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La and Sr Substituted $Pr_2NiO_{4+\delta}$: Oxygenation and Electrical Properties

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We report herein results concerning the solid solutions $Pr_{2-x}M_xNiO_{4+\delta}$, $M =$ La, Sr. These two cations are larger than praseodymium and lead to a structural stabilization. The oxygen excess δ decreases with x for La and Sr substituted $Pr_2NiO_{4+\delta}$. Both cases suggest that structural strain is a leading factor for the oxygenation ability of the title compounds. From the evolution of cell parameters, we suggest a phase transition for La substituted compounds occurring for $x \sim 1$–1.2. Surprisingly, this transition has a negligible effect on transport properties. On the other hand, a charge localization linked to the presence of praseodymium is observed. Owing to charge compensation, the Sr substituted compounds have a quasi-constant hole concentration (formally 50%) for $x < 0.5$. The $Pr_{2-x}Sr_xNiO_{4+\delta}$ solid solution shows an anomalous behavior for $x = 0.5$ corresponding to $Ni^{2+}/Ni^{3+} = 1$. This anomaly combines an enhancement of the c/a ratio, a larger resistivity, and a peak for the activation energy of the resistivity versus T. © 1997 Academic Press

INTRODUCTION

$La_{2-x}M_xCuO_{4+\delta}$-type compounds have extremely interesting physical properties which depend greatly on M, x, and δ (δ can be positive or negative). A leading example is high T_c superconductivity arising in these cuprates. It is well known that T_c increases in $La_{2-x}Sr_xCuO_4$ with the Sr content up to a maximum temperature of 35 K when $x = 0.15$ while a sudden decrease in T_c occurs for $x = 1/8$ in the case of Ba substitution (1, 2). Recently possible analogies have been suggested in $La_2NiO_{4+\delta}$ (3). In this system, complex surstructures changing with δ (4–8) are suspected to give rise to abnormal transport and magnetic properties. To find confirmation of such effects in the praseodymium nickelate analogues, we have undertaken a systematic exploration of transport and magnetic properties versus the dopant nature, its concentration, and δ.

It is well known that the structural strain is a very important parameter in determining the properties of K_2NiF_4-type oxides (9) described as the intergrowth of "LnO" layers with "NiO_6" layers. Due to the small size of Pr^{3+}, large strain (extension) applies on the rock salt "PrO" layer and combines with the compressed NiO_6 layer to severely distort the structure. Several mechanisms can relax the strain. In oxygen stoichiometric compounds, the tilting of NiO_6 octahedra triggers structural transitions (10–12). On the other hand, the introduction of extra oxygen in the rock salt layer fills the space and lowers the structural strain. Oxidation could form Pr^{4+} species; they are however unexpected in this structure because its size is too small. In fact $PrNiO_3$, a strongly oxidized perovskite, involves Pr^{3+} ions (13) and not Pr^{4+}. Hence, oxygenation in $Pr_2NiO_{4+\delta}$ promotes oxidation of Ni^{2+} to the smaller Ni^{3+}, also releasing compression in the NiO_6 layer. The substitution of a larger cation for the rare earth element obviously occurs in the same manner. Alkaline earth substitution has been used extensively in this way; it also dopes the NiO_6 layer by injecting holes for charge compensation (1, 6, 14, 15).

In the present paper, we report on the aliovalent solid solution $Pr_{2-x}La_xNiO_{4+\delta}$, $0 \leq x \leq 2$, and compare it with the charge-compensated Sr-doped $Pr_2NiO_{4+\delta}$. Structural data, oxygen uptake, and electrical properties of these compounds are discussed.

EXPERIMENTAL

Precursor of $Pr_{2-x}A_xNiO_{4+\delta}$ ($A =$ La, Sr) are made from precalcinated Pr_6O_{11} (Rhône-Poulenc 99.9%), La_2O_3 (Strem Chemical, 99.99%), $SrCO_3$ (Rhône-Poulenc 99.9%), and NiO (Labosi 99.9%). The cations are dissolved separately in nitric acid, and then citric acid is added to stabilize the solutions. They are then mixed in the appropriate stoichiometry and gelified using a modified sol–gel route described elsewhere (16). A fine powder is formed by drying the gel at 700°C; it is then heated at 1200°C in air with one intermediate grinding step, providing a pure phase powder. The samples are furnace cooled in static air using an identical thermal program. This provides valid conditions for comparing the oxygen content. Phase purity is checked by X-ray powder diffraction on an automated Philips

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diffractometer using a Ni-filtered Cu$K\alpha$ wavelength. Lattice parameters are refined by a least-squares refinement program. Sintering is achieved at high temperature (1520 K) after the powder is isostatically compacted (300 MPa). The final density is in the range 80–95% of the theoretical density, even with Sr substitution which inhibits sintering.

The oxygen content of sintered samples is deduced from the weight loss measured during total reduction of the sample in a thermobalance (Setaram TAG 24, sensitivity ± 1 μg). The reduction is achieved at 900°C in an atmosphere of Ar + 5% H_2 and is certified by the presence of lanthanide oxide, alkaline earth oxide, and metallic nickel at the end of the procedure. The oxygen excess δ is calculated from this weight loss as in most publications. In addition, the existence of a plateau in the weight evolution versus temperature is an interesting source of information. When the nominal cation stoichiometry is respected in the chemical preparation ($Pr + A/Ni = 2$), the plateau corresponds to oxygen stoichiometry ($O_{4.0}$) (17). In some cases the plateau is observed for a different value; this is thought to be the case when the cation stoichiometry differs from the nominal value ($Pr + A/Ni \neq 2$) (18). We used this peculiarity to check unwanted differences in cation ratio. Iodometric titrations are used in addition as a measure of the formal valence of nickel ions. Pr^{4+} could contribute to this measurement if present but as said in the Introduction Pr^{4+} is highly unexpected in $Pr_2NiO_{4+\delta}$. Therefore, the eventual contribution from Pr^{4+} would come from second phases. In fact, there is an excellent agreement of the formal valence of Ni measured by iodometric titration to that deduced from the oxygen excess and electroneutrality equation.

Electrical resistivity (dc) is measured on sintered pellets with an automated setup using the classical four-probe method; measurements are performed in the temperature range 4–800 K. The rather small residual porosity of our samples is not expected to affect the measurement of the resistivity. Temperature is measured below 300 K with a silicon-doped sensor on which the sample is fixed. They are inserted into a copper tube which ensures the thermal homogenization. This system is fixed at the bottom of a rod moving vertically in a bottle of liquid helium. The temperature varies simply as a function of elevation above the liquid.

RESULTS AND DISCUSSIONS

$Pr_{2-x}La_xNiO_{4+\delta}$

Substituting lanthanum into praseodymium gives rise to a solid solution as expected. Indeed, lanthanum and praseodymium have very close ionic radii ($r(Pr^{3+}) = 1.126$ Å and $r(La^{3+}) = 1.16$ Å for coordination number VIII according to Shannon and Prewitt) and both $Pr_2NiO_{4+\delta}$ and $La_2NiO_{4+\delta}$ have similar structures. This solid solution is an interesting system to investigate rare earth element size effects on oxygenation because Pr and La have the same oxidation number.

Let us first comment on the oxygen stoichiometry. Slow cooling in air leads to $\delta = 0.22$ for $Pr_2NiO_{4+\delta}$ whereas $\delta = 0.16$ is obtained for $La_2NiO_{4+\delta}$ under identical conditions. This is a significant difference, larger than experimental scattering. Increasing the substitution rate of lanthanum into praseodymium induces a progressive decrease in δ from 0.22 to 0.16 as shown in Fig. 1; δ decreases

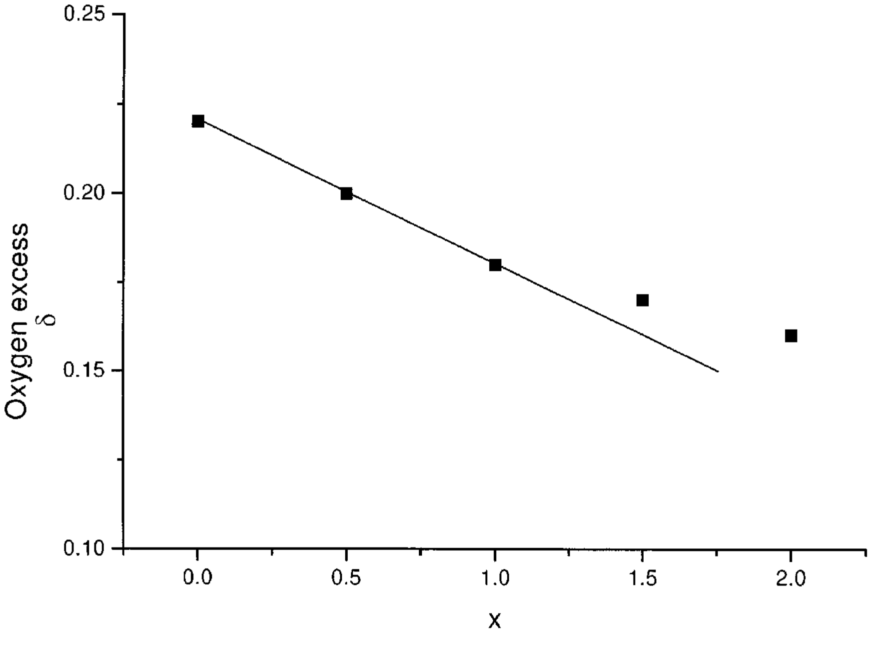

FIG. 1. Oxygen excess $Pr_{2-x}La_xNiO_{4+\delta}$ versus x for furnace cooled samples in air.

linearly with x up to values of $x \sim 1$ and then more slowly for $x > 1$. This evolution is expected to arise from the larger ionic radius of lanthanum. The difference between the bond lengths of both PrO and NiO_6 layers decreases when substituting La and consequently the lanthanum compound needs a smaller excess of oxygen to reach an equivalent state of strain to that in the praseodymium compound. This qualitative explanation suggests a driving force for oxygenation controlled by structural strain and then correlated with the tilting angle of NiO_6 octahedra.

All compositions are single phase and can be indexed in an orthorhombic unit cell. The evolution of parameters is reported in Fig. 2a (data at room temperature). The substitution by lanthanum leads to an overall increase of the cell volume consistent with their respective ionic radii. An abrupt change is evidenced for b and c in the range $x \sim 1$–1.2 while a increases more smoothly. This suggests a phase transition in the region $x \sim 1$–1.2. This is expected since the average structure of $Pr_2NiO_{4+\delta}$ ($\delta \geq 0.16$) is described in the *Bmab* space group (21) while $La_2NiO_{4+\delta}$ crystallizes in the *Fmmm* space group (19, 20) when $\delta \geq 0.14$.

Aliovalent substitution on the rare earth element is a good choice to investigate structural strain effects on transport properties. Minor modifications of T dependency are observed in the temperature range 30–800 K (18) due to La substitution and here we focus on room temperature resistivity versus x (Fig. 2b). Error bars in this figure reproduce differences observed between several samples. The resistivity decreases first smoothly with La content up to $x = 1.5$ and then more rapidly to $x = 2$. Praseodymium compounds belong to the *Bmab* space group, which allows the tilting of the NiO_6 octahedra such that in-plane oxygen positions can be out of the plane; this modifies the transfer integral and is expected to affect the in-plane conduction. In contrast, the *Fmmm* structure of $La_2NiO_{4+\delta}$ does not allow such movements and thus a more efficient transfer integral is likely in the conducting plane. From this, an overall decrease in the resistivity is anticipated when introducing lanthanum as it has been observed. Also one expects an abrupt variation at the phase transition for $x \sim 1$ which is not seen. However, the data require closer inspection. As the hole density is modified between $Pr_2NiO_{4.22}$ and

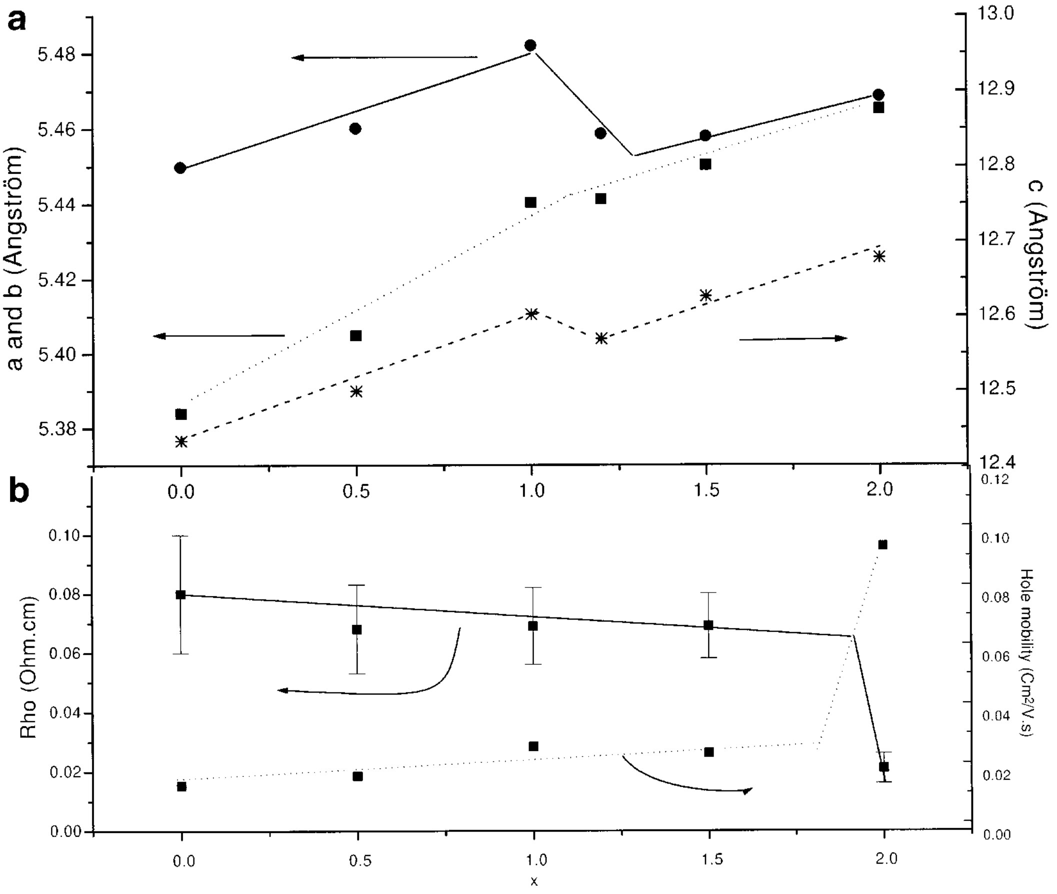

FIG. 2. (a) Cell parameters a, b, and c (in Å) versus x in $Pr_{2-x}La_xNiO_{4+\delta}$ at room temperature. (b) Room temperature resistivity and calculated hole mobility versus x in $Pr_{2-x}La_xNiO_{4+\delta}$. Lines are only guides for the eyes. Scale for resistivity is in Ω cm and that for carrier mobility is in $cm^2\ V^{-1}\ s^{-1}$.

$La_2NiO_{4.16}$ (variation is smaller than 30%), the relevant parameter is the hole mobility versus x. Assuming a conductivity proportional to the hole density, i.e., twice the oxygen excess, the corresponding carrier mobility has been plotted in Fig. 2b (dotted line). It is in close agreement with Hall mobility measured at 300 K in $La_2NiO_{4+\delta}$ (22). While the mobility increases when La is introduced as expected for a reduced buckling in the conducting plane, the onset of the sharp increase in the mobility is clearly in the *Fmmm* range, for $x > 1.5$. This suggests an additional effect of praseodymium in localizing charge carriers not related to a structural effect. We suggest a possible magnetic origin of this phenomenon in a forthcoming paper.

$Pr_{2-x}Sr_xNiO_{4+\delta}$

The stable oxidation state of strontium is 2 +; this diamagnetic ion has a ionic radius of 1.26 Å when the coordination is VIII (Shannon and Prewitt). It is therefore interesting to compare its substitution with that of La^{3+}. This cation is larger than Pr^{3+} and is expected to increase the average (Pr, Sr)–O distance; this will contribute to an increase in the structural stability and then reduce the oxygenation trend. This effect is investigated first.

The substitution of Pr^{3+} for Sr^{2+} is accompanied by a partial oxidation of Ni^{2+} into Ni^{3+} for charge compensation. Oxygen stoichiometry should also be modified because SrO brings less oxygen than the rare earth element; oxygen vacancies are effectively frequently reported in air-prepared $La_{2-x}Sr_xNiO_4$ compounds. However annealing is generally performed in air (or even in pure oxygen) and it is supposed to contain more oxygen than needed to fill the vacancies. Thus, an additional constrain in oxygenation should exist. In agreement with Chen *et al.* (15) single phases $Pr_{2-x}Sr_xNiO_{4+\delta}$ have been prepared with values of x up to $x = 1$. Their oxygen content has been measured for all compositions by thermogravimetric analysis and plotted in Fig. 3. An oxygen excess is noticed which decreases linearly with x for $x < 0.5$. Following the same arguments as previously used for the $Pr_{2-x}La_xNiO_{4+\delta}$ solid solution, this result suggests the structural strain to be a leading factor for the oxygenation of these compositions. For $x > 0.5$ the compounds remain quasi-stoichiometric in oxygen. The formal valence of nickel ions has been measured by iodometric titration; it is also reported in Fig. 3. This agrees with the electroneutrality criterion. The formal valence of nickel is nearly constant up to $x = 0.5$ indicating a constant hole density, an interesting property for comparing resistivities. For $x = 1$, these chemical analyses point to $PrSrNiO_{4.09}$ suggesting the presence of Ni^{4+} species as already reported (14, 23).

Cell parameters versus x are shown in Fig. 4a at room temperature (the equivalent tetragonal cell is used to compare samples with $Pr_2NiO_{4.22}$ which is orthorhombic). We observe the existence of a minimum for a corresponding to a maximum for c at $x = 0.5$ while the volume decreases continuously from $x = 0$ to $x = 1$. Such singularity in c/a has already been observed in the same compound (15) but also in $La_{2-x}Sr_xNiO_{4+\delta}$ (14, 24) or $Nd_{2-x}Sr_xNiO_{4+\delta}$ (25, 26). According to Takeda *et al.* (14, 26) this phenomenon

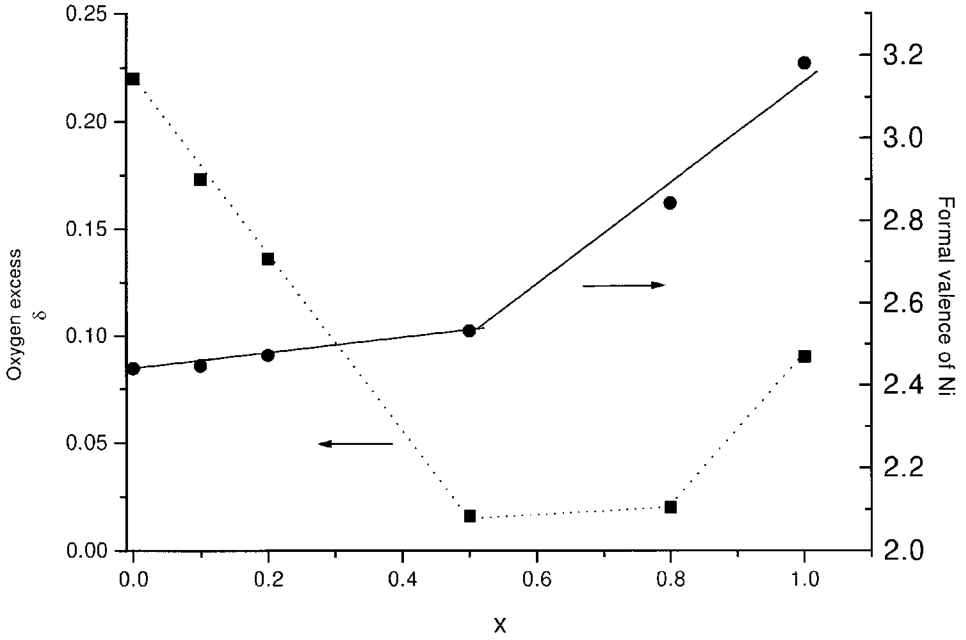

FIG. 3. Excess oxygen content δ and formal nickel valence (right-hand scale) versus strontium fraction x in $Pr_{2-x}Sr_xNiO_{4+\delta}$.

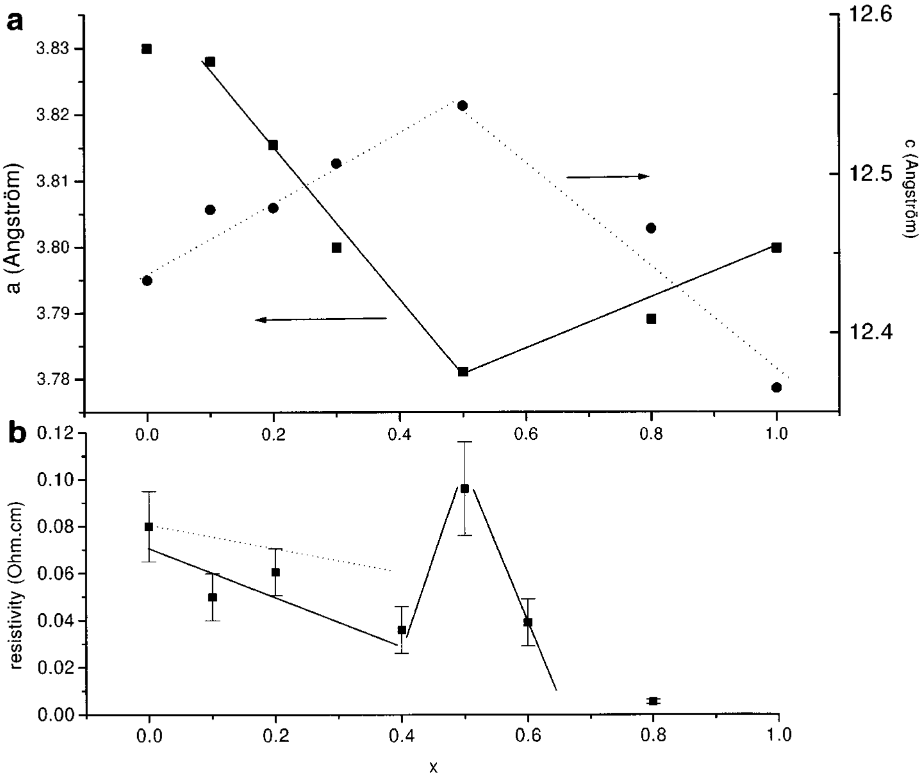

FIG. 4. (a) Cell parameters a (Å) and c (Å) at room temperature versus x in $Pr_{2-x}Sr_xNiO_{4+\delta}$. (The equivalent tetragonal cell is used for $x < 0.2$). (b) Room temperature resistivity versus strontium x in $Pr_{2-x}Sr_xNiO_{4+\delta}$. The dotted line shows the expected variation for a resistivity inversely proportional to the hole density imposed by the Sr concentration.

is linked with a very anisotropic change in RE(Sr)–O(2) bond length (RE = rare earth) and not to any noticeable anomaly in the variation of Ni–O(2) (//c)/Ni–O(1)(ab) ratio at room temperature. In our case, the maximum of c/a occurs when the valence in Ni 2.5, that is for an equal fraction of Ni^{2+} and Ni^{3+}. This effect has thus a presumed electronic origin.

Room temperature resistivity is shown in Fig. 4b. The error bars have the same meaning as explained above and the lines are only guides for the eyes. The dotted line shows the evolution assuming a resistivity inversely proportional to the hole density. The resistivity does not vary according to this simple law; this is particularly obvious for the composition with $x = 0.5$, the resistivity of which is noticeably larger than expected. The resistivities have been in fact measured from 80 to 800 K (18); it is thermally activated below a temperature T_m where it changes to a metal-like behavior (14, 18) (This is also the case for other rare earth nickelates (25, 26)). In our case $T_m = 600$ K for $x = 0.1$ and 400 K for $x = 0.8$. The thermal evolution in this semiconducting range has been analyzed according to $\rho = (1/A)T\exp(W/kT)$ which correctly fits the temperature range 100 K–T_m. Figure 5 plots W versus x and shows a clear anomaly for $x = 0.5$ while W decreases smoothly for other compositions and tends to a very small value when $x = 0.8$. The anomaly at $x = 0.5$ has been related to charge–spin ordering in strontium substituted lanthanum nickelate (5, 27), resulting from holes interacting with a 2D antiferromagnetic spin lattice (28). The above result suggests that a similar effect might be possible in the praseodymium nickelate.

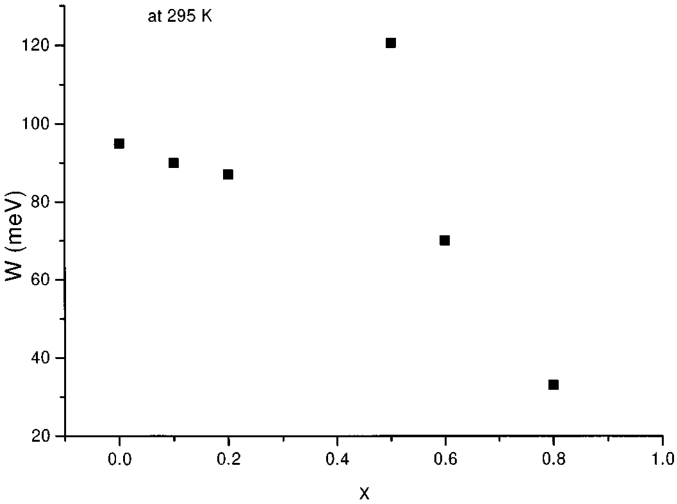

FIG. 5. Activation energy for the thermally activated part of the resistivity in $Pr_{2-x}Sr_xNiO_{4+\delta}$ versus x.

CONCLUSIONS

The comparison of $Pr_{2-x}La_xNiO_{4+\delta}$ with $Pr_{2-x}Sr_xNiO_{4+\delta}$, supports the idea that structural strain is a leading factor for oxygenation of these compounds. This may be a key factor in searching for compounds which have wider oxygen exchange capacities.

A phases transition ($Bmab \rightarrow Fmmm$) occurs in the $Pr_{2-x}La_xNiO_{4+\delta}$ solid solution; it modifies the oxygenation capacities but has no dramatic effect on transport properties. Conversely, Pr appears to have a localization effect on the charge carriers.

The $Pr_{2-x}Sr_xNiO_{4+\delta}$ solid solution shows anomalous behavior for $x = 0.5$ corresponding to $Ni^{2+}/Ni^{3+} = 1$. This anomaly combines an enhancement of the c/a ratio, a larger resistivity, and a peak for the activation energy of the resistivity versus T. It may have the same origin as in La nickelate.

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