Chem. Mater. **1991,** *3,* 1060–1063

Synthesis of Nickel Cobaltite Spinel from Coprecipitated Nickel–Cobalt Hydroxide Carbonate

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Received May 14, 1991. Revised Manuscript Received July 12, 1991

A nickel–cobalt hydroxide carbonate precursor for the synthesis of nickel cobaltite was obtained by a coprecipitation technique. Thermal analysis and IR spectroscopy were used in the characterization of the basic carbonate and in the evaluation of some aspects of the spinel formation mechanism. The thermal decomposition of precursors with different Ni/Co ratio yields solid solutions $Ni_xCo_{3-x}O_4$, $0 < x < 1$ with a spinel structure and of high dispersity. The unit-cell parameter of $NiCo_2O_4$ synthesized at 570 K is 0.810 (6) nm. The specific surface area measured by the BET method is 90 m^2/g, and the particle sizes range from 8.0 to 12.0 nm. A temperature-programmed reduction with hydrogen is also performed, and the resulting spectrum is interpreted.

Introduction

Among the binary cobaltites of transition metals with the general formula $MeCo_2O_4$, where Me is a divalent cation of a d element, nickel, copper, and zinc cobaltites are of definite interest due to their catalytic activity in complete oxidation reactions[1] and their application as oxide electrode materials.[2-4] The high activity of nickel cobaltite in the oxidation of saturated, aromatic hydrocarbons[5] and carbon monoxide allows its application as a catalyst for the neutralization of waste gases from diesel internal-combustion engines. In this connection, it is important to obtain a material with a high specific surface area. This is achieved by using different precursors which should ensure the preset stoichiometry and the absence of impurities as well as homogeneity and high dispersion of the final product. Until now coprecipitated oxalates,[6] hydroxide nitrates,[7] and complexes such as hydrazine carboxylate hydrates, acetate hydrazines, and oxalate hydrazinates[8-10] have been used as precursors for the synthesis of nickel cobaltite. Spinels with a high specific surface area above 50 m^2/g have been obtained by the first two methods. Nevertheless, in the use of oxalates special care must be taken to avoid the reduction to elementary cobalt or CoO. The third method using complex compounds has been applied even more successfully with other binary spinels, e.g., Zn, Mg, Mn, and Fe cobaltites, but in the case of nickel cobaltite, samples with lower specific surface areas (12.5 m^2/g are obtained. The application of other hydroxide salts as precursors to spinel cobaltites is of interest. The choice of a suitable precursor is restricted by the low thermal stability of the binary cobaltites, which decompose, evolving oxygen and MeO above a certain temperature, in the range 620–1050 K. The relative cobalt content increases in the remaining decomposed spinel phase. The hydroxide carbonates obtained by coprecipitation have some advantages in comparison with the above-mentioned precursors: they decompose at a low temperature without evolving toxic gases.[11,12] In addition, no oxidation medium is required as is the case with the oxalates.

The possibility of synthesis of nickel cobaltite as a high-dispersity material, using coprecipitated nickel–cobalt hydroxide carbonate as a precursor is studied in the present paper.

Experimental Section

Hydroxycarbonates with different Ni/Co ratios ranging from 0 to 0.5 were prepared by coprecipitation from solutions of Ni(II) and Co(II) nitrates. The coprecipitation process is performed as follows: a solution containing Ni(II) and Co(II) nitrates was heated to 340–350 K and was added rapidly with continuous stirring into a Na_2CO_3 solution having a concentration of 1.4 mol/dm^3 and pH 9, heated to the same temperature. To ensure a constant pH during the coprecipitation, the sodium carbonate solution had a volume twice as large as that of the nitrate solutions. The precipitate was formed immediately and remained in the mother solution, which was stirred for 30 min at the same temperature. After cooling, the precipitate was filtered, washed with hot water until negative reaction for nitrate ions was obtained, and then dried at 380 K for 24 h.

The hydroxide carbonates were decomposed at various temperatures ranging from 570 to 770 K to spinel oxides with different Ni content. The samples were characterized by the following methods: (a) Chemical analysis of the coprecipitated hydroxide carbonates for carbonate content by gravimetrical determination of the CO_2 evolved during thermal decomposition; the CO_2 was absorbed by natron asbestos. (b) Atomic absorption analysis of nickel and cobalt in the hydroxide carbonate samples and X-ray fluorescence analysis of the two elements in the final spinel products. (c) Thermal analysis of the nickel–cobalt hydroxide carbonate and the pure Ni and Co hydroxide carbonates, obtained by the same method, in air at a heating rate of 10 K/min. (d) IR spectroscopy in KBr using a Perkin-Elmer 983 G spectrometer. (e) X-ray analysis using a Dron 3 diffractometer with Cu $K\alpha$ monochromatic radiation. (f) BET method for specific surface area measurements. (g) TEM (transmission electron microscopy) for determination of the mean particle size using a JEOL 100. (h) Temperature-programmed reduction (TPR) with hydrogen at a heating rate of 25 K/min.

Results and Discussion

The nickel–cobalt hydroxide carbonate was obtained as a violet-blue colored amorphous precipitate, hydrated to a certain extent. The DTA and DTG plots (Figure 1)

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(1) Golodetz, G. *Heterogennokataliticeskie reakcii s ycastiem moleculjarnogo kisloroda*; Naukova Dumka: Kiev, 1977, pp 198, 258 (Russian).

(2) Tarasevich, M. R.; Effremev, B. N. *Electrodes of Conductive Metallic Oxides*; Trasatti, S., Ed.; Elsevier: New York, 1980; p 221.

(3) Carapuca, H. M.; Pereira, M.; Da Costa, F. *Port. Electrochim. Acta* **1989,** *7,* 11.

(4) Singer, J.; Fielder, W. *J. Power Sources* **1990,** *29,* 443.

(5) Papadatos, K.; Shelstad, K. A. *J. Catal.* **1973,** *28,* 116.

(6) Peshev, P.; Toshev, A.; Gyurov, G. *Mater. Res. Bull.* **1989,** *24,* 33.

(7) Markov, L.; Petrov, K. *Reactiv. Solids* **1986,** *1,* 319.

(8) Mahesh, G.; Patil, K. *Reactiv. Solids* **1987,** *4,* 117.

(9) Ravindranathan, P.; Mahesh, G.; Patil, K. *J. Solid State Chem.* **1987,** *66,* 20.

(10) Patil, K. C.; Gajpathy, D.; Pai Verneker, V. *J. Mater. Sci. Lett.* **1983,** *2,* 272.

(11) Klissurski, D. G.; Uzunova, E. L. *J. Mater. Sci. Lett.* **1990,** *9,* 576.

(12) Klissurski, D. G.; Uzunova, E. L. *J. Mater. Sci. Lett.* **1990,** *9,* 1255.

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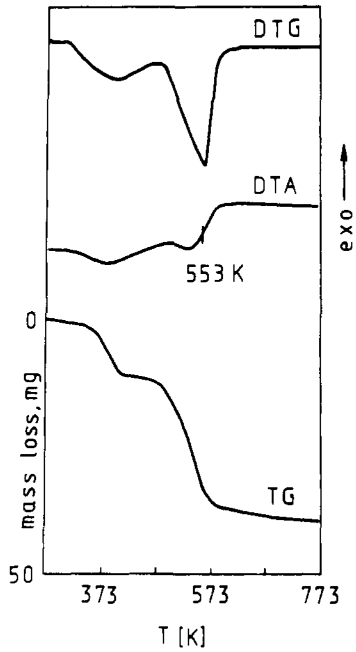

Figure 1. TG, DTG, and DTA of coprecipitated nickel–cobalt hydroxide carbonate, $NiCo_2(OH)_3(CO_3)_{1.5}\cdot 1.74H_2O$.

exhibit two endothermal transitions at 380 and 553 K, the former being due to the evolution of hydration water and the latter to thermal decomposition of the hydroxide carbonate, accompanied by evolution of carbon dioxide and water. Simultaneously, oxidation of the Co(II) ions to Co(III) proceeds and compensates for the endothermal effect of decomposition, which as a result is weak. The same behavior is exhibited by the pure cobalt hydroxycarbonate, whose thermal dissociation takes place at 503 K. In the case of nickel hydroxycarbonate this transition is established at higher temperature, 563 K.

The basic carbonates of nickel and cobalt are amorphous compounds; this is also the case for the mixed nickel–cobalt hydroxide carbonate. Depending on the conditions of coprecipitation, this compound can have different OH^-/CO_3^{2-} ratios. The weight loss during the second endothermal transition is 21.4%. Taking into account the results from atomic absorption analysis and the CO_2 content, a $NiCo_2(OH)_3(CO_3)_{1.5}\cdot 1.74H_2O$ formula can be ascribed to the precursor for synthesis of $NiCo_2O_4$.

The IR spectrum of the coprecipitated compound, Figure 2, contains the bands characteristic for the CO_3 group vibrations, valid for a mono- or polydentate CO_3 ligand,[13] and is rather similar to the spectra of pure nickel and cobalt hydroxide carbonates.[14-16] At 3440 (strong) and 1630 cm^{-1} (shoulder), the vibrational and bending modes of adsorbed water molecules are registered. The carbonate group vibrations are observed at 1531 (str, ν_{OCO_2}), 1406 (str, ν_{CO_3}), 1095 (sh, $\nu_{C=O}$), 830 (sharp, δ_{CO_3}), 745 (m, δ_{OCO}) and 682 cm^{-1} (m, ρ_{OCO}). The band at 976 cm^{-1} (weak) can be ascribed to δ_{M-OH} bending vibrations, while that at 520 cm^{-1} is caused by $\rho_{w(MOH)}$ vibrations. In the range 450–350 cm^{-1} the ν_{MO} frequencies appear, where M = Ni, Co.

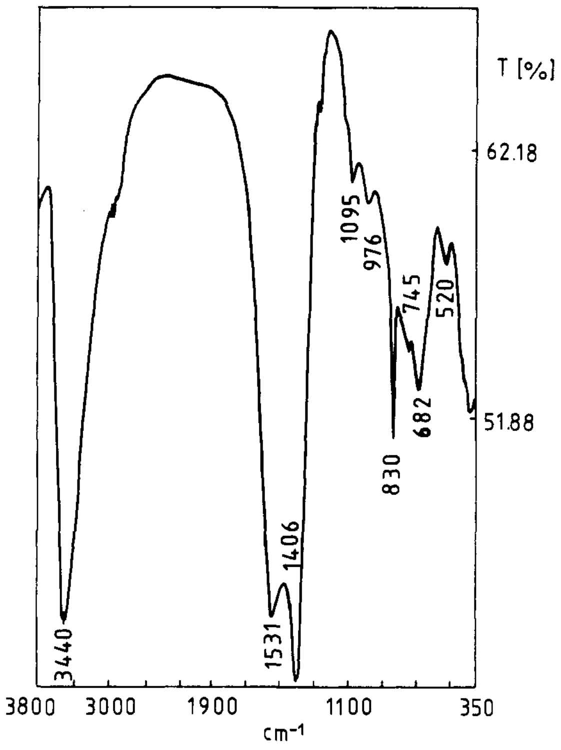

Figure 2. IR spectrum of nickel–cobalt hydroxide carbonate.

Table I. Ni and Co Contents in Synthesized $Ni_xCo_{3-x}O_4$ Samples According to X-ray Fluorescence Analysis Data and Specific Surface Areas

nominal spinel composition	Ni,[a] wt %	Co,[a] wt %	*S*, m^2/g
$Ni_{0.2}Co_{2.8}O_4$	5.1 (4.88)	68.4 (68.54)	
$Ni_{0.4}Co_{2.6}O_4$	10.0 (9.75)	63.5 (63.65)	56
$Ni_{0.6}Co_{2.4}O_4$	14.8 (14.64)	58.5 (58.77)	63
$Ni_{0.8}Co_{2.2}O_4$	19.3 (19.55)	53.5 (53.88)	70
$Ni_{0.9}Co_{2.1}O_4$	21.5 (21.96)	51.1 (51.44)	82
$NiCo_2O_4$	24.2 (24.40)	48.6 (48.99)	90

[a] The values given in brackets correspond to the nominal Ni/Co ratio.

The IR spectra of nickel–cobalt hydroxide carbonate at different stages of thermal decomposition permit an insight into the spinel formation mechanism, as the short-range order in the material under investigation may be recognized in this way. The partly decomposed basic salt shows new strong bands at 570 (strong) and 444 cm^{-1} (medium). The first one corresponds to the BOB_3 vibrations in the spinel lattice (B, metal cation in octahedral coordination) and the second to ν_{NiO} vibrations.[17] Since the crystal structure formation is not yet complete, it may be concluded that an intermediate of randomly oriented octahedra precedes the formation of the spinel structure. Further heating causes diminishing of the carbonate bands and of the ν_{NiO} band as well, and a band at 645 cm^{-1}, due to AOB_3 vibrations, appears (A, metal cations in tetrahedral coordination). The IR spectrum of the final spinel product contains only two bands at 645 and 563 cm^{-1} of approximately equal intensities (Figure 3).

Upon variance of Ni/Co ratio in the initial nitrate solutions between 0 and 0.5, hydroxide carbonates are precipitated, from which, after thermal decomposition, spinel products $Ni_xCo_{3-x}O_4$ with different *x* values are obtained. The Ni and Co content determined by X-ray fluorescence analysis are shown in Table I. The spinel unit cell parameter of the stoichiometric $NiCo_2O_4$ sample is 0.810 (6) nm. Both in the X-ray patterns and in the IR spectra no

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(13) Busca, G.; Lorenzelli, V. *Mat. Chem.* **1982**, *7*, 89.

(14) Nakamoto, K. *Infrared and Raman Spectroscopy of Inorganic and Coordination Compounds*; Wiley: New York, 1978; p 380.

(15) Minkova, M.; Krusteva M.; Nikolov, G. *J. Mol. Struct.* **1984**, *115*, 23.

(16) Baraldi, P.; Davolio, G.; Fabbri, G.; Manfredini, T. *Mater. Chem. Phys.* **1989**, *21*, 479.

(17) Farmer, V. C. *Infrared Spectra of Minerals*; Mineralogic Society: London, 1974; p 189.

Figure 3. IR spectra of nickel–cobalt hydroxide carbonate at intermediate stages of thermal decomposition: (a) after heating at 515 K for 20 min; (b) after heating at 555 K for 20 min.

byproducts are established over the whole range of possible x values. Comparison with the nominal value of Ni/Co ratio shows that the use of co-precipitated hydroxycarbonates as precursors allows attaining of the desired stoichiometry in the final spinel product over the whole range of x values.

The temperature interval of stability of nickel cobaltite is, however, limited and depends on the nickel ion concentration in the spinel structure. Above 870 K, $NiCo_2O_4$ is no longer stable, and nickel oxide traces are registered in the diffractograms. A phase segregation process begins that leads to a spinel with lower Ni content and a NiO phase.

The concentration interval of the nitrate and alkali-metal carbonate solutions is limited to the range 0.15–1.2 mol/dm^3 M^{2+} and 0.4–2.0 mol/dm^3 Na_2CO_3. The use of more diluted solutions leads to a gellike precipitate with higher OH^-/CO_3^{2-} ratio, from which, after thermal decomposition spinel products of lower dispersity were obtained with specific surface areas below 65 m^2/g. At higher nitrate salt concentrations, the precipitate is contaminated with adsorbed nitrate ions, which are recognized in the IR spectra by the sharp band at 1372 cm^{-1}, partly overlapping the CO_3 band in the same region.

The cobaltites obtained have a high specific surface area and consist of particles with shapes close to the spherical and sizes between 8.0 and 12.0 nm. The specific surface area of $NiCo_2O_4$ synthesized at 570 K reaches 90 m^2/g and depends on the temperature of synthesis as shown in Figure 4. As expected, a decrease of Ni content in the samples brings about a lowering of the specific surface area, as shown in Table I.

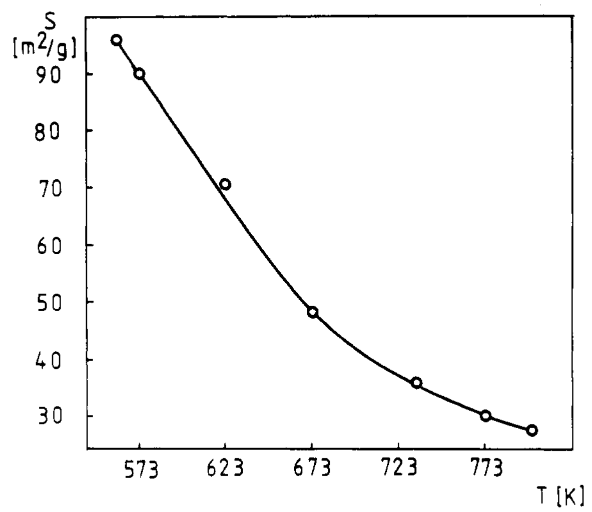

Figure 4. Dependence of the specific surface area of nickel cobaltite on the temperature of synthesis.

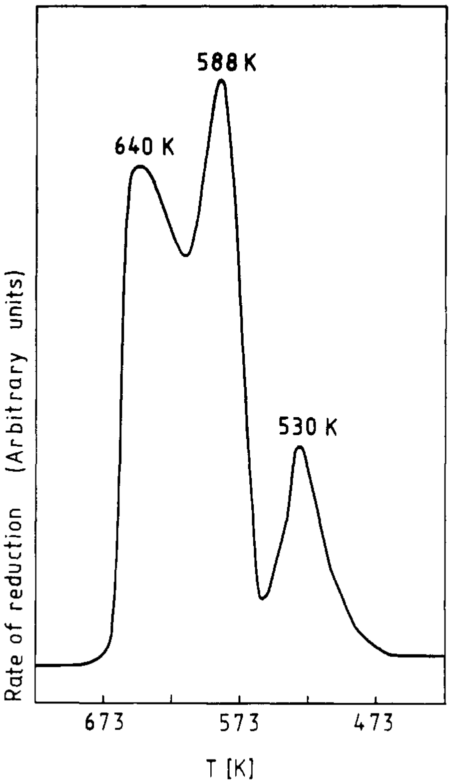

Figure 5. TPR spectrum of $NiCo_2O_4$.

Since the Ni–Co–O system is used in different catalytic reactions and electrochemical processes, an important characteristic of the synthesized spinel compound is the TPR spectrum, Figure 5. In the temperature interval 300–1000 K three peaks are distinguished that probably correspond to the consecutive stepwise reduction of Ni^{2+}, Co^{3+}, and Co^{2+} cations, statistically distributed among tetrahedral and octahedral spinel positions. The peaks with maxima at 588 and 640 K may be due to the reduction steps $Co^{3+} \rightarrow Co^{2+}$ and $Co^{2+} \rightarrow Co$. The latter two peak maxima values are in accordance with the data for pure Co_3O_4 (593 K and 663 K), reported in ref 18. The first peak with maximum at 530 K eventually corresponds to the reduction of Ni^{2+} cations. Another possible interpretation is that the three maxima account for the reduction

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(18) Bhatia, S.; Beltramini, J.; Do, D. D. *Catal. Today* **1990**, *7*, 360.

of surface, tetrahedral, and octahedral sites of the spinel structure.

Conclusion

Nickel–cobalt hydroxide carbonate obtained by coprecipitation with Na_2CO_3 at pH 9 is an appropriate precursor in the synthesis of nickel cobaltite. The thermal decomposition is performed at low temperatures, and as a result spinel products of high dispersity are obtained, with no impurities being found in the IR spectra and X-ray diffractograms. Cobaltites with a preset stoichiometry are obtained, possessing a thermal stability over a considerably wide temperature interval (up to 870 K).

Acknowledgment. Special thanks are due to Dr. L. Minchev from the Institute of Kinetics and Catalysis for the temperature-programmed reduction experiment.

Registry No. $NiCoO_4$, 12017-35-5; $NiCo_2(OH)_3(CO_3)_{1.5}\cdot 1.74H_2O$, 136826-96-5; $Ni(NO_3)_2$, 13138-45-9; $Co(NO_3)_2$, 10141-05-6; Na_2CO_3, 497-19-8; $Ni_{0.2}Co_{2.8}O_4$, 136826-94-3; $Ni_{0.4}Co_{2.6}O_4$, 136826-93-2; $Ni_{0.6}Co_{2.6}O_4$, 136826-92-1; $Ni_{0.8}Co_{2.2}O_4$, 136826-91-0; $Ni_{0.9}Co_{2.1}O_4$, 136826-90-9; nickel–cobalt hydroxide carbonate, 136826-89-6.

Effect of Isomeric Ions on the Contact Charge of Polymers

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Received May 16, 1991. Revised Manuscript Received August 9, 1991

The contact charge of styrene-*co*-butyl methacrylate powder containing a small fraction of a styrene-*co*-*N*-methylvinylpyridinium toluenesulfonate is found to depend on whether the nitrogen in the vinylpyridinium cation is ortho or para to the polymer chain. This is a particularly interesting result because the contact charge is proposed to develop from the transfer of the toluenesulfonate anion (OTs^-) to the second surface, thus, giving it a negative charge while the powder develops a positive charge. The cation is not involved in the transfer, yet it clearly affects the mobility and transfer of the anion. These results are explained in terms of differences in ion aggregation in this highly nonpolar medium.

Introduction

When two dissimilar materials are contacted and then separated, opposite sign charges are often generated on the two surfaces. This phenomenon has been widely observed, and in the specific case of two metals, it is generally accepted that contact charging occurs by electron transfer, where the direction of the transfer is determined by the relative Fermi levels.[1] In polymers, charge transfer is often attributed to electron transfer;[2-8] however, in the case with polymer blends containing a minor amount of *N*-methylpyridinium toluenesulfonate ions where the cation is "anchored" to the polymer by covalent bonding and the anion is mobile, the charging behavior is more readily explained by ion transfer.[9-11] The conclusion was based on the observation of a sulfur signal for the toluenesulfonate anion (OTs^-) on the surface of the second surface by XPS after the contact, and the correspondence between the sign of the charge and of the ion (negative). Thus, the polymer blend acquires the charge of the "anchored" cation (positive), and the second surface acquires the charge of the mobile ion (negative). This result is not limited to polymer-bound ions (ionomers). Similar results were observed with a polymer containing cetylpyridinium bromide.[12] This polymer charged positively against indium while the indium acquired a negative charge. SIMS analysis of the indium surface after the contact revealed the presence of both the cation and the anion (both mobile); however, the anion content was much greater. These results were explained by ion transfer where the sign reflected the higher mobility of the Br^- ion. In contrast with these studies, earlier reports with organic materials (molecular and polymer) explained the charging in terms of electron transfer because of the correlation between the charge and a substituent parameter for a series of substituted structures.[3,13] Even the charging results with ionomers containing methyltriphenylphosphonium arylsulfonate ions were explained by electron transfer because the charge correlated with a substituent parameter and because of the mismatch between the sign of the charge

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(1) Harper, W. R. *Contact and Frictional Electrification*; Oxford University Press: Oxford, 1967.

(2) Nanya, T.; Tsubuko, K. *Japan Hardcopy '88, The Society of Electrophotography of Japan, 30th Conference*, 1988, 9.

(3) Gibson, H. W. *J. Am. Chem. Soc.* **1975**, *97*, 3832.

(4) Gruber, R. J. *SID 87 Digest* **1987**, 272.

(5) Matsui, N.; Oka, K.; Inaba, Y., *The Sixth International Congress on Advances in Non-Impact Printing Technologies Black and White and Color* **1990**, 45.

(6) Duke, C. B.; Salaneck, W. R.; Fabish, T. J.; Ritsko, J. J.; Thomas, H. R.; Paton, A. *Phys. Rev. B* **1978**, *28*, 5717.

(7) Duke, C. B.; Fabish, T. J. *J. Appl. Phys.* **1978**, *49*, 315.

(8) Gibson, H. W. *Polymer* **1984**, *25*, 3.

(9) Diaz, A.; Fenzel-Alexander, D.; Miller, D. C.; Wollmann, D.; Eisenberg, A. *J. Polym. Sci., Polym. Lett. Ed.* **1990**, *28*, 75.

(10) Diaz, A.; Fenzel-Alexander, D.; Wollmann, D.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.*, in press.

(11) Unpublished results from this laboratory.

(12) Mizes, H. A.; Conwell, E. M.; Salamida, D. P. *Appl. Phys. Lett.* **1990**, *56*, 1597.

(13) Cressman, P. J.; Hartmann, G. C.; Kuder, J. E.; Saeva, F. D.; Wychick, D. *J. Chem. Phys.* **1974**, *61*, 2740.