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Preparation and Thermochemical Properties of $BaNiO_{2+x}$

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Single crystals of $BaNiO_3$ have been synthesized in molten KOH. The enthalpies of formation from the component oxides at 25°C of $BaNiO_2$, $BaNiO_{2.63}$, and $BaNiO_3$ have been measured using high temperature reaction calorimetry. As the value of x increases in $BaNiO_{2+x}$, the enthalpy of formation becomes more exothermic. From the enthalpy of formation data, an enthalpy of oxidation of -196 ± 20 kJ/(mole O_2) was obtained. This value is very similar to the values of -202 ± 18 and -220 ± 50 kJ/(mole O_2) obtained for $YBa_2Cu_3O_{7-y}$ and $La_{2-x}Ba_xCuO_{4-y}$, respectively Z. Zhou, and A. Navrotsky, *J. Mater. Res.* 7(11), 2920 (1992); J. DiCarlo, J. Bularzik, and A. Navrotsky, *J. Solid State Chem.* 96, 381 (1992). Energetic and structural data are discussed in terms of a model in which the holes have significant oxygen character [A. Mehta, J. DiCarlo, and A. Navrotsky, *J. Solid State Chem.* 101, 173 (1992).] © 1994 Academic Press, Inc.

INTRODUCTION

Recently much attention has been focused on superconducting copper compounds with perovskite related structures. Generally, the highest critical temperature superconductors contain mobile holes. Whether the holes should be considered to reside predominantly on copper or oxygen atoms is still a matter of debate (4–7). Mehta *et al.* (3) proposed a model in which a fraction of the holes produced upon oxidation reside in peroxide-like states and cause contractions in O–O distances. Previous measurements of several barium-containing cuprates with perovskite related structures showed that they all had similar oxidation enthalpies. The result suggests that copper plays no unique role in the energetic properties of these materials but that the specific alkaline earth ion (barium) largely determines the magnitude of the energetic properties. It was previously found that perovskite related cuprates containing barium all had similar oxidation enthalpies. To further investigate this argument, the perovskite related phases $BaNiO_{2+x}$ have been measured for comparison with the copper system.

The $BaNiO_{2+x}$ system was first investigated by Lander (8). $BaNiO_3$ crystallizes with a perovskite related structure in which the BaO_3 layers are hexagonal closed packed. Nickel atoms occupy octahedral sites which share faces to form chains along the hexagonal c axis. The structure determination (12) indicates that some O–O distances are shorter (2.5 Å) than those normally observed in other ABO_3 perovskites. $BaNiO_3$ formally contains nickel in the oxidation state of +4 and is insulating and diamagnetic to 4 K (9). Single crystals of $BaNiO_3$ have previously been synthesized but only at high pressure (9).

The previous studies of $BaNiO_3$ show that it exists over a range of composition and therefore it is an excellent material to compare to the superconducting cuprate compounds. We have investigated the analogy between the energy of oxidation of $BaNiO_2$ to $BaNiO_3$ with the energy of oxidation of $YBa_2Cu_3O_6$ to $YBa_2Cu_3O_7$ and the oxidation of $La_{2-x}Ba_xCuO_{4-y}$ to $La_{2-x}Ba_xCuO_4$.

EXPERIMENTAL

Preparation of $BaNiO_3$

Single crystals of $BaNiO_3$ were prepared by a flux technique using molten KOH. Stoichiometric amounts of $BaCO_3$ (Aldrich reagent grade), and NiO (Aldrich 99.99%) were ground in an agate mortar, placed in a platinum crucible and heated for 24 hr at 900, 1000, and 1050°C with additional grinding after each heating. Approximately 400 mg of this material were then placed in a 100-ml alumina crucible with 50 g of KOH and 400 mg of $Ba(OH)_2 \cdot 8H_2O$ (Aldrich reagent grade). The crucible was then heated at 700°C for 24 hr and cooled at a rate of 0.33°C/min to room temperature. The KOH was slowly dissolved by adding deionized water. The undissoved material was filtered and

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found to be single crystals of $BaNiO_3$ with an average crystal size of 4 × 0.1 × 0.1 mm. Extra barium hydroxide was required to suppress the formation of NiO as a second phase. The formation of NiO was also observed when the concentration of nickel in the melt was increased.

Preparation of $BaNiO_2$ and $BaNiO_{2.63}$

$BaNiO_2$ was prepared by treating $BaNiO_3$ in a flow of predried nitrogen gas at 900°C. Approximately 50 mg of $BaNiO_3$ crystals were placed on a Dupont 951 thermobalance and purged with nitrogen gas at room temperature for approximately 30 min at a flow rate of 50 cm^3/min. The temperature was then raised at a rate of 10°C/min to 900°C and held at 900°C for 1 hr while maintaining the flow rate. Experiments were performed in triplicate. From the weight lost, the oxygen content was found to be 2.0 ± 0.02.

$BaNiO_{2.63}$ was prepared by treating $BaNiO_3$ at 900°C in an 80% N_2 : 20% O_2 atmosphere at a flow rate of 50 cm^3/min. The gases were predried and mixed using MKS electronic mass flow meters. Approximately 50 mg of $BaNiO_3$ were placed on the thermobalance and heated in the 80% N_2 : 20% O_2 atmosphere at a rate of 10°C/min to 900°C and held isothermal for 1 hr. Experiments were performed in triplicate. From the weight lost the oxygen content was found to be 2.63 ± 0.02.

Characterization of Products

Powder diffraction patterns were obtained with a Scintag XDS 2000 diffractometer using Cu*Kα* radiation. Phases were identified from diffraction data measured over the range $10° \leq 2\theta \leq 70°$ with the scan rate of 1°/min. All of the peaks in the diffraction pattern of $BaNiO_3$ and $BaNiO_2$ are in agreement with literature data (8). The results for $BaNiO_{2.63}$ can be indexed with a unit cell similar to that observed for $BaNiO_3$. However, the presence of oxygen vacancies introduces disorder into the lattice and is reflected in significant line broadening.

The oxygen content of $BaNiO_3$ was determined by a programmed temperature reduction cycle using a Dupont 951 thermobalance. Approximately 50 mg of sample were placed on the balance and purged at room temperature in a stream of 5% H_2 in nitrogen until a constant weight was reached. The flow rate of the gas was 50 cm^3/min. The temperature was then increased to 900°C at a rate of 10°C/min and held at 900°C for 1 hr. The reaction products were determined from X-ray analysis to be BaO and Ni metal. The oxygen stoichiometry of $BaNiO_3$ was ascertained from the weight loss on reduction to be 3.0 ± 0.02.

Calorimetry

Thermochemical measurements were performed in flowing air using a high temperature Tian Calvet twin calorimeter operating at 702°C. Molten lead borate ($2PbO \cdot B_2O_3$) was used as a solvent for solution calorimetry (details of the measurement techniques and thermochemical cycles employed are given elsewhere (2, 10)). The calorimeter was calibrated using the known value of the heat content of platinum. The final oxidation state of nickel atoms in the solvent was determined previously (11) to be +2 regardless of its formal oxidation state in the starting material. Materials which contain formal oxidation states of nickel greater than +2 liberate oxygen upon dissolution in lead borate at 702°C (11). Oxygen evolution is accounted for in the thermochemical cycle (see below).

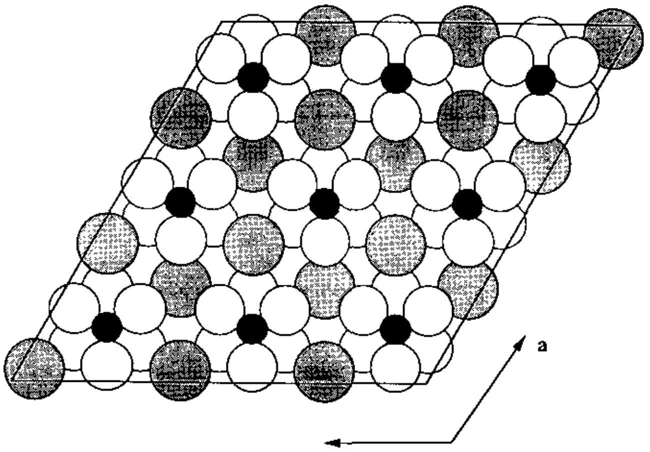

FIG. 1. Projection of the $BaNiO_3$ structure. Large shaded circles are barium, large empty circles are oxygen, and small shaded circles are nickel.

RESULTS AND DISCUSSION

$BaNiO_3$ crystallizes with a 2H hexagonal variant of the cubic perovskite structure (12). The compound is hexagonal, space group $P6_3/mmc$ with $a = 5.629$ and $c = 4.811$ Å. A projection of the structure looking down the *c* axis is shown in Fig. 1. Nickel atoms are octahedrally coordinated by oxygen atoms and the NiO_6 octahedra form a face-sharing chain along the *c* axis. The O–O distances in a NiO_6 octahedron are 2.466 Å within a BaO_3 layer and 2.795 Å between adjacent layers. The structure of $BaNiO_2$ is very similar to that of $BaNiO_3$ and is shown in the same orientation in Fig. 2. In $BaNiO_2$ the nickel atoms are in square–planar coordination and form zizag chains along the *c* axis. The square–planar NiO_4 chains in $BaNiO_2$ are obtained from the NiO_6 chains in $BaNiO_3$ by removing two oxygen atoms from *trans* vertices. In $BaNiO_2$, none of the O–O distances is uncharacteristically short (<2.7 Å). The intermediate compositions can be derived from $BaNiO_3$ or $BaNiO_2$ by progressive removal or addition of

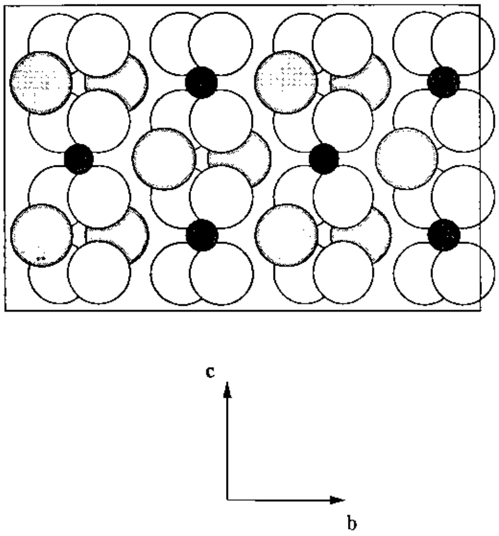

FIG. 2. Projection of the $BaNiO_2$. Large shaded circles are barium, large empty circles are oxygen, and small shaded circles are nickel.

oxygen atoms without substantially changing the positions of the other atoms in the structure. However, electron microscopy data suggest (13) that discrete phases may exist at some intermediate compositions as a result of oxygen vacancy ordering along the NiO_{6-x} chains. The X-ray data for our $BaNiO_{2.63}$ sample show no evidence for long range vacancy order.

Table 1 shows the thermochemical data for the $BaNiO_{2+x}$ compounds. The enthalpy of formation from the component oxides is obtained using the following thermodynamic cycle:

$$BaNiO_{2+x}(\text{xtl, 25°C}) \Rightarrow BaNiO_2\ (\text{soln, 702°C}) + x/2\ O_2\ (\text{g, 702°C}) \quad [1]$$

$$BaO\ (\text{xtl, 25°C}) \Rightarrow BaO\ (\text{soln, 702°C}) \quad [2]$$

$$NiO\ (\text{xtl, 25°C}) \Rightarrow NiO\ (\text{soln, 702°C}) \quad [3]$$

$$x/2\ O_2\ (\text{g, 25°C}) \Rightarrow x/2\ O_2\ (\text{g, 702°C}) \quad [4]$$

$$BaO\ (\text{xtl, 25°C}) + NiO\ (\text{xtl, 25°C}) + x/2\ O_2\ (\text{g, 25°C}) \Rightarrow BaNiO_{2+x}\ (\text{xtl, 25°C}). \quad [5]$$

The enthalpy of formation from the component oxides (reaction 5) is the sum of reactions [2], [3], and [4] minus reaction [1]. Reaction [1] represents the heat solution and the heat content from 25 to 702°C of the given compound, while reactions [2] and [3] are the corresponding values for BaO and NiO, respectively. Reaction [4] corrects for the heat content of O_2 (14).

Figure 3 shows the relationship between the enthalpy of formation from the component oxides and oxygen content for $BaNiO_{2+x}$. From Fig. 3 it appears that there is a linear relationship between the enthalpy of formation from the component oxides and oxygen content over the entire range between $BaNiO_2$ and $BaNiO_3$. From the slope of the line the enthalpy of oxidation represented by the reaction

$$BaNiO_2 + (x/2)\, O_2 \Rightarrow BaNiO_{2+x} \quad [6]$$

is -196 kJ/(mole O_2).

The magnitude of the enthalpy of oxidation of $BaNiO_{2+x}$ (-196 kJ/mole O_2) and its composition dependence resemble the corresponding data for $YBa_2Cu_3O_6$ and $La_{2-x}Ba_xCuO_{4-x/2}$ previously studied (1, 2). The enthalpy of oxidation of $YBa_2Cu_3O_{6+y}$ was found to be -202 ± 20 kJ/(mole O_2), and also there was a linear relationship between the enthalpy of formation from the component oxides and oxygen content from $YBa_2Cu_3O_6$ to $YBa_2Cu_3O_7$. In $La_{2-x}Ba_xCuO_{4-x/2}$, the enthalpy of oxidation was found to be -220 ± 50 kJ/(mole O_2). The enthalpy of oxidation of $BaNiO_{2+x}$ is different from the enthalpy of oxidation previously found for $La_{2-x}A_xNiO_{4-y}$ (A =

TABLE 1
Thermochemical Data for $BaNiO_{2+x}$

Compound	ΔH_{ds} (kJ/mole)[a]	ΔH_f(25°C)(kJ/mole)
NiO	$+69.9 \pm 0.8$ (7)[b]	—
BaO	-90.8 ± 2.2 (6)	—
$BaNiO_{2.00}$	$+11.1 \pm 2.2$ (4)	-32.0
$BaNiO_{2.63}$	$+76.3 \pm 5.4$ (4)	-90.4
$BaNiO_{3.00}$	$+121 \pm 3.3$ (4)	-131

[a] ΔH_{ds} represents the enthalpy of drop solution (see Ref. [1]). ΔH_f is the enthalpy of formation from the component oxides at 25°C. The heat content of O_2 used to calculate ΔH_f is 21.9 (kJ/mole O_2) (14).

[b] Uncertainty is 2 s.d. of mean, value in ( ) is number of experiments.

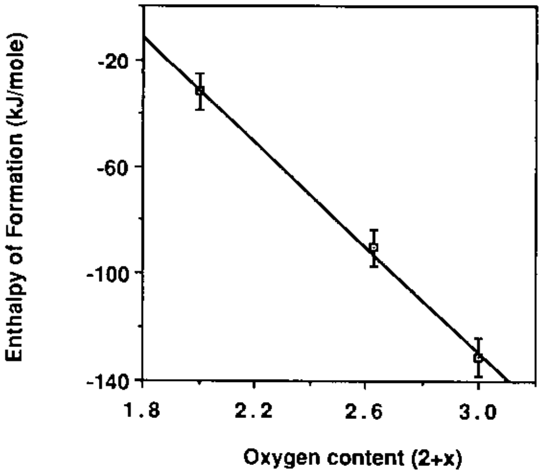

FIG. 3. Enthalpy of formation from the component oxides versus oxygen content for $BaNiO_{2+x}$.

Ba, Sr) (11) and $La_{2-x}Sr_xCuO_{4-x/2}$ (2). In these studies, the enthalpies of oxidation were found to be −296 ± 36 kJ/(mole O_2) and −129 ± 20 kJ/(mole O_2) for vacancy filling oxidation processes of the nickelate and cuprate, respectively.

The energetic arguments made previously (3, 11) suggest that the holes in the compounds $YBa_2Cu_3O_{7-x}$, $La_{2-x}Ba_xCuO_{4-y}$, and $BaNiO_{2+x}$ all reside in similar energy states (barium peroxide-like states) which are different in energy from the hole states of $La_{2-x}Sr_xCuO_{4-y}$ (strontium peroxide-like states) and $La_{2-x}A_xNiO_{4-y}$ (A = Ba, Sr)(Ni^{3+} states). If the hole states in $BaNiO_{2+x}$ system are in peroxide-like states, a contraction in the O–O bond distances would be expected based on the simple counting formula proposed by Mehta *et al.* (3). Application of the counting formula to the structural data of $BaNiO_3$ (8) predicts that holes added above the formal oxidation state of $Ni^{+2.48}$ produce O–O contractions. This result is consistent with the previous study on $La_{2-x}A_xNiO_{4-y}$ (A = Ba, Sr) (11) which suggested that holes reside predominantly on nickel for oxidation states $2 \leq y \leq 2.4$. Thus, we suggest that if the formal oxidation state of nickel in La_2NiO_4 could be made higher than +2.48, the holes formed would go primarily on oxygen atoms, causing contractions in the O–O distances. We are currently testing this hypothesis.

CONCLUSION

Synthesis of relatively large amounts (0.4 g) of pure single crystals of $BaNiO_3$ can easily be accomplished by the use of a molten salt method where KOH is used as a flux. Thermochemical and structural studies have shown that the trends in the energetic properties of $BaNiO_{2+x}$ and the superconducting $La_{2-x}Ba_xCuO_{4-y}$ and $YBa_2Cu_3O_{7-y}$ systems are similar.

ACKNOWLEDGMENTS

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