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## High Pressure Synthesis and Physical Properties of the Solid Solution, $\text{SrLaAl}_{1-x}\text{Ni}_x\text{O}_4$ ( $0 < x < 1$ )

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*Received July 22, 1995*

A complete solid solution ( $\text{SrLaAl}_{1-x}\text{Ni}_x\text{O}_4$ ) between insulating  $\text{SrLaAlO}_4$  and metallic  $\text{SrLaNi(III)O}_4$  oxides were prepared under high oxygen pressure (1.5 kbar, 800 °C). They have tetragonal  $\text{K}_2\text{NiF}_4$ -type structure in all the solid solution range. Compared with lattice parameters of the same solid solution prepared under normal condition (1 bar, 1200 °C), large decrease in the *c*-parameter was induced by high pressure treatment while no noticeable variation of the *a*-parameter was observed. Although marked changes of structural parameters, magnetic susceptibilities, and electron paramagnetic resonance spectra were consistently occurred before and after  $x=0.5$ , overall behaviors were essentially the same with those of solid solution prepared under normal condition. Such a phenomenon is explained by assuming the formation of partially filled narrow  $\sigma^*_{x^2-y^2}$  band for  $x>0.5$ . Lattice contraction along the *c*-axis by high pressure treatment seems not to broaden this band. Particularly, the continuous absorption characteristic of a high free carrier concentration for  $x>0.5$  and the absence of Ni-O in-plane stretching mode in the infrared absorption spectra supports this picture. However, the conductivities increasing with temperature for all solid solution suggest that some localization character, of probably Anderson type, remains for  $x>0.5$ .

### Introduction

Layered perovskite-type oxides of the general formula  $\text{A}_2\text{BO}_4$  have been intensively studied because they exhibit typical two-dimensional magnetism,<sup>1-3</sup> metal-insulator transition,<sup>4-6</sup> and superconductivity.<sup>7-9</sup> The large variety of the properties that these compounds with so-called  $\text{K}_2\text{NiF}_4$ -type structure show is derived from the possibility of synthesis of multicomponent layer-type compounds. Partial substitution of cations in *A* and *B* positions, for example, gives rise to the  $\text{A}_{2-x}\text{A}'_x\text{B}_{1-x}\text{B}'_x\text{O}_{4-6}$ . The probability of solid solution formation in

the entire compositional range is very high when the cation (*A* or *B*) is substituted by another cation (*A'* or *B'*) with the same charge and a similar ionic radius.<sup>10</sup> In contrast, when there is a large difference in charge and/or ionic radius, ordered structures are formed and only certain compositions are allowed. In addition, this type of compounds are good candidates for the stabilization of a mixed or unusual oxidation states with anisotropic electronic configuration.<sup>11-13</sup>

Several studies have been carried out on the physical properties of the perovskite and the layered perovskite compounds with  $\text{K}_2\text{NiF}_4$ -type structure containing Ni(III). Although

in most of them Ni(III) is stabilized in the low-spin state ( $t_{2g}^6 e_g^1$ ), the high-spin state ( $t_{2g}^5 e_g^2$ ) had been postulated in  $\text{NiCrO}_3$ <sup>14</sup> and  $\text{BaLaNiO}_4$ .<sup>15</sup> J. B. Goodenough, P. M. Raccah,<sup>16</sup> and G. Demazeau *et al.*<sup>17</sup> had discussed the metallic character of  $\text{LaNiO}_3$  perovskite on the basis of its Pauli-paramagnetic behavior and the absence of Jahn-Teller distortion. When La(III) is replaced by a smaller rare-earth cation ( $\text{Nd(III)} \rightarrow \text{Lu(III)}$ ), due to the increase of the structural distortion, the electronic localization increases and Curie-Weiss behavior is observed for  $\text{YNiO}_3$  and  $\text{LuNiO}_3$ . For all  $\text{SrLnNiO}_4$  ( $\text{Ln} = \text{La} \rightarrow \text{Gd}$ ) of the two-dimensional character, on the other hand, the strengthening of Ni(III)-O bond in the perovskite-type layer leads to a metallic behavior.<sup>18</sup>

In this study, the solid solution ( $\text{SrLaAl}_{1-x}\text{Ni}_x\text{O}_4$ ) between insulating  $\text{SrLaAlO}_4$  and metallic  $\text{SrLaNiO}_4$  have been investigated. The substitution of Ni(III) for Al(III) would be expected to induce two different phenomena;

1) stabilization of the low-spin Ni(III) configuration accompanying Jahn-Teller distortion with low  $x$  value. This is because the smaller Al(III) (0.535 Å) compared with the low-spin Ni(III) (0.56 Å) will increase crystal-field strength on the nickel site.

2) increase of electronic delocalization with high  $x$  value, giving rise to a disappearance of Jahn-Teller distortion.

Such a solid solution had been already reported by Mohanram *et al.*<sup>19</sup> They have prepared all the solid solutions under bar of  $\text{O}_2$  pressure and high temperature (1200 °C) and observed unusual changes in structural data and physical properties. An abrupt decrease of the lattice  $c$ -parameter for  $x > 0.75$  has been explained by a change in the electronic configuration of the Ni(III) ions. Considering that  $3+$  state

Ni is one of the unusual oxidation state in oxide lattice, we have prepared this solid solution under the high oxygen pressure (1.5 kbar) and much lower temperature (800 °C) in comparison with that prepared under normal condition at high temperature. Such a high pressure condition is more appropriate for the stabilization of unusual oxidation state  $3+$  for Ni as well as very effective to increase the transfer integral  $b$ <sup>10</sup> and the possibility of electronic transfer between  $d$  ions through anionic orbitals. Therefore it is envisaged that if an abrupt structural change of  $\text{SrLaAl}_{1-x}\text{Ni}_x\text{O}_4$  attributed to the electronic delocalization, the behavior localized  $\rightarrow$  collective electron transition will be strongly influenced by high pressure treatment. This electronic delocalization would be evidenced by the absence of electron paramagnetic resonance signal, Pauli-paramagnetic behavior, metallic like conduction behavior, and the continuous absorption in infrared spectra.

## Experimental

Stoichiometric mixtures of corresponding nitrates for  $\text{SrLaAl}_{1-x}\text{Ni}_x\text{O}_4$  ( $x = 0.1, 0.3, 0.5, 0.7, 0.9, 1.0$ ) were slowly decomposed in air. The residual powders were heated under oxygen flow at 950 °C for 48 hours with intermittent heating. In the next step, the stabilization of Ni(III) ion in the lattice was induced by the final high oxygen pressure (5 kbar, 800 °C) treatment.

The oxidation states of nickel ion in the final products were determined by the chemical iodometric titration. The samples were dissolved in small amount of about 4 N HCl

**Table 1.** The oxidation states of Ni determined by the iodometric titration for  $\text{SrLaAl}_{1-x}\text{Ni}_x\text{O}_4$

Compounds	Oxidation states
$\text{SrLaAl}_{0.9}\text{Ni}_{0.1}\text{O}_4$	—
$\text{SrLaAl}_{0.7}\text{Ni}_{0.3}\text{O}_4$	3.02(2)
$\text{SrLaAl}_{0.5}\text{Ni}_{0.5}\text{O}_4$	3.01(3)
$\text{SrLaAl}_{0.3}\text{Ni}_{0.7}\text{O}_4$	2.97(2)
$\text{SrLaAl}_{0.1}\text{Ni}_{0.9}\text{O}_4$	2.98(2)
$\text{SrLaNiO}_4$	2.98(2)

solution and diluted with distilled water. After the addition of potassium iodide solution, the liberated iodine was titrated with sodium thiosulfate solution using starch as an indicator. Determined oxidation states of nickel ion in the solid solution are listed in Table 1. In case of  $x = 0.1$ , the standard deviation of experimental error was too large to determine the oxidation number of nickel ion.

The structural types and the lattice constants were determined at room temperature by the powder X-ray diffraction method using a monochromatized  $\text{CuK}\alpha$  radiation. The electron paramagnetic resonance (EPR) spectra of all solid solution were recorded at liquid helium temperature in the X-band region (9.5 GHz). The magnetic susceptibility for  $\text{SrLaAl}_{1-x}\text{Ni}_x\text{O}_4$  was measured from 4.2 to 300 K using a Faraday-type microbalance. The instrument was calibrated with  $\text{Hg}[\text{Co}(\text{NCS})_4]$ . The infrared (IR) absorption spectra for polycrystalline samples  $\text{SrLaAl}_{1-x}\text{Ni}_x\text{O}_4$  ( $x = 0.1, 0.3, 0.5, 0.7, 0.9, 1.0$ ) in CsBr pellets were obtained at room temperature. The electrical conductivity measurements were carried out in the range of 80 K ~ room temperature by the typical four-probe method.

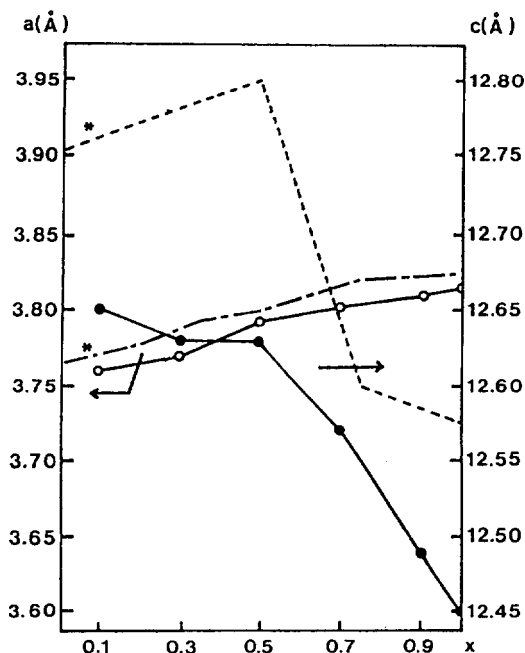
## Results and Discussion

As far as powder X-ray diffractions are concerned, all the patterns for solid solutions were indexed on the basis of tetragonal  $\text{K}_2\text{NiF}_4$ -type structure ( $I_4/mmm$ ). No extra diffraction lines, resulting from a long range ordering between Al(III) and Ni(III) in the perovskite-type planes, were detected on the Guinier film, even after a long exposure time. Since there was no evidence of superstructure, they may be assumed to have a random or near-random distribution of Al and Ni on the  $B$  sites. Considering that  $\text{Al}^{3+}$  and  $\text{Ni}^{3+}$  have the same charge and similar ionic radii, a disordering between two cations in the perovskite-type plane would be rationalized. If they have different charges and sizes each other, an 1:1 ordering of  $B$  and  $B'$  cations have been observed for several kinds of cationic pairs such as ( $\text{Li}^I, \text{Mn}^{IV}$ ), ( $\text{Li}^I, \text{Fe}^{IV}$ ), ( $\text{Li}^I, \text{Co}^{III}$ ), ( $\text{Li}^I, \text{Ni}^{III}$ ), ( $\text{Mg}^{II}, \text{Mn}^{IV}$ ), ( $\text{Mg}^{II}, \text{Fe}^{IV}$ ), ( $\text{Mg}^{II}, \text{Co}^{III}$ ), ( $\text{Mg}^{II}, \text{Ni}^{III}$ ), ( $\text{Zn}^{II}, \text{Mn}^{IV}$ ), ( $\text{Zn}^{II}, \text{Fe}^{IV}$ ), ( $\text{Zn}^{II}, \text{Co}^{III}$ ), and ( $\text{Zn}^{II}, \text{Ni}^{III}$ ).<sup>20-24</sup> Although two cations have different charges, on the contrary, a random distribution is induced if they have similar sizes as ( $\text{Ti}^{IV}, \text{Ni}^{III}$ ) and ( $\text{Ti}^{IV}, \text{Co}^{III}$ ) pairs.<sup>22,25</sup> These results indicate that the main factor determining the ordering between two different cations in the lattice is the size difference of them and the difference in size of ( $\text{Al}^{III}, \text{Ni}^{III}$ ) pair is not sufficient to induce an ordering.

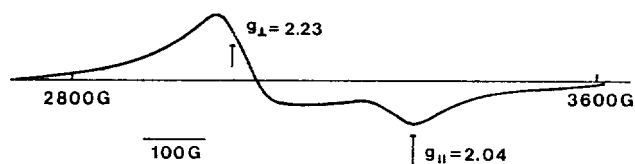
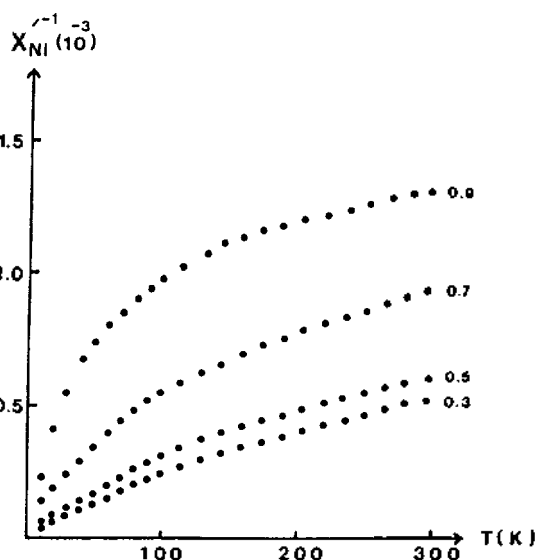
The estimated lattice constants are given in Table 2 and

**Table 2.** Unit cell parameters of SrLaAl<sub>1-x</sub>Ni<sub>x</sub>O<sub>4</sub>

Compounds	<i>a</i> (Å)	<i>c</i> (Å)	<i>c/a</i>
SrLaAl <sub>0.9</sub> Ni <sub>0.1</sub> O <sub>4</sub>	3.760(3)	12.65(1)	3.36
SrLaAl <sub>0.7</sub> Ni <sub>0.3</sub> O <sub>4</sub>	3.768(3)	12.63(1)	3.35
SrLaAl <sub>0.5</sub> Ni <sub>0.5</sub> O <sub>4</sub>	3.793(4)	12.63(1)	3.33
SrLaAl <sub>0.3</sub> Ni <sub>0.7</sub> O <sub>4</sub>	3.802(4)	12.57(1)	3.31
SrLaAl <sub>0.1</sub> Ni <sub>0.9</sub> O <sub>4</sub>	3.814(4)	12.54(1)	3.29
SrLaNiO <sub>4</sub>	3.826(4)	12.52(1)	3.25

**Figure 1.** Lattice parameters vs *x* for SrLaAl<sub>1-x</sub>Ni<sub>x</sub>O<sub>4</sub>. (\*Comparison with those for the same solid solution prepared under normal O<sub>2</sub> pressure and at high temperature.<sup>19</sup>).

compared with those of the same solid solution prepared under normal O<sub>2</sub> flowing condition in Figure 1. As shown in this figure, the unit cell *c*-parameters are much smaller for the pressure treated solid solution. But there is no marked change in the *a*-parameters, the small differences being within experimental errors. From these structural data, it was expected that all the properties associated with the chemical bonding along the *c*-axis will be strongly influenced by high pressure treatment of the solid solution. In spite of such a difference in absolute values of the *c*-parameters, in contrast, its variation tendency remains similar; the *c* values remarkably decrease for *x*>0.5. In the K<sub>2</sub>NiF<sub>4</sub>-type structure, the *c/a* ratio could be a good criterion for the local distortion of the octahedral site. When there is no considerable distortion, the *c/a* ratio is generally close to 3.30. If the octahedral site is deformed by Jahn-Teller effect, on the contrary, we observe largely different *c/a* ratio depending on the distortion type. For example, the *c/a* value is close to 3.10 when a hole is localized on *d*<sub>z<sup>2</sup>-orbital as in Nd<sub>2</sub>CuO<sub>4</sub> and Sm<sub>2</sub>CuO<sub>4</sub><sup>4</sup> or close to 3.45 when occupy *d*<sub>z<sup>2</sup>-y<sup>2</sup>-one as in La<sub>2</sub>CuO<sub>4</sub>.<sup>26</sup> The *c/a* ratios for SrLaAl<sub>1-x</sub>Ni<sub>x</sub>O<sub>4</sub> listed in Table 2, therefore, seems to show that Jahn-Teller distortion</sub></sub>

**Figure 2.** EPR spectra at liquid helium temperature for SrLaAl<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>4</sub>.**Figure 3.** Inverse magnetic susceptibilities per Ni(III) ion vs temperature for SrLaAl<sub>1-x</sub>Ni<sub>x</sub>O<sub>4</sub> (*x*=0.3, 0.5, 0.7, and 0.9).

is alleviated for *x*>0.5. Such a crystallographic comparison would suggest some delocalization of *e<sub>g</sub>*-electrons for *x*>0.5 as in metallic LaNiO<sub>3</sub> perovskite with no Jahn-Teller distortion.<sup>17</sup>

Electron paramagnetic resonance spectroscopy was very useful to elucidate the oxidation state and the spin state of Ni, the electronic delocalization behavior, and the local distortion of the site occupied by Ni(III). An anisotropic signal was observed for *x*=0.1, 0.3, and 0.5 of which EPR signal for *x*=0.5 is represented in Figure 2. The estimated *g* values (*g*<sub>⊥</sub>=2.23 and *g*<sub>∥</sub>=2.04) correspond to the low-spin Ni(III) ions stabilized in the tetragonally elongated octahedral site. Jahn-Teller type distortion could result from a localized *e<sub>g</sub>*-electron for the phases with higher aluminum content. It is noticeable that no signal was detected with *x*>0.5 in spite of the measurements with maximum gain. This absence of EPR signal indicates the electronic delocalization in such a solid solution range. Considering that an anisotropic EPR signal had not been observed with *x*>0.5 either for the solid solution prepared under normal condition,<sup>19</sup> the electronic delocalization is likely to be independent on the variation of the lattice along the *c*-axis.

Figure 3 shows the inverse molar magnetic susceptibility as a function of temperature for the high pressure treated solid solution SrLaAl<sub>1-x</sub>Ni<sub>x</sub>O<sub>4</sub>. Each plot of  $\chi_m^{-1}$  vs. temperature for *x*<0.5 after the diamagnetic corrections can be fitted into an equation,

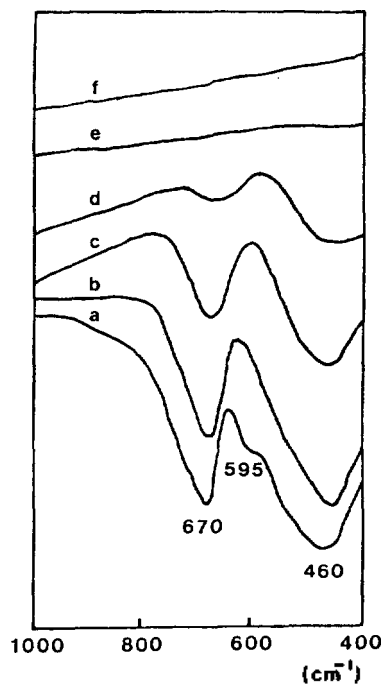


Figure 4. Infrared absorption spectra for SrLaAl<sub>1-x</sub>Ni<sub>x</sub>O<sub>4</sub>,  $x=0.1$  (a), 0.3(b), 0.5(c), 0.7(d), 0.9(e), and 1.0(f).

$$\chi_m' = \frac{C}{T - \theta_p} + N_a$$

where  $C$  is Curie constant,  $\theta_p$  Curie-Weiss constant, and  $N_a$  van-Vleck constant paramagnetism ( $2N\beta^2k^2/\Delta E$ ). The values of  $C$  and  $N_a$  obtained by the fit of the experimental magnetic curves are  $C=0.12-0.29$  which are smaller than the theoretical spin-only value (0.375) per one low-spin Ni(III) ion and  $N_a=600-680 \times 10^{-6}$  emu which are close to those observed in SrLaNiO<sub>4</sub> ( $667 \times 10^{-6}$  emu) and BaLaNiO<sub>4</sub> ( $633 \times 10^{-6}$  emu).<sup>15</sup> Such quite high  $N_a$  values imply delocalization character induced by the presence of a low-lying excited state. As shown in Figure 3, the magnetic susceptibility considerably decreases to show Pauli-paramagnetic behavior for  $x > 0.5$ , which is generally observed with the metallic phases. This variation is consistent with the abrupt decrease of  $c$  parameter and the absence of EPR signal for  $x > 0.5$ . Such a behavior of magnetic property is also quite similar with those of same solid solution prepared under normal oxygen pressure.

The metallic-like properties were also reflected in the infrared absorption spectra of SrLaAl<sub>1-x</sub>Ni<sub>x</sub>O<sub>4</sub> shown in Figure 4. Infrared spectra of A<sub>2</sub>BO<sub>4</sub> oxides in the region 1000-400 cm<sup>-1</sup> have been studied by several workers.<sup>23,27,28</sup> In general, the A<sub>2</sub>BO<sub>4</sub> oxides show three prominent bands in this region. The assignment of absorption bands based on factor group analysis in these oxides has not been successful as in the fluorides.<sup>29</sup> Fair success has been obtained, however, by considering the internal modes of BO<sub>6</sub> octahedra.<sup>30</sup> According to these reports, the highest frequency band in the region 660-680 cm<sup>-1</sup> could be assigned to a A-O stretching frequency along the  $c$ -axis and the lower frequency bands at around 580-600 cm<sup>-1</sup> and 400-500 cm<sup>-1</sup> to a B-O in-plane

stretching and BO<sub>6</sub> octahedral deformation modes, respectively.

If we assume the metallic property, the absorption coefficients of vibrational modes are determined by both charge carriers and the localized modes. Therefore, infrared spectrum can be another tool to obtain information at a microscopic level on the nature of metal-oxygen bonding at the metal-insulator transition.<sup>31</sup> The compounds with  $x < 0.5$  show typical strong absorption bands, corresponding to the semiconducting behavior. The intensities of absorption bands are strongly decreased from  $x=0.5$  and a continuous absorption characteristic of a high free carrier concentration as in a metal is shown for  $x > 0.7$ , in agreement with the metallic conduction. Moreover, it is interesting that absorption band at around 595 cm<sup>-1</sup> assigned to Al-O activity is disappeared with increasing  $x$  while a mode related to Ni-O in-plane stretching is absent for all over the  $x$  range. This observation would suggest that the short range order in these disordered materials encompasses clusters of corner-shared NiO<sub>6</sub> octahedra with delocalized electrons and the electrical conductivity takes place *via* Ni-O band states. Such a consideration agrees with high  $N_a$  values for even  $x < 0.5$ . The changes of IR absorption bands are quite consistent with the results of the crystallographic, EPR, and magnetic susceptibility measurements.

From the structural, EPR, magnetic susceptibility, and IR absorption data, it could be temporarily concluded that the electronic delocalization is not related to the nature of chemical bonding along the  $c$ -axis. In this view point, it is referable the fact that in the phases with K<sub>2</sub>NiF<sub>4</sub>-type structure, the intra-perovskite layer interactions are predominant on the inter-layer interaction. With La<sub>2</sub>NiO<sub>4</sub>, for instance, an antiferromagnetic ordering between Ni<sup>2+</sup> ions in the perovskite layer results in a splitting of narrow  $\sigma_{x^2-y^2}^*$  band below 500 K (that is, semiconducting).<sup>4</sup> But magnetic moments of Ni<sup>2+</sup> ions become disordered above 600 K and a single  $\sigma_{x^2-y^2}^*$  band that is half filled is formed, giving rise to the metallic conduction. When we compare the Ni(II)-O bond with the Ni(III)-O one, the higher covalency of the latter would induce  $b_o$  (covalence parameter)  $>$   $b_m$  (critical value for the collective electrons) and therefore the formation of  $\sigma_{x^2-y^2}^*$  band.<sup>10</sup> Thus, it is agreeable that the decrease of Jahn-Teller distortion with increasing  $x$  is likely to result from the electronic configurational change from  $t_{2g}^6 d_{x^2-y^2}^1 d_{z^2}^0$  to  $t_{2g}^6 d_{x^2-y^2}^1 d_{z^2}^1$  then the  $d_{z^2-y^2}$  electrons will form a partially filled  $\sigma_{x^2-y^2}^*$  band.<sup>19</sup> Since the structural, magnetic, and EPR properties vary before and after  $x=0.5$ , the electrical conductivities were measured. A considerable increase of electrical conductivity was observed for  $x > 0.7$ , which showed quite similar behavior with SrLaNiO<sub>4</sub>,<sup>18</sup> but their conductivities still increased with temperature until  $x=0.9$ . This result suggests that although we assume the formation of the  $\sigma_{x^2-y^2}^*$  band, such a band is narrow and a strong lattice contraction along the  $c$ -axis by high pressure treatment does not broaden effectively this band. If we calculate thermal activation energy  $E_a$  defined by  $\rho = \rho_0 \exp(E_a/kT)$ , where  $\rho$  is the resistivity,  $E_a \sim 0.01$  eV is found for  $x > 0.5$ . Such an activation energy is too low to be characteristic of even semiconductor dopant levels in metal oxides. Therefore, it could be proposed that some localization character (probably Anderson type) remain for  $x > 0.5$ .

### Conclusion

If we consider metallic  $\text{LnNiO}_3$  perovskite ( $\text{Ln}=\text{La, Sm, Eu, and Gd}$ ), a localization of Ni  $e_g$ -electrons is increased by the bending of Ni-O-Ni angle when the lanthanide ion becomes smaller. On the contrary, the Ni-O-Ni bond angle is  $180^\circ$  for all  $\text{SrLnNiO}_4$  phases and their metallic conduction behaviors are similar. In this paper, we have observed that the lattice contraction along the  $c$ -axis of  $\text{SrLaAl}_{1-x}\text{Ni}_x\text{O}_4$  solid solution by high pressure treatment could not induce any difference in EPR and magnetic susceptibility as long as a bending of the Ni-O-Ni bond is not accompanied. Such a difference between two types of oxides says that in  $\text{K}_2\text{NiF}_4$ -type structure, the electronic delocalization should take place in perovskite-type layer and thus the  $\sigma_{x^2-y^2}^*$  band would be responsible for this delocalization. The conductivities increasing with temperature and their weak activation energies for  $x>0.5$  indicate the formation of a narrow band that is not broadened by the lattice contraction along the  $c$ -axis. All the change in physical properties from  $x>0.5$  would involve percolation of the electrons among the connected networks of  $\text{NiO}_6$  octahedra.

**Acknowledgment.** This work was supported by the '94 research fund of Kyung Hee University and Basic Science Research Institute program, Ministry of Education (BSRI-94-3421).

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