.342 | 2 0 3, 3 0 2 | W |
| 1.293 | 1.293 | 3 1 1 | W |
| 1.209 | 1.209 | 2 2 2, 2 1 3, 0 0 4 | W |

[a] Nominal formula. Cell dimensions match those reported for $BaNiO_{2.5}$ (12).

[b] Includes contribution from NiO 111 reflection.

TABLE II

CATION COMPOSITION $Ba_{1-x}Sr_xNi$, $x = 0.6$

(MAJOR PHASE, $a = 5.53$ Å, $c = 20.84$ Å)

| $d_{obs}$ | $d_{calc}$ | $h k l$ | $I_{obs}$ |
|---|---|---|---|
| 3.40 | 3.40 | 1 0 1[a] | M- |
| 3.14[b] | 3.15 | 1 0 5 | M+ |
| 2.764 | 2.766 | 1 1 0 | S+ |
| 2.149 | 2.145 | 2 0 1[a] | M- |
| 2.078[c] | 2.077 | 2 0 5 | M+ |
| 1.975 | 1.972 | 2 0 6 | W- |
| 1.697 | 1.694 | 2 1 1[a] | W |
| 1.657 | 1.661 | 2 1 5 | W |
| 1.595 | 1.597 | 3 0 0 | W |
| 1.523 | 1.527 | 3 0 4 | W |
| 1.383 | 1.383 | 2 2 0 | W |

[a] Lines of barium-rich phase, $a \simeq 5.53$ Å, $c \simeq 4.81$ Å.

[b] Probably an unresolved doublet.

[c] Includes contribution from NiO 200 reflection.

phases in a single solid-state reaction would have no difficulty in accepting the plausibility of this hypothesis. The pattern for $x = 0.6$ with an accounting of the lines is given in Table II.

The difficulty in attaining equilibrium is well brought out in a comparison of the patterns for $x = 0.8$, $x = 0.9$, and $x = 1.0$. For $x = 0.8$, lines at $\sin^2 \theta = 0.0594$ and $0.0616$ form a close doublet with about equal intensity. For $x = 0.9$, the low-angle line of the doublet is much the stronger, but at $x = 1.0$ the high-angle line is much stronger. Again two phases are called for, but which phase dominates may be determined by uncontrolled variables. It may also be noted that, judging from line intensities, the amount of NiO impurity decreased from $x = 0.8$ to $x = 0.9$ but increased quite sharply at $x = 1.0$. An accounting for the patterns for $x = 0.7$, $x = 0.8$, $x = 0.9$, and $x = 1.0$ is given in Tables III, IV, V, and VI.

## Discussion and Summary

The cell dimensions for the 100% Ba preparation correspond to those given for $BaNiO_{2.5}$ (*12*), an analysis also matching that determined by Gushee *et al.* (*4*). This two-

### TABLE III

CATION COMPOSITION $Ba_{1-x}Sr_xNi$, $x = 0.7$

(MAJOR PHASE, $a \simeq 5.52$ Å, $c \simeq 20.60$ Å)

| $d_{obs}$ | $d_{calc}$ | $h\,k\,l$ | $I_{obs}$ |
|---|---|---|---|
| 3.41 | 3.40 | 1 0 1[a] | W[+] |
| 3.14[b] | 3.12 | 1 0 5 | S |
| 2.762 | 2.758 | 1 1 0 | S[+] |
| 2.167[c] | 2.167 | 2 0 4 | W |
| 2.146 | 2.145 | 2 0 1[a] | W |
| 2.067[b] | 2.066 | 2 0 5 | M[+] |
| 1.975[c] | ? | ? | W[-] |
| 1.696 | 1.694 | 2 1 1[a] | W[-] |
| 1.653 | 1.654 | 2 1 5 | W[+] |
| 1.594 | 1.592 | 3 0 0 | W[+] |
| 1.523[c] | 1.521 | 3 0 4 | W[-] |
| 1.379 | 1.379 | 2 2 0 | W |

[a] Lines of barium-rich phase, $a \simeq 5.52$ Å, $c \simeq 4.80$ Å.
[b] Probably an unresolved doublet.
[c] May be impurity lines. See text.

### TABLE IV

CATION COMPOSITION $Ba_{1-x}Sr_xNi$, $x = 0.8$

(MAJOR PHASE, $a \simeq 5.51$ Å, $c \simeq 20.52$ Å)

| $d_{obs}$ | $d_{calc}$ | $h\,k\,l$ | $I_{obs}$ |
|---|---|---|---|
| 3.16 | 3.17 | 1 0 1[a] | S |
| 3.11 | 3.11 | 1 0 5 | S |
| 2.755 | 2.755 | 1 1 0 | S[+] |
| 2.167[b] | 2.163 | 2 0 4 | W[-] |
| 2.084[c] | 2.080 | 2 0 1[a] | S[-] |
| 2.062 | 2.063 | 2 0 5 | S[-] |
| 1.977[b] | ? | ? | W[-] |
| 1.653 | 1.651 | 2 1 5 | W |
| 1.590 | 1.591 | 3 0 0 | W |
| 1.521[b] | 1.519 | 3 0 4 | W[-] |
| 1.377 | 1.377 | 2 2 0 | W |

[a] Lines of second-phase, small-cell dimensions $a \simeq 5.51$ Å, $c \simeq 4.24$ Å.
[b] May be impurity lines. See text.
[c] Includes contribution from NiO 220 reflection.

### TABLE V

CATION COMPOSITION $Ba_{1-x}Sr_xNi$, $x = 0.9$

(MAJOR PHASE, $a \simeq 5.49$ Å, $c \simeq 4.05$ Å)

| $d_{obs}$ | $d_{calc}$ | $h\,k\,l$ | $I_{obs}$ |
|---|---|---|---|
| 3.10 | 3.09 | 1 0 1 | S |
| 3.04 (shoulder) | 3.04 | 1 0 5[a] | M |
| 2.741 | 2.743 | 1 1 0 | S[+] |
| 2.373 | 2.376 | 2 0 0 | W[-] |
| 2.172[b] | ? | ? | W |
| 2.051 | 2.049 | 2 0 1 | S[-] |
| 1.975[b] | ? | ? | W |
| 1.640 | 1.641 | 2 1 1 | M |
| 1.583 | 1.583 | 3 0 0 | M |
| 1.519[b] | ? | ? | W |
| 1.371 | 1.371 | 2 2 0 | M[-] |
| 1.260[b] | ? | ? | W |
| 1.253 | 1.253 | 3 1 1 | W |

[a] Minor component, $a \simeq 5.45$ Å, $c \simeq 19.85$ Å.
[b] May be impurity lines. See text.

layer phase is the only one observed in the system $Ba_{1-x}Sr_xNiO_{3-y}$ from $x = 0$ to $x \simeq 0.25$ (except for some NiO which was observed in all of our preparations). At $x = 0.3$, a new line appears at about $d = 3.17$ Å. As pointed out earlier, with only one new line to account for, a variety of explanations could be

| $d_{obs}$ | $d_{calc}$ | $h\,k\,l$ | $I_{obs}$ |
|---|---|---|---|
| 4.74 | 4.74 | 1 0 0 | W |
| 3.02 | 3.03 | 1 0 5 | S |
| 2.732 | 2.732 | 1 1 0 | S$^+$ |
| 2.368 | 2.366 | 2 0 0 | W$^-$ |
| 2.182$^a$ | 2.187 | 1 0 8 | W$^+$ |
| 2.028 | 2.029 | 0 2 5 | S |
| 1.983$^a$ | 1.989 | 1 0 9 | W |
|  | 1.973 | 0 0 10 |  |
| 1.957 | 1.962 | 1 1 7 | W |
| 1.813 | 1.812 | 2 0 7 | W |
| 1.628 | 1.628 | 2 1 5 | M |
| 1.577 | 1.578 | 3 0 0 | M$^-$ |
| 1.520$^a$ | 1.518 | 0, 0, 1 3 | W |
| 1.366 | 1.366 | 2 2 0 | W |
| 1.260$^a$ | 1.261 | 2 2 6 | W |
| 1.246 | 1.245 | 1 3 5 | W |

$^a$ May be impurity lines. See text.

offered; however, since this line increases in intensity with increasing Sr until it becomes one of the strongest lines on the pattern, distortion of the cell is not so reasonable an explanation as the appearance of a new phase. This line becomes about equal in intensity to the strongest line of the barium-rich phase (101) at $x \simeq 0.55$. By $x = 0.6$, the barium-rich phase is a minor constituent, and it has almost disappeared at $x = 0.7$. With our method of preparation, then, the two-layer phase with layer thickness about 2.4 Å does not persist across the composition range.

At $x = 0.6$ and $x = 0.7$, the line at $d = 3.14$ Å is fairly broad and could accommodate a close doublet; that this is so becomes clear at $x = 0.8$, where the two lines occur at about $d = 3.16$ and $d = 3.11$ Å. At $x = 0.9$, the pattern is very similar to that obtained by Takeda at 600°C under oxygen pressure of 50 atm, except that we observe four more lines. These same four lines were observed in Takeda's 1000°C product prepared in a wet oxygen gas flow. They were not accounted for, but it was suggested that they might be due to some

lattice distortion produced by oxygen deficiency. A number of efforts were made to account for these four lines, which occurred at about $d = 2.17$, 1.98, 1.52, and 1.26 Å. They can be indexed on the basis of various cells. For instance, the $x = 0.9$ pattern can be indexed quite well with $a = 9.49$ (5.48 × 3$^{1/2}$) and $c = 6.53$ Å, or, if the 1.26 Å line is assumed to be an NiO impurity line, the cell $a = 9.49$, $c = 6.12$ Å can account for the pattern. However, these indexings have the previously mentioned defect of accounting for strong lines as lines resulting from cell distortion. In addition, the extra lines do not change position at different compositions, so that the same kind of cell could not be used to account for them at different values of $x$. It thus appears more likely that they are due to an unidentified impurity.

For $x = 1.0$, i.e., for SrNiO$_{3-y}$, the pattern we obtained matched Takeda's 1000°C oxygen gas flow product quite well. There is a discontinuity in our results in that the doublet lines are of equal intensity at $x = 0.8$, the low-angle line is much the stronger at $x = 0.9$ with only an unresolved shoulder at higher angle, but the high-angle line is much stronger at $x = 1.0$ with only an unresolved shoulder at lower angle. We thus observe a pair of phases beginning at $x \simeq 0.6$. At $x = 0.9$ one of these phases is dominant, at $x = 1.0$ the other is the major constituent. (It should also be mentioned that at $x = 1.0$ there is a substantial amount of NiO impurity and several weak lines attributable to SrO$_2$ decomposition appear in the X-ray pattern.) It is thus clear that equilibrium conditions were not attained, a fact which is also brought out by cell size changes even when more than one phase is present.

The 100% Sr pattern can be indexed almost completely using a cell with $a = 5.47$, $c = 19.73$ Å (Table VI). This cell could correspond to a nine-layer structure with a short layer spacing of 2.19 Å. With this assumption, the same phase with $a = 5.49$, $c = 19.85$ is a minor constituent at $x = 0.9$, and with longer $c$

axes is one of a pair of phases at $x = 0.8$, 0.7, and 0.6. The other phase is a very minor constituent at $x = 1$, the major phase at $x = 0.9$, and is a co-equal phase at $x = 0.8$, 0.7, and 0.6; $c$-axis values are 4.05, 4.05, 4.24, 4.24, and 4.24 Å, respectively. However at $x = 0.7$ and $x = 0.6$ the patterns of the two phases are not resolved and only the nine-layer description is used in Tables II and III. A summary of the observations is given in Table VII.

Takeda has shown that a two-layer $SrNiO_3$ can be made with a normal layer spacing of about 2.4 Å at 600°C and oxygen pressures from 50 to 2000 atm. Indeed the $c$ axis is as long as any observed for two-layer $BaNiO_3$ and is much longer than the values reported by Arjomand and Machin (*12*). It thus seems

### TABLE VII

PHASES ASSUMED PRESENT IN SYSTEM $Ba_{1-x}Sr_xNiO_{3-y}$

| $x$ | Phase | Cell dimensions[a] (Å) | Comment |
|---|---|---|---|
| 0.0 | 2-Layer | $a = 5.59, c = 4.85$ | |
| 0.1 | 2-Layer | $a = 5.59, c = 4.85$ | |
| 0.2 | 2-Layer | $a = 5.58, c = 4.83$ | |
| 0.3 | 2-Layer | $a = 5.58, c = 4.81$ | |
|  | 9-Layer[b] | $a = 5.58, c = 21.1$ | Trace |
| 0.4 | 2-Layer | $a = 5.57, c = 4.81$ | |
|  | 9-Layer | $a = 5.57 \ c = 21.0$ | Trace |
| 0.5 | 2-Layer | $a = 5.55, c = 4.81$ | |
|  | 9-Layer | $a = 5.55, c = 20.95$ | Minor phase |
| 0.6 | 2-Layer | $a = 5.53, c = 4.81$ | Minor phase |
|  | 9-Layer | $a = 5.53, c = 20.60$ | |
| 0.7 | 2-Layer | $a = 5.52, c = 4.81$ | Last trace |
|  | 9-Layer | $a = 5.52, c = 20.60$ | Unresolved |
|  | 2-Layer[c] | $a = 5.52, c = 4.24$ | Unresolved |
| 0.8 | 9-Layer | $a = 5.51, c = 20.52$ | |
|  | 2-Layer | $a = 5.51, c = 4.24$ | |
| 0.9 | 9-Layer | $a = 5.49, c = 19.85$ | Minor phase |
|  | 2-Layer | $a = 5.49, c = 4.05$ | Major phase |
| 1.0 | 9-Layer | $a = 5.47, c = 19.73$ | Major phase |
|  | 2-Layer | $a = 5.47, c = 4.05$ | Trace |

[a] At each composition only one $a$ value given since $h k 0$ reflections were not resolved.

[b] Except at $x = 1.0$, there is no unambiguous X-ray evidence.

[c] This two-layer phase could be similar to Lander's "$Ba_3Ni_3O_8$," (*2*).

likely that under appropriate conditions this two-layer phase would be stable across the barium–strontium composition range. However, conditions suitable for preparing two-layer $BaNiO_3$ are not necessarily sufficient to preserve this phase when Sr is substituted for Ba. In our experience phases with much reduced layer spacings are produced. One of these may be a nine-layer structure, in which the continuous strings of face-sharing $NiO_6$ octahedra are replaced by corner-connected strings of three face-sharing octahedra. The other may be a phase of the compressed two-layer variety with oxygen deficiencies which would reduce the number of oxygen atoms coordinated to each nickel. At the strontium-rich end, these phases are close to those observed by Takeda and designated $Sr_2Ni_2O_5$. The "compressed" two-layer phase is probably analogous to the "$Ba_3Ni_3O_8$" reported by Lander and others (*2, 8, 9*).

A referee has noted the instability of $SrNiO_3$; oxygen-deficient variants of $SrNiO_3$ are obtained as decomposition products. It is clear that definitive answers to questions of identification would require suitable single crystals. Unfortunately, we have not succeeded in growing them.

### Acknowledgment

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