Physical Properties of the Nonstoichiometric Perovskite $Dy_{1-x}Sr_xCoO_{3-y}$ System

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Solid solutions of the nonstoichiometric $Dy_{1-x}Sr_xCoO_{3-y}$ system with the compositions of $x=0.00$, 0.25, 0.50, 0.75, and 1.00 have been synthesized by the solid state reaction at 1000 ℃ under atmospheric air pressure. The crystallographic structures of the solid solutions are analyzed by the powder X-ray diffraction patterns at room temperature. The analyses assign the compositions of $x=0.00$ and 0.25 to the orthorhombic system with space group of $Pbnm/D_{2h}{}^{16}$, the compositions of $x=0.50$ and 0.75 to the tetragonal system like a typical $SrCoO_{2.86}$, and the composition of $x=1.00$ or $SrCoO_{2.50}$ to the brownmillerite type system with space group of $I**a$. The reduced lattice volumes increas with x value due to the larger radius of Sr^{2+} ion than that of Dy^{3+} ion. The mole ratio of Co^{4+} ion to total Co ion with mixed valence state between Co^{3+} and Co^{4+} ions at B sites or τ value has been determined by an iodometric titration. All the samples except for the $DyCoO_3$ compound show the mixed valnce state and thus the composition of $x=0.50$ has the maximum τ value in the system. The oxygen vacancies increasing with x value are randomly distributed over the crystal lattice except for the composition of $x=1.00$ which have the ordering of the oxygen vacancies. The nonstoichiometric chemical formulas of the $Dy_{1-x}Sr_xCo^{3+}{}_{1-\tau}Co^{4+}{}_\tau O_{3-(x-\tau)/2}$ system are formulated from the x, τ, and y values. The electrical conductivity in the temperature range of 100 to 900 K increases with the τ value linearly because of positive holes of the Co^{4+} ions in π^* band as a conducting carrier. The activation energy of the $x=0.50$ as $E_a \cong 0.17$ eV is minimum among other compouds. Broad and high order transition due to the overlap between σ^* and π^* bands broadened by the thermal activation is observed near 1000 K and shows a low temperature-semiconducting behavior. Magnetic properties following the Currie-Weiss law show the low to high spin transition in the cobaltate perovskite. Especially, the composition of $x=0.75$ presents weak ferromagnetic behavior due to the Co^{3+}-O^{2-}-Co^{4+} indirect superexchange interaction.

Introduction

Various funtional properties of perovskite-type oxides (ABO_3) have been extensively studied in the aspect of total cations substitutions at A and/or B sites by many investigators.[1~13] The unique properties due to the mixed valence state of B ion and the oxygen vacancies are usually controlled by the substitution of lower valence cations such as Ca^{2+}, Sr^{2+}, and Ba^{2+} ions in place of La^{3+} ions in A sites as well as heating temperature and oxygen pressure. In the systems such as rare-earth chromites, manganites, and ferrites, d-electrons are localized. Whereas, in $LnCoO_3$ system,[2] since crystal field energy and exchange energy are similar, the low spin and high spin states can coexist. Thus, the $LnCoO_3$ systems are most interesting in the study of the B cation states which may be applicable in the catalytic process.

Raccah and Goodenough reported that the $LaCoO_3$ system with some unique electrical and magnetic properties shows the first order transition between localized and collective electrons at 1210 K.[1] Thornton suggested the high-order transition at the high temperature metallic phase resulted from the overlap of the primarily occuppied Co 3d derived $\pi^*(t_{2g})$ and empty $\sigma^*(e_g)$ bands.[5,9] Bhide *et al.* reported a detailed investigation for the novel oxide system of $La_{1-x}Sr_xCoO_3$ ($0.00 \leq x \leq 0.50$) which was partially substituted by Sr^{2+} ions and a 180° superexange interaction by covalent mixing between the transition metal d and oxygen 2p orbitals.[2] Through Mössbauer study in the composition of $0.125 \leq x \leq 0.50$, it is proved that the ferromagnetism occurs in the $La_{1-x}Sr_xCoO_3$ with the Sr^{2+}-rich regions and paramagnetism with the La^{3+}-

rich regions.

The $SrCoO_{2.50}$ compound prepared at 1000 ℃ in air atmospheric has the brownmillerite structure with the space group $I**a$ and antiferromagnetic ordering below the Néel temperature of 570 K,[14] and the cobalt ions in the octahedal sites are in only high spin Co^{3+} ion ($s=2$) due to the small crystal fields in loose lattice.

In the present study, the solid solutions of the nonstoichiometric $Dy_{1-x}Sr_xCoO_{3-y}$ ($x=0.00$, 0.25, 0.50, 0.75, and 1.00) system were synthesized and their structures were analyzed by the X-ray powder diffraction method. The nonstoichiometric formulas for the $Dy_{1-x}Sr_xCo^{3+}{}_{1-\tau}Co^{4+}{}_\tau O_{3-y}$ system were determined by iodometric titration. Their electrical and magnetic properties are discussed on the bases of the structures and nonstoichiometric compositions.

Experimental

The compounds of the $Dy_{1-x}Sr_xCoO_3$ system with the compositions of $x=0.00$, 0.25, 0.50, 0.75, and 1.00 have been prepared with the starting materials such as spectroscopically pure $Co(NO_3)_2 \cdot 6H_2O$, Dy_2O_3, and $SrCO_3$ by the ceramic method or solid-state reaction. Appropriate amounts of the mixtures are dissolved in diluted nitric acid and evaporated in a sand bath and then decomposed at 800 ℃ for 4 hrs. The heating at 1000 ℃ for 24 hrs, weighing, and grinding processes are repeated several times in order to produce homogeneous solid solution. The crystallographic structures are analyzed by the powder X-ray diffraction with monochromatized Cu $K\alpha$ ($\lambda=1.5406$ Å) radiation at room temperature.

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The iodometric titration has been carried out to determine the oxidation state of cobalt ion in each solid solution. The I_2 molecules will be produced when Co^{3+} and Co^{4+} ions are all reduced into Co^{2+} ions in excess KI and dilute HCl solution. The I_2 concentration has been titrated by the potentiometric method in the N_2 atmosphere in order to prevent any oxidation of the I^- ion with the oxygen in air. Thus the mixed valence state between Co^{3+} and Co^{4+} ions or the τ value can be calculated from the titration.

Electrical conductivities are measured by means of a four probe dc-technique using Kiethley Model 236 Source Measure Unit (SMU) at temperature range of 100 to 900 K in the air. For the measurement of electrical conductivities, each powder sample is pressed into a pellet under a pressure of 3 ton/cm², and the pellets are sintered under the same preparation condition. Magnetic susceptibilities of all powder sample are also measured by Faraday method with DSM-8 apparatus at the condition of zero field cooling.

Results and Discussion

In this work, the $Dy_{1-x}Sr_xCoO_{3-y}$ system with the compositions of $x=0.00$, 0.25, 0.50, 0.75, and 1.00 were found to be homogeneous by X-ray powder diffraction analysis. The XRD patterns of all compositions are shown in Figure 1. The spectra analyses assigned the compositions of $x=0.00$ and 0.25 to the orthorhombic system as a distorted prerovskite-type structure with the space group $Pbnm/D_{2h}^{16}$, the compositions of $x=0.50$ and 0.75 to the tetragonal system, and the composition of $x=1.00$ to the brownmillerite type with space group of $I^{**}a$. The brownmillerite-type compound contains ordered oxygen vacancies which result in alternating layers of the distorted octahedral and tetrahedral sites along the b-axis.[15,16] Since the $SrCoO_3$ itself is not stable at 1000 °C in air, it
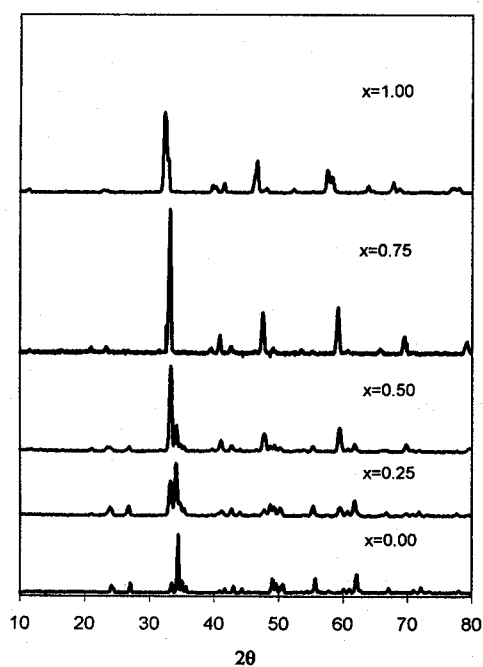
losses oxygen down to approximately $SrCoO_{2.50}$ for the electrical neutrality.[8] In general, B cations are octahedrally coordinated with oxygen ions and thus, they form bonding with a d^2sp^3 hybridized orbital.

Lattice parameters, reduced lattice volume, and crystal system for the $Dy_{1-x}Sr_xCoO_{3-y}$ system are listed in Table 1. The reduced lattice volume of the system increases with x value as shown in Figure 2. The substitution of the larger Sr^{2+} ion (158 pm) in place of the Dy^{3+} ion (105.2 pm) enhances the volume of unit cell and the tilting of oxygen octahedra decreases as the content of Sr^{2+} ions increases. This system followed the Vegard rule which is show the linearty of the lattice constant as Sr^{2+} ion substitute. The increase in lattice constant is caused by two factors: increase of oxygen deficiencies and the content of Sr^{2+} ions. The decrease in lattice constant is caused by the difference in ionic radii between Co^{3+} (HS; 75 pm, LS; 68.5 pm) and Co^{4+} (67 pm) ions. The Co^{4+} ion is formed due to a relatively deep acceptor Sr^{2+} ion and the Co^{4+} ion formed exist as low-spin state in an isolated six-coordinated site of an oxide lattice by Buffat *et al.*[19] However, the XRD data in Table 1 show that the lattice constant has influence on the increasing factor rather than the decreasing factor.[16]

The mole ratio of Co^{4+} ion (τ), oxygen vacancy (y) and the nonstoichiometric chemical formulas are listed in Table 2. The samples are all oxygen nonstoichiometric compounds except for the composition of $x=0.00$ with the stoichiometric formula. The oxygen vacancies for the compositions of 0.25 $\leq x \leq 0.75$ are randomly distributed in the unit cell. In the

Table 1. Lattice Parameters, Reduced Lattice Volume, and Crystal system for the $Dy_{1-x}Sr_xCoO_{3-y}$ System

x	Lattice parameter (Å)			Reduced lattice volum (Å³)	Crystal system
	a	b	c		
0.00	5.178	5.418	7.394	51.86	Orthorhombic
0.25	5.180	5.427	7.410	52.03	Orthorhombic
0.50	7.619	—	15.300	55.37	Tetragonal
0.75	7.660	—	15.387	56.42	Tetragonal
1.00	5.468	15.748	5.575	60.01	Orthorhombic

Figure 1. X-ray diffraction patterns of the $Dy_{1-x}Sr_xCoO_{3-y}$ system.
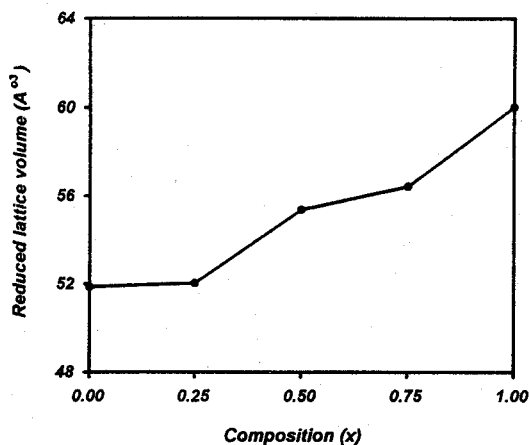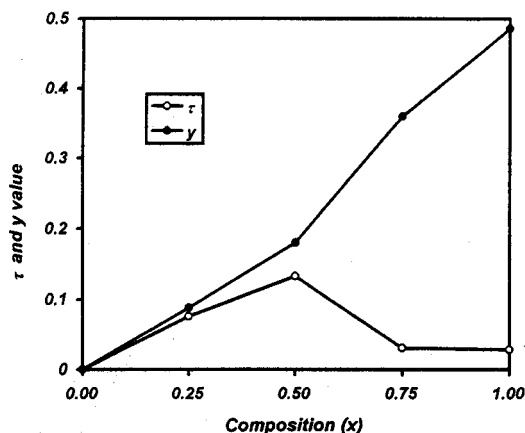

Figure 2. Plot of reduced lattice volume *vs* x value for the $Dy_{1-x}Sr_xCoO_{3-y}$ system.

Table 2. x, τ, and y Values and Nonsoichiometric Chemical Formulas for the $Dy_{1-x}Sr_xCoO_{3-y}$ System $(y = (x-\tau)/2)$

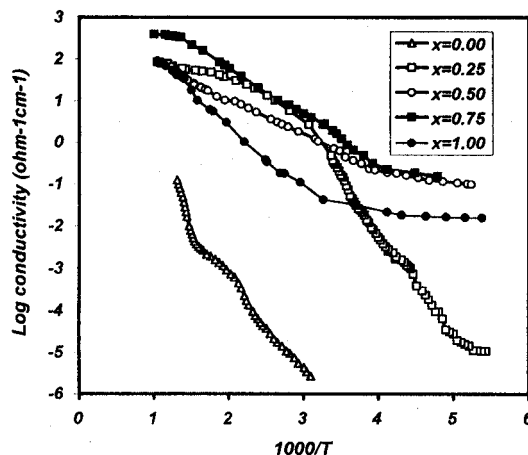| x	τ	y	Nonstoichiometric chemical formula
0.00	0.000	0.000	$DyCoO_3$
0.25	0.076	0.088	$Dy_{0.75}Sr_{0.25}Co^{3+}_{0.925}Co^{4+}_{0.076}O_{2.912}$
0.50	0.133	0.180	$Dy_{0.50}Sr_{0.50}Co^{3+}_{0.867}Co^{4+}_{0.133}O_{2.820}$
0.75	0.031	0.360	$Dy_{0.25}Sr_{0.75}Co^{3+}_{0.969}Co^{4+}_{0.031}O_{2.640}$
1.00	0.028	0.486	$SrCo^{3+}_{0.972}Co^{4+}_{0.028}O_{2.514}$

Figure 4. Plots of log electrical conductivity *vs* 1000/T for the $Dy_{1-x}Sr_xCoO_{3-y}$ system.

Table 3. Activation Energy of the Electrical Conductivity for the $Dy_{1-x}Sr_xCoO_{3-y}$ System

x	Temperature range (K)	Activation energy (eV)
0.00	323<T<442	0.390
	442<T<662	0.370
	662<T<761	1.350
0.25	184<T<198	0.140
	198<T<284	0.430
	284<T<477	0.382
	477<T<962	0.075
0.50	191<T<253	0.053
	253<T<690	0.170
	690<T<813	0.056
0.75	209<T<255	0.064
	255<T<737	0.220
	737<T<1000	0.062
1.00	186<T<309	0.400
	309<T<800	0.310
	800<T<868	0.097

Figure 3. Plots of the τ and y values *vs* x value for the $Dy_{1-x}Sr_x$-CoO_{3-y} system.

compositions of $0.00 \le x \le 0.50$, the τ value increases with x value up to the maximum at $x = 0.50$ and then decreases in the $x \ge 0.75$ as shown in Figure 3.

Grenier *et al.* suggested the increase of lattice volume due to the oxygen vacancies in the $CaTiO_3$-$Ca_2Fe_2O_5$ systems in which the formation of oxygen vacancies enhance the electrostatic repulsive force between Co cations.[17] In the composition of $x = 0.75$, the formation of oxygen vacancies is more favorable than that of Co^{4+} ions under the present conditions. Therefore the oxygen vacancies result in an increase of lattice constant.[18] In similar way, the composition of $x = 1.00$ or $SrCoO_{2.5}$ have a very samll τ value and then large y value. The chemical formula which was determined by the iodometry titration is the same as the brownmillerite structure identified by the x-ray powder diffraction analysis. The compositions which are heated under various oxygen pressures have the different y values of $0.00 \le y \le 0.50$,[21] and thus the composition of $x = 1.00$ has the y value of 0.49.

The $LaCoO_3$ compound is an insulator which has only the partially intrinsic semiconducting character.[8,20] However, the mixed valence state of Co ions due to the substituted Sr^{2+} ions plays an important role in physical properties (catality and conductivity for instance) of the $Dy_{1-x}Sr_xCoO_{3-y}$ system. The electronic conduction is based on the gradual delocalized 3d-electron behavior over the temperature range. For all the compositions, the electrical conductivities have shown in a semiconducting behavior, increaseing with temperatures, as shown in Figure 4. The conductivity curve of the $DyCoO_3$ compound show the plateau which is the activate range of the electron excitation t_{2g} level to e_g level. Especially, the

conducting types of the $x = 0.00$ and 0.25 which have same crystal system show a similarity with anomalous character. Also, those of the $x = 0.50$ and 0.75 show the same result. Therefore, structural ordering between two mixed valence Co ions and O^{2-} ions can influence the electronic properties.

All the samples showed the minute increasing of the conductivity with temperature at very low temperature range, so-called a low temperature semiconduction.[2] It is in accordance with an exponential increase of a conductivity, $\sigma = \sigma_0 e^{-E_a/kT}$, up to about 200 K.

The activation energies of the electrical conductivity for all the compositions in the given temperature range are listed in Table 3 and plotted in Figure 5. The overlap integrals between π^* band derived from t_{2g} level of Co 3d and σ^* band derived from e_g level grow on by thermal activation at high temperature and thus, show the semiconducting behavior with the temperature.
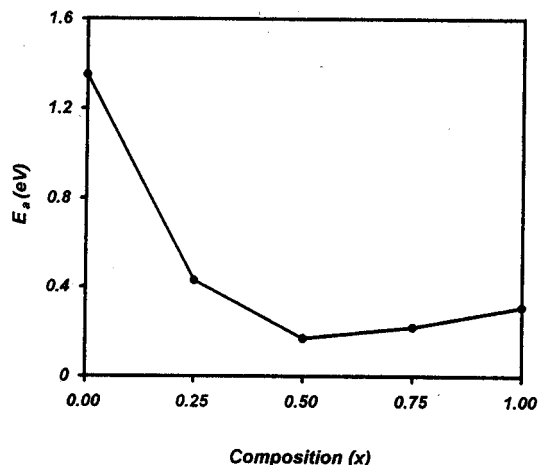
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Figure 5. Plot of the activation energy *vs* x value for the Dy_{1-x}-Sr_xCoO_{3-y} system.

Figure 6. Plots of $1/\chi_M$ *vs* absolute temperature for the $Dy_{1-x}Sr_x$-CoO_{3-y} system ($0.00 \leq x \leq 0.75$).

The covalency of the Co-O bond which can induce the localized-collective electron transition at higher temperature increases as the radius of the central metal ion increases.[5] Since the strong Co-O covalency stabilizes more the low-spin ion sites, Co-3d and O-2p interactions result in decrease of the energy difference between σ^* and π^* levels. Therefore, the introduction of weak Sr-O bonds competing with the Co-O covalency[17] and the structural effect plays an important role in electrical properties as the above statements. The electron transport property of the $x = 0.75$ at very high temperatures shows high conductivity. Other compounds of this system except for the $DyCoO_3$ and $SrCoO_{2.51}$ compounds show the high-order transition of semiconductor to matal phase which shows the predominant high-spin state instead of the low spin of Co^{3+} ion.

The energy gap of the kT order between low spin ($t_{2g}^6 e_g^0$; $s=0$) and high spin ($t_{2g}^4 e_g^2$; $s=2$) states is very small and thus, a gradual spin state transition ($Co^{ls} \rightarrow Co^{hs}$) as the function of temperature is observed. For the compositions of $x=$ 0.00 and 0.25, electrical anomalies due to slowly spin state transition are observed as shown in Figure 4. However, the phenomenon is not observed in magnetic measurement. The result may established that magnetic properties are more affected by the unpaired spin of Dy^{3+} ion than that of Co ion. The composition of $x=0.50$ has the minimum activation energy, $E_a \cong 0.17$ eV and shows an onset of matallic behavior above 700 K. Although the composition of $x=1.00$ has a small τ value, the sharp increasing conductivity with temperature can be explain by the long-range ordering of oxygen vacancies affecting to conduction mechanism. Existence of only large radius Sr^{2+} ion in A sites may relax the distortion of sublattice.

The inverse molar magnetic susceptibilities as a funtion of temperature for the $Dy_{1-x}Sr_xCoO_{3-y}$ system are shown in Figures 6 and 7. The magnetic parameters, the observed effective magnetic moment, and the calculated one are listed in Table 4. As a result, magnetic properties for all compositions coincide with Currie-Weiss law and pauli paramagnetism. Since magnetic moment of Dy^{3+} ion (10.65 BM) in ground state is prominent to that of only Co ion in the compositions of $0.00 \leq x \leq 0.50$, they show paramagnetic behavior.
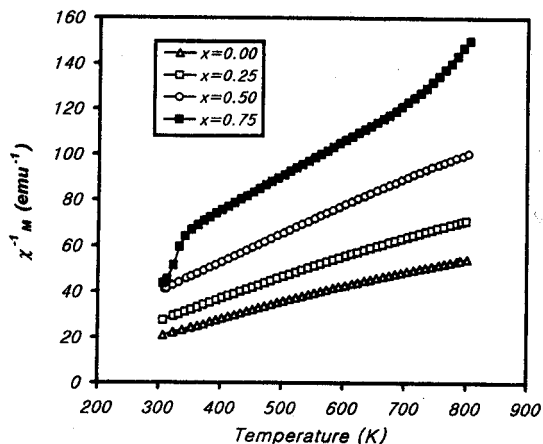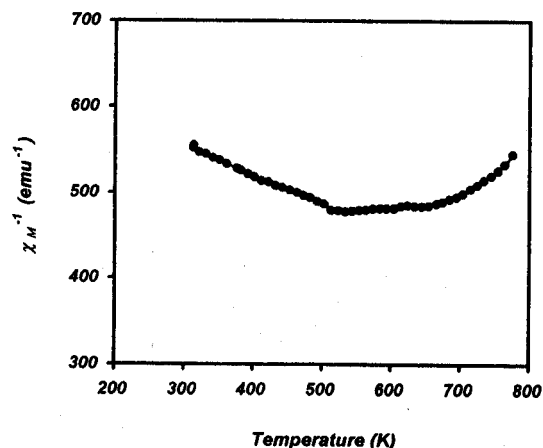

Figure 7. Plot of $1/\chi_M$ *vs* absolute temperature for the $SrCoO_{2.51}$ system.

Table 4. Magnetic Parameters and Observed and Calculated Effective Magnetic Moments of Co for the $Dy_{1-x}Sr_xCoO_{3-y}$ System

x (Co^{4+})	Temperature range (K)	C	θ_p	μ_{eff} (BM)	$\mu_{eff}^{(Co)}$ (BM)
0.00	T<575	14.29	−1.94	10.69	0.00
(0.00)	T<575	17.18	7.79	11.72	1.16
0.25	T<573	10.50	14.18	9.16	1.17
(0.076)	T<573	12.83	−110.85	10.13	2.14
0.50	T<634	8.50	−22.44	8.00	2.67
(0.133)	T<634	9.04	−105.59	8.50	3.17
0.75	342<T<725	6.40	−78.4	7.15	4.48
(0.031)	T<342	1.67	235.12	3.65	0.98
	T<725	3.44	289.68	5.25	2.58
	T<513	−2.88	−	−	−
1.00	513<T<674	16.88	−	−	−
(0.028)	T>674	1.55	−197.94	3.52	3.52

Small slope change by the spin transition between low spin and high spin states is observed in intermediate temperature

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as spin state transition in electrical conductivity. The composition of $x = 0.75$ shows weak ferromagnetic behavior due to Co^{3+}-O^{2-}-Co^{4+} indirect superexchange interaction below 300 K (T_c) in the Sr^{2+} ion rich region.

The $SrCoO_{2.5}$ compound shows antiferromagnetic behavior with the plateau and the magnetic structure is the G-type in which near-neighbouring Co^{3+} ions have always opposite spins,[14,16] the Néel temperature (T_N) of the compound is about 550 K. Since Co^{3+} ions are only high spin state which results from the small crystal field (10Dq) due to the loose lattice, it is found that antiferromagnetic Co^{3+}-O^{2-}-Co^{3+} interaction represents the electrical and magnetic behaviors. Finally, the mixed valence of Co ions at B sites depending on the x-value and the spin transition between two Co ion states plays an important role in the physical properties of the $Dy_{1-x}Sr_xCoO_{3-y}$ system.

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Photolysis of Aqueous Ammonia in the Absence and the Presence of O₂

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The photochemical decomposition of aqueous ammonia in the absence (saturated with argon) and the presence of O_2 (saturated with air or oxygen) has been investigated using 184.9 nm UV light. The decomposition of ammonia depended on the concentration of oxygen in the solution. With increasing the concentration of oxygen, the decomposition of ammonia diminishes. Hydrazine is found the major product from the irradiation. In the presence of oxygen, hydrogenperoxide was also produced. The product yields depended also on the concentration of oxygen in the solution. The initial quantum yield of the products and of the ammonia decomposed were determined. Probable reaction mechanisms for the reaction were presented from the products analysis.

Introduction

Ammonia is produced in huge quantities worldwide for use as a primary source of nitrogen in the production of

many commercial chemicals such as a fertilizer. However, ammonia with foul oder, generated from decomposition of a large amount of garbage, causes a serious environmental pollution. Therefore, it is interesting to study on the decom-