Thermo-transport properties of Zn-substituted layered Li-nickel oxide, LiNiO_2

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Abstract. The layered Li-TM-O₂ materials have been investigated extensively due to their application as cathodes in Li batteries. The electrical properties of these oxides can be tuned or controlled either by non-stoichiometry or substitution. Hence the thermo-transport properties of Zn-substituted $\text{LiNi}_{1-x}\text{Zn}_x\text{O}_2$ for $0 \leq x \leq 0.16$ have been investigated in the temperature range of 300–900 K for potential application as a high-temperature thermoelectric material. For $x < 0.08$, the compounds were of single phase belonging to the space group R-3mH while for $x > 0.08$ an additional minority phase, ZnO forms together with the main layered phase. All the compounds exhibit a semiconducting behaviour with electrical resistivity, varying in the range of $\sim 10^{-4}$ to $10^{-2} \Omega\text{m}$ between 300 and 900 K. The electrical resistivity is found to increase with increasing Zn-substitution predominantly due to a decrease in the charge carrier hole mobility. The activation energy remains constant, ~ 10 meV, with Zn-substitution. The Seebeck coefficient of the compounds is found to decrease with increasing temperature and increase with increasing Zn-substitution. The Seebeck coefficient decreases from ~ 95 to $35 \mu\text{V K}^{-1}$ and the corresponding power factor is $\sim 12 \mu\text{W m}^{-1} \text{K}^{-2}$ for the $x = 0.16$ compound.

Keywords. Thermoelectricity; layered oxides; Seebeck coefficient; conductivity.

1. Introduction

The concept of oxides for high-temperature thermoelectric application is relatively new compared with Si–Ge alloys which have been the semiconductors of choice for power modules [1,2]. The main advantages of oxides are they are stable against oxidation at high temperatures, have low density compared with heavy metal alloys and are of low cost. The disadvantages however are several: (a) low charge carrier concentration which results in low-electrical conductivity, (b) brittle nature which makes them difficult to handle and (c) selecting high-temperature non-reactive electrical contact materials is difficult. However, attempts are being made to overcome these limitations and one such attempt is to increase the charge carrier concentration to enhance the electrical conductivity. In this context, layered transition metal oxides containing alkali metal ions such as Li and Na have become prominent for several reasons. The spin and orbital degrees of freedom are strongly coupled to the lattice which facilitates independent control of thermoelectric parameters such as the Seebeck coefficient, electrical conductivity and thermal conductivity [3–6]. Specifically, Co-oxides with Na became popular after they were found to have high thermoelectric figure-of-merit at high temperatures [7,8]. Li-containing transition metal oxides which are well known as electrodes for solid-state batteries, however, have not been investigated extensively for high-temperature thermoelectric application

[9–11]. The electrical conductivity of these oxides can be changed either by manipulating the oxidation state of the transition metal ion by substitution or by varying the quantity of Li in the oxide to above or below a stoichiometric limit. The most common type of charge carriers in these oxides is of p-type with semiconducting temperature dependence. This is because, the dominant charge carriers in these oxides are the small alkali metal cations, specifically at high temperatures. These oxides have a high Seebeck coefficient of $300 \mu\text{V K}^{-1}$ and a low-thermal conductivity of $1 \text{ W m}^{-1} \text{K}^{-1}$ which are both desirable to achieve a high figure-of-merit. Their electrical conductivity, however, is still low for realization of high power delivery capabilities. Among all the Li-transition metal oxides, LiCoO_2 has been extensively investigated both for low- and high-temperature application. In these oxides, it has been observed that substitution of non-isovalent ions such as Ni^{2+} and Mg^{2+} for Co^{3+} results in increasing the electrical conductivity while isovalent substitution with Fe^{3+} results in decreasing the electrical conductivity [4,12,13].

In the present work, LiNiO_2 , the layered compound has been chosen for investigation as it has been well studied for its electrochemical performance in rechargeable batteries. The Ni-ions in this oxide should have an effective valence of 3+ to compensate the charge on oxygen ions [14]. However, it is most stable in a Ni^{2+} configuration which results in the formation of charged defects. The Ni–O bonding therefore becomes strong compared with the Li–O bond which moves

the O-ions closer to Ni^{2+} leaving the Li^+ ions relatively free to move in the presence of electric fields. The presence of these charged defects results in the oxide having a relatively high-electrical conductivity due to which it has been used as an electrode in batteries. Substitution of divalent Zn^{2+} for Ni^{2+} should result in changing the nature of oxygen and thus expected to alter the electrical conductivity. Hence in this work, $\text{LiNi}_{1-x}\text{Zn}_x\text{O}_2$ compounds with $0 \leq x \leq 0.16$ have been synthesized and their high-temperature thermo-transport properties in the range of 300–900 K have been studied in detail.

2. Experimental

$\text{LiNi}_{1-x}\text{Zn}_x\text{O}_2$ compounds have been synthesized by a solid-state reaction using high-purity lithium carbonate (Li_2CO_3), nickel oxide (NiO) and zinc oxide (ZnO) as starting materials. After mixing Li_2CO_3 , NiO and ZnO in a stoichiometric ratio in an agate mortar for 20–30 min, the mixed samples were calcined at 1073 K for 12 h. After calcination, the samples are ground for ~ 10 min to make it more homogeneous. The calcined powder was made into pellets of diameter 12.5 mm and sintered at 1123 K for 12 h under an air atmosphere. The pellet was cut into a rectangular bar for electrical resistivity and Seebeck coefficient measurement. Crystallographic and phase structure analysis of the sintered powder was performed by X-ray diffraction using PAN analytical X-ray analytical instrument with $\text{CuK}\alpha 1$ radiation. Morphological and microstructural analysis is done using a field emission gun equipped secondary electron microscope. Carrier concentration, Hall mobility and Hall coefficient have been determined using a Lake Shore Model 8404 Hall Effect Measurement System. To measure temperature dependent Seebeck coefficient (S) and resistivity (ρ) at high temperature, rectangular bar samples were used in a ZEM-3 ULVAC RIKO system. The density of all the samples was measured using the specific gravity bottle to determine the net porosity present after sintering the pellets.

3. Results and discussion

The phases present and their crystal structure was determined by analysing and refining the X-ray diffraction patterns and are shown in figure 1. For $x \leq 0.08$, the oxides have a single phase with an $\alpha\text{-NaFeO}_2$ -type-layered rhombohedral structure belonging to the R-3mH space group. The lattice parameters ' a ' and ' c ' are found to be 0.288 and 1.4199 nm, respectively. The compound with $x = 0.16$ has two phases – rhombohedral layered LiNiO_2 and ZnO as the minor second phase. These results clearly show that the solubility limit of ZnO in LiNiO_2 is ≤ 0.08 and for compositions in excess of 0.08, ZnO precipitates as a second minor phase. The microstructure present in the oxides was studied by scanning

Figure 1. X-ray diffraction patterns from $\text{LiNi}_{1-x}\text{Zn}_x\text{O}_2$ for $0 \leq x \leq 0.16$, compounds at room temperature. The compounds are single phase with the R-3mH structure except for the $x = 0.16$ compound which has a minor ZnO phase.

Figure 2. Secondary electron image shows formation of large grains together with some porosity. The structure shown is for $x = 0.04$ and is typical for all compounds.

electron microscopy and figure 2 shows a secondary electron image of $x = 0.04$ single phase oxide. The microstructure shows the presence of large grains with a plate-like layered morphology. The microstructure also shows some porosity in the samples. The density of different compositions was measured and it was found to vary between 4.1 and 4.42 g cm^{-3} compared with the theoretical density of $\sim 4.6 \text{ g cm}^{-3}$ for the base LiNiO_2 compound. These results clearly show that the porosity in these compounds is $< 10\%$.

Table 1. Electrical transport parameters, charge carrier concentration n_H and mobility μ_H of all the compounds, determined by measuring the Hall coefficient.

Compounds	Hall mobility μ_H , $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$	Carrier concentration n_H , cm^{-3}	Hall coefficient R_H , $\text{cm}^3 \text{C}^{-1}$
LiNiO_2	0.44	9.49×10^{19}	0.066
$\text{LiNi}_{0.96}\text{Zn}_{0.04}\text{O}_2$	0.18	1.6×10^{20}	0.042
$\text{LiNi}_{0.92}\text{Zn}_{0.08}\text{O}_2$	0.14	1.46×10^{20}	0.043
$\text{LiNi}_{0.84}\text{Zn}_{0.16}\text{O}_2$	0.14	8.83×10^{19}	0.071

Figure 3. Variation of (a) electrical resistivity ρ with temperature, (b) $\ln \sigma$ vs. T^{-1} for the compounds $\text{LiNi}_{1-x}\text{Zn}_x\text{O}_2$ and (c) change in activation energy with increasing Zn^{2+} substitution. The compounds exhibit a semiconducting behaviour and ρ increases with increasing Zn in the compounds.

Figure 4. (a) Temperature dependence of the Seebeck coefficient S and (b) thermoelectric power factor of $\text{LiNi}_{1-x}\text{Zn}_x\text{O}_2$. The S increases with increasing Zn in the compounds and variation of power factor with T for each of the compounds is low.

The charge carrier concentration and their mobility at room temperature was determined by measuring the Hall coefficient and the results are given in table 1. The charge carriers are predominantly holes and their concentration does not vary significantly with the amount of Zn-substitution. The charge carrier concentration in all the oxides is $\sim 10^{20} \text{ cm}^{-3}$. The carrier mobility on the other hand decreases significantly due to Zn-substitution from ~ 0.44 to $0.14 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $x = 0$ and $x = 0.08$, respectively. These results clearly show that Zn^{2+} -substitution for Ni^{2+} decreases the charge carrier mobility by ~ 2.5 times not while changing the carrier concentration. This should result in a reduction in electrical conductivity due to Zn^{2+} substitution and it is indeed observed in the electrical resistivity variation with temperature. The variation of electrical resistivity ρ with T in the range of 300–900 K is shown in figure 3a. The resistivity decreases with increasing T in all the compounds, a typical semiconducting behaviour. The magnitude of decrease however is small, an order of magnitude over the range of 300–900 K indicating that resistivity saturation is nearly complete, $\sim 10^{-4} \Omega \text{ m}$. The resistivity increases with increasing Zn^{2+} substitution, in agreement with the charge carrier mobility's determined by measuring the Hall coefficient. The decreased charge carrier mobility with Zn^{2+} substitution results in increased resistivity at all temperatures. The electrical conductivity of the oxides is found to be thermally activated as seen in figure 3b which shows an Arrhenius behaviour. The change in thermal activation behaviour for $T > 723 \text{ K}$ is probably due to a change in conduction mechanism as it tends to saturate. The electrical conductivity variation can be fitted to the Arrhenius law given by [15,16]

$$\sigma = \sigma_0 \exp \left[-\frac{E_a}{k_B T} \right], \quad (1)$$

where E_a , σ_0 and k_B are the conduction activation energy, pre-exponential factor and Boltzmann constant, respectively. The conductivity variation for all the compositions exhibits a nearly identical behaviour, near parallel fits with no significant change in slope with increasing Zn^{2+} substitution. The variation of activation energy with Zn^{2+} substitution is plotted in figure 3c and it is found that the activation energy of $\text{LiNi}_{1-x}\text{Zn}_x\text{O}_2$ for all x remains almost unchanged, $\sim 10 \text{ meV}$ indicating that the energy barrier for charge transport does not change. These results indicate that a decrease in mobility observed with Zn^{2+} substitution is plausibly due to an increase in effective mass of the carriers across the energy barrier. The variation of the Seebeck coefficient S with T in the range of 300–900 K is shown in figure 4a. It is observed that S decreases with increasing T from ~ 95 to $\sim 35 \mu\text{V K}^{-1}$. The magnitude of S however increases with increasing Zn^{2+} substitution at any given temperature, in agreement with the behaviour of the electrical resistivity. The parameter of importance for thermoelectric energy conversion is the power factor given by S^2/ρ and variation of power factor with T for all the different $\text{LiNi}_{1-x}\text{Zn}_x\text{O}_2$ compounds is shown in figure 4b. It is found that the power factor of all the compounds is low and the unsubstituted compound has the highest power factor at all temperatures compared with the substituted compounds. The highest power factor achieved is around $\sim 12 \mu\text{W m}^{-1} \text{ K}^{-2}$, a low value for application. The concentration of charge carriers as well as their mobility in the LiNiO_2 compound is strongly correlated with charge balance and the associated defect concentration. In the unsubstituted compound, the charge balance is due to $\text{L}^{1+}\text{Ni}^{2+}\text{O}^{2-}$ and O-ions are polarized towards the Ni^{2+} in order to keep this charge balance. Substitution of Zn^{2+} for Ni^{2+} changes this charge balance severely leading not only to extreme polarization of O-ions but also creation of O-ion

vacancies. The resulting vacancy formation reaction can be written as

where $\square$ denotes vacancies. The substitution of Zn^{2+} appears to retain the equilibrium concentration of O-ion vacancies rather than creation of additional charge carriers as originally envisaged. This can be clearly seen in Hall parameters and electrical resistivity. The small changes in the electrical conductivity and Seebeck coefficient with increasing Zn^{2+} substitution is due to a combination of increase in charge carrier mass as well as scattering by charge defects.

4. Conclusions

The thermo-transport behaviour of Zn-substituted LiNiO_2 has been studied in the range of 300–900 K for Zn-substitution varying from 0 to 16 at.%. It is found that the $\text{LiNi}_{0.84}\text{Zn}_{0.16}\text{O}_2$ compound has an additional ZnO minority phase together with the layered compound belonging to the R-3mH space group, while $\text{LiNi}_{0.92}\text{Zn}_{0.08}\text{O}_2$ exhibits a single phase belonging to the parent compound structure. This clearly shows that the solubility limit of ZnO in LiNiO_2 is between 8 and 16 at.%. The thermo-transport properties of the substituted compounds are found to be inferior compared with the parent compound due to the formation of charged defects which increase their effective mass. These results clearly show that the Zn-substituted LiNiO_2 compounds are not ideally suited for high-temperature thermoelectric energy conversion and a different substitution strategy needs to be adapted to enhance the applicability of LiNiO_2 for thermoelectric energy conversion.

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