

PEROVSKITE VERSUS SPINEL TYPE NTC MATERIALS FOR APPLICATION AT ELEVATED TEMPERATURES

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Abstract: Commercial NTC's made of spinel type NiMn_2O_4 materials cannot be used at elevated temperatures because of different reasons, e.g. too low resistivity and activation energy, poor thermal stability. Searching for proper materials we investigated Al and Ti doped LaCoO_3 with the composition $\text{LaMe}_x\text{Co}_{1-x}\text{O}_3$ ranging from $x = 0,1$ to $0,7$. In contrast to NiMn_2O_4 the DC conductivity of the perovskite type material can be tuned by Ti doping within a wide range of applicability. The conduction mechanism was studied with impedance spectroscopy and leads to the conclusion, that both kinds of materials conduct via small polaron hopping. Relaxation phenomena are observed in the frequency range 1 to 1000 kHz and interpreted with theories of Holstein, Sewell and Appel. To explain the difference of the DC response upon doping of spinel and perovskite type materials the conventional probability factor had to be modified.

Perovskitni in spinelni NTC za uporabo pri visokih temperaturah

Ključne besede: NTC koeficienti temperaturni negativni, materiali tipa spinel, materiali tipa perovskite, prevodnost materiala, polaroni, spektroskopija impedančna, spektri impedančni, pojav relaksacije, frekvenca preskoka polarona, verjetnost preskoka polarona

Povzetek: Komercialni NTC upori na osnovi spinela NiMn_2O_4 iz več razlogov niso uporabni pri visokih temperaturah. Imajo prenizko upornost, previsoko aktivacijsko energijo in so toplotno slabo obstojni. Z namenom dobiti primernejše materiale smo raziskovali prevodnost perovskitov na osnovi LaCoO_3 s sestavo $\text{LaMe}_x\text{Co}_{1-x}\text{O}_3$, kjer je Me: Ti, Al in $0,1 \leq x \leq 0,7$. V nasprotju s spinelnimi materiali na osnovi NiMn_2O_4 se da z dodatkom Ti prevodnost perovskitov na osnovi LaCoO_3 spreminjati v širokem območju.

Mehanizem prevajanja, ki smo ga študirali z impedančno spektroskopijo, se da pri obeh tipih materialov pojasniti s takojmenovanim "small polaron hopping". Relaksacijske pojave v frekvenčnem območju 1 do 1000 kHz smo razložili s Holstein, Sewell, Appel teorijo. Pri razlagi razlike v prevajanju dopiranih spinelov in perovskitov je bilo potrebno spremeniti standardni faktor verjetnosti.

INTRODUCTION

NTC materials are usually based on inverse spinels of the type $\text{Ni}_{1-x}\text{Mn}_{2+x}\text{O}_4$. In air they are thermally stable only in the range $x = -0,2$ to 1 above 700°C /1/. Therefore, conventionally sintered materials are always composed of quenched high temperature phases reflecting consequently the technology of processing.

The temperature dependent inversion between cations on tetrahedral and octahedral sites is said to be connected with a disproportion of Mn^{3+} ions, and leads to rather complicated cation distributions /2, 3, 4/. The inversion phenomenon is also a main reason for aging problems, which can be overcome by stabilizing bivalent ions on tetrahedral sites. For instance, a sufficient improvement can be obtained by substitution with Zn^{2+} ions /5, 6, 7/.

The application of sintered materials demands a stable DC conductivity with respect to temperature changes. In many cases, at high enough temperatures the DC conductivity displays an exponential temperature dependence, which can be fitted well by

$$\sigma = \sigma_0 \exp\left[\frac{-E_A}{kT}\right] \quad (1)$$

σ	specific conductivity
σ_0	preexponential factor
E_A	activation energy
k	Boltzmann's constant
T	absolute temperature

However, at lower temperatures the DC conductivity deviates from this exponential behaviour in a rather intrinsic manner, i.e. different processing steps or even doping are not very effective. Up to now little attention has been paid to this low temperature deviations, although they are already observable in the undoped materials like NiMn_2O_4 and CoMn_2O_4 /8, 9/.

In general, manganite materials cannot be used for applications at elevated temperatures because of too low resistivity, too small activation energy and poor

thermal stability. Aiming at proper materials, we investigated the perovskite system $\text{LaMe}_x\text{Co}_{1-x}\text{O}_3$ by substituting Al^{3+} and Ti^{4+} for Co^{3+} ions. Ti and Mg doping was first studied by Ramadass et al. /10/. They reported, that in contrast to the above mentioned manganites, the DC conductivity of the perovskite LaCoO_3 can be modified within a wide range. In this work we compare DC and AC conductivities of spinel and perovskite type materials and apply small polaron models for their interpretation. We anticipated, that both types of materials conduct via a similar process of small polaron hopping.

EXPERIMENTAL

Powders of different spinel and perovskite type materials were produced by coprecipitation of hydroxides from chloride solutions at about pH 11 and calcination at 900°C for 30 minutes. They were pressed into pellets and sintered between 1100 and 1200°C in air for several hours. Electrical contacts were made with a silver paste (E 4031 Demetron) fired at 750°C . Characterization of powders and pellets were made by XRD, REM and titration of the Co^{3+} content. Experimental details are described elsewhere /5,6/.

DC measurements within the temperature range -30 to $+400^\circ\text{C}$ were carried out potentiostatically using platinum clamps. For AC measurements we used the HP impedance analyser 4192A, operative in the frequency range 5 Hz to 13 MHz.

DC CONDUCTIVITY

Typical examples of DC conductivities for both kinds of materials are shown in figs.1 to 3. Whereas Zn doping of NiMn_2O_4 has rather little influence on the

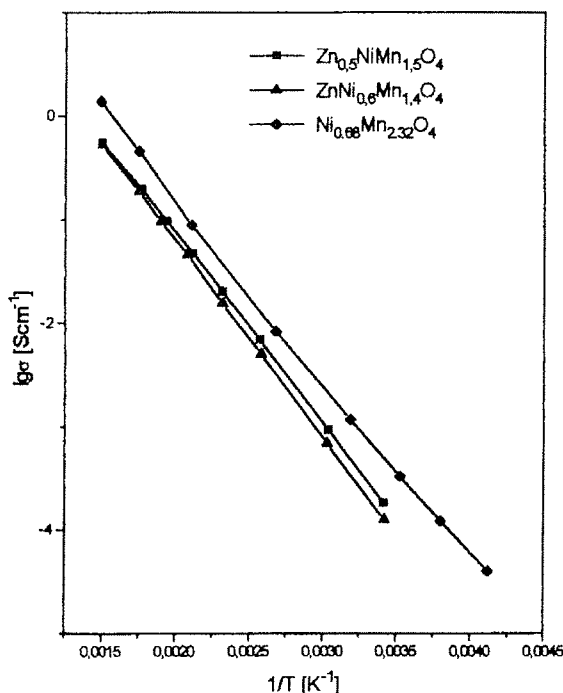


Fig. 1: DC conductivity of Zn doped manganites

conductivity, Ti and Al doping of LaCoO_3 leads to a dramatic decrease of conductivity at $x > 0.1$. The effect is unexpectedly high (fig. 4) and demands for a reasonable explanation. Many conductivity curves deviate at low temperatures from the exponential dependence.

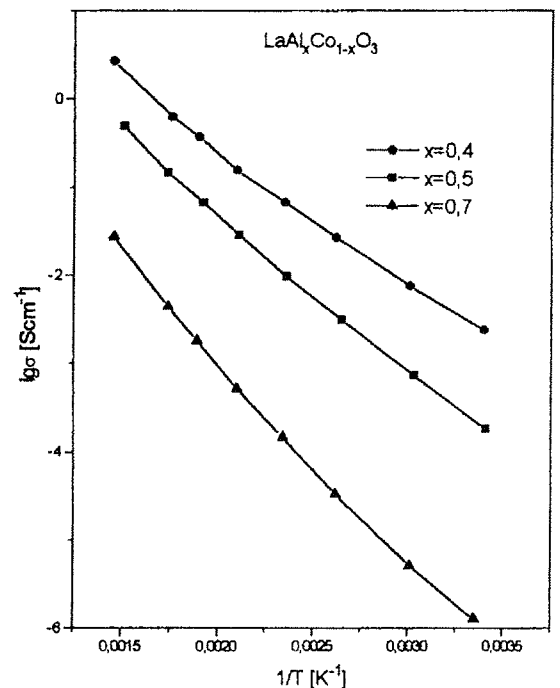


Fig. 2: DC conductivity of Al doped cobaltites

The simplest explanation for the observed exponential conductivity is based on the idea, that charges are hopping over an energy barrier (activation energy) located between neighbouring cations of different valency, similar to the activated motion of ions in solids (jump model, /11/). A theory developed by Holstein /12/ describes the charge transfer as a phonon assisted hopping of (localized) electrons i.e. polarons, leading to deviations from pure exponential behaviour below the Debye temperature. For the diffusion coefficient of activated electrons in a linear chain Holstein obtains two solutions, one due to the diffusion of localized states at higher temperatures (D_{loc} with NTC character), and one due to the motion in a band at very low temperatures (D_{band} with PTC character):

$$D_{\text{loc}} = a^2 2\pi v_0 \left(\frac{J^2}{\hbar^2 v_0^2} \right) \sqrt{\frac{2\pi}{2Y \cosh(\hbar v_0 / 2kT)}} \exp \left[-2Y \tanh \left(\frac{\hbar v_0}{4kT} \right) \right] \quad (2)$$

$$D_{\text{band}} = a^2 2\pi v_0 \sqrt{\frac{2Y \text{csch}(hv_0 / 2kT)}{\pi}} \quad (3)$$

$$\exp\left[-2Y \text{csch}\left(\frac{hv_0}{4kT}\right)\right]$$

v_0 vibrational frequency
 $Y = E_b/hv_0$
 a jump distance
 E_b polaron binding energy
 J overlap integral
 hv_0 vibrational energy

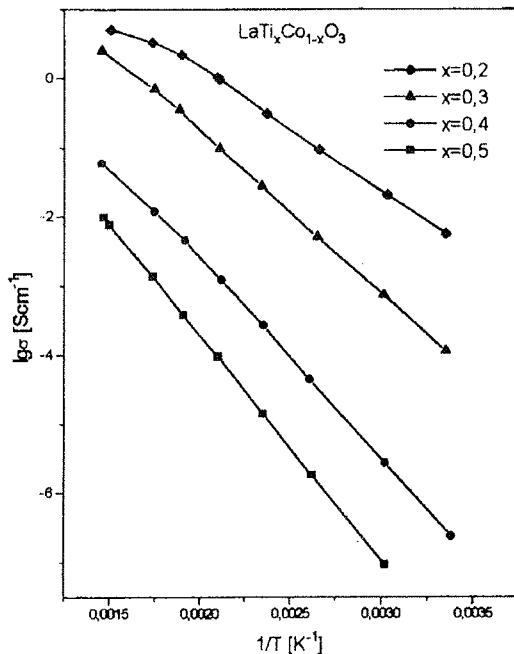


Fig. 3: DC conductivity of Ti doped cobaltites

In the high temperature case with $hv_0 \ll kT$ the exponent $\tanh(hv_0/4kT)$ can be replaced by its argument. With n for the polaron density, $E_A = E_b/2$ for the activation energy, $J = hv_0$ and the Nernst relation $\sigma = (ne^2/kT)D$ one obtains for the DC conductivity

$$\sigma_{\text{loc}} = \frac{ne^2 a^2}{kT} P v_0 \exp\left[\frac{-E_A}{4kT}\right] \quad (4)$$

The factor P contains all preexponential D_{loc} terms except $a^2 v_0$. In the classical adiabatic limit of hopping P equals 1. Assuming that n is approximately given by $c(1-c)N$ ion pairs of different valency (N density of cations, c fraction of donor ions, $1-c$ fraction of acceptor ions) one obtains

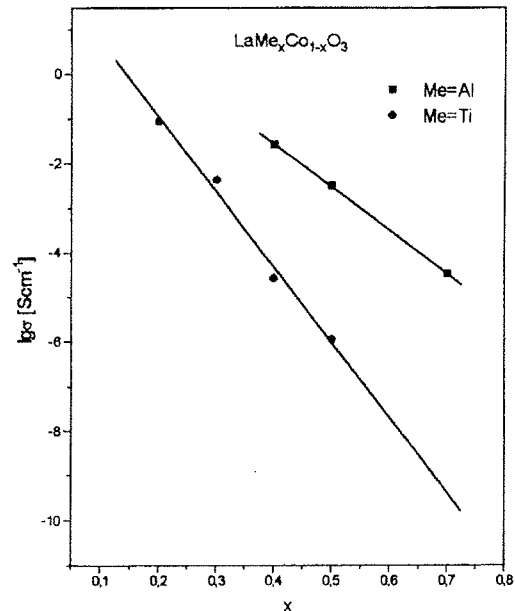


Fig. 4: Composition dependence of DC conductivity at 400 K

$$\sigma_{\text{loc}} = \frac{ne^2 a^2}{kT} c(1-c) v_0 \exp\left[\frac{-E_A}{kT}\right] \quad (5)$$

At this stage one can roughly estimate the DC conductivity of manganites and compare it with the experimental value. Use of the data $v_0 = 10^{13}$ Hz, $N = 2.7 \times 10^{28} \text{ m}^{-3}$, $c = 0.5$, $a = 3 \text{ \AA}$, $E_A = 0.35 \text{ eV}$, $e =$ electron charge and $T = 300 \text{ K}$ gives $s = 4.9 \times 10^{-4} \text{ Scm}^{-1}$. The measured value is about $5.4 \times 10^{-4} \text{ Scm}^{-1}$.

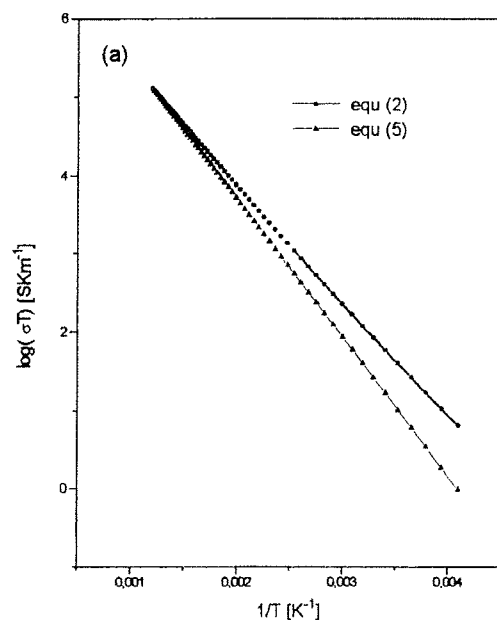


Fig. 5a: Schematic representation of Holstein formulae (2) and (5)

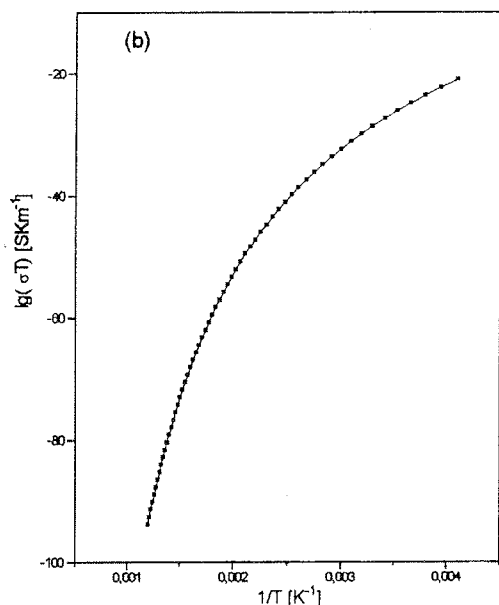


Fig. 5b: Holstein formula (3) on the basis of manganite data

As shown in fig. 5a the Holstein formulae (2) and (5) seem to be a good approach for explaining not only the intrinsic low- but also the exponential high-temperature regimes.

IMPEDANCE SPECTRA

To prove the overall applicability of the small polaron model, we searched for a possibility to measure independently the polaron jump frequency. From impedance spectra we found relaxation phenomena between 1 kHz and 1 MHz. As can be seen from the dispersion curves in figs. 6 and 7 the relaxation effects of both perovskite and spinel type materials are quite similar. In the region around 1 MHz an electrical dispersion is observed, which is caused by the common oxide properties.

The relaxation effects can be simulated electrically by Randles' equivalent circuits, which are sometimes used in electrochemistry. The circuits consist of a series combination of a resistor (R_1) and a parallel condenser (C_1) - resistor (R_2):

$$G_p = \frac{1/(R_1 + R_2) + (1/R_1)(\omega t)^2}{1 + (\omega t)^2}$$

$$t = \frac{R_1}{R_1 + R_2} R_2 C_1 \quad (6)$$

Although such equivalent circuits yield a good data fit for the complex properties, it is not possible to assign the circuit elements to conductive and capacitive

regions within the ceramic material. Thus we tried to find an atomistic interpretation.

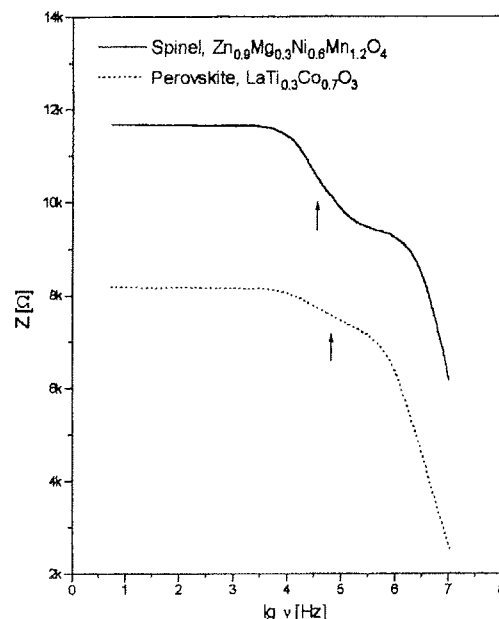


Fig. 6: Comparison of impedance spectra of spinel and perovskite type material

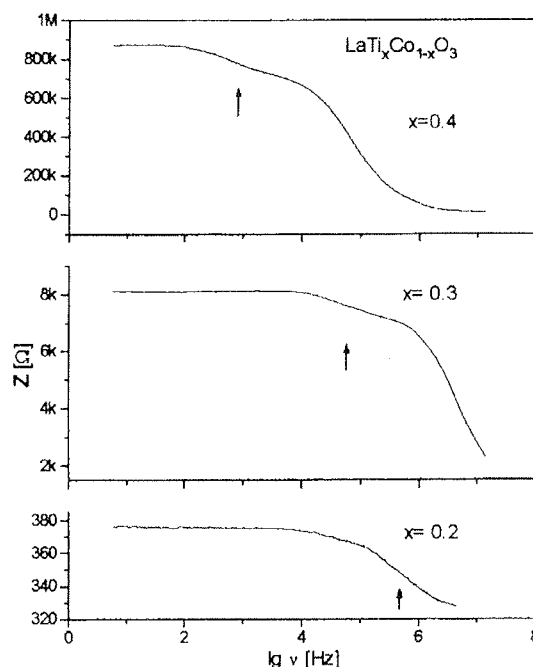


Fig. 7: Impedance spectra of Ti doped cobaltites

Sewell /13/ calculated the complex conductivity of small polarons from first basic principles. In a Debye-like way Appel /14/ applied the two-site model for hopping charges (equivalent to a dipolar flip-flop process) and obtained a frequency dependence, which equals Sewell's and Randles' formulae:

$$\operatorname{Re}(\sigma) \equiv G_p = \frac{ne^2a^2}{kT} \frac{1}{\tau} \frac{\omega^2\tau^2}{1+\omega^2\tau^2} + \sigma_0 \quad (7)$$

Thus from the inflection point of G_p or Z dispersion curves (indicated by arrows in figs. 6 and 7) the relaxation time $\tau = 1/\omega$ can be obtained and interpreted as the reciprocal mean jump frequency given by $c(1-c)v$. The temperature dependence of the DC conductivity and of the mean jump frequency are equal:

$$\frac{1}{\tau} = \frac{1}{\tau_0} \exp\left[\frac{-E_A}{kT}\right] \quad (8)$$

The independently measured data are compared in fig. 8. $1/\tau_0$ ranges from 10^{12} to 10^{13} Hz and has the expected order of magnitude.

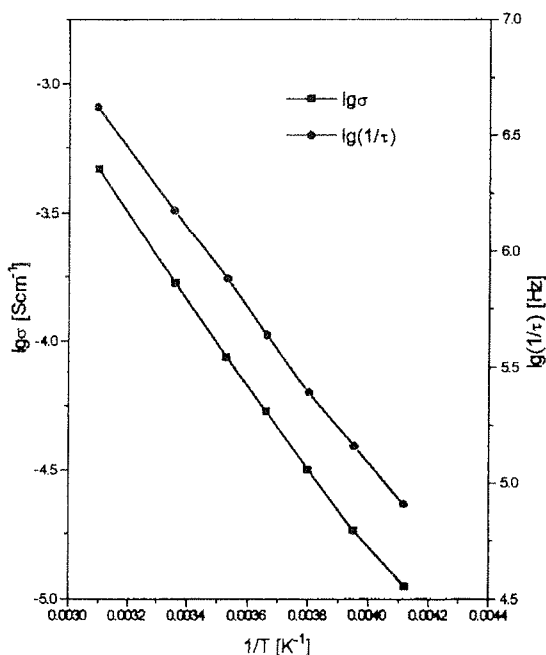


FIG. 8: Comparison of temperature dependence of DC conductivity and mean jump frequency of Zn doped manganite

Besides the temperature shift of the impedance dispersion curves a similar shift with composition x is observed, that is also directly connected with DC conductivities (fig. 9). Both shifts give strong evidence, that relaxation sets in when the AC frequency ν exceeds the mean jump frequency $1/\tau$.

From the experimental results of DC and AC conductivities and the applied dynamic models a phenomenological picture of hopping charges in NTC materials can be drawn. They conduct via polarons, that are able to diffuse through the lattice. At low enough frequencies

the real part is given by independently diffusing charges. At frequencies higher than the mean jump frequency the dipoles cause an additive part to the conductivity by localized relaxation. The dispersion curves are broader by about 25% than predicted by the applied formulas, probably due to the strong coupling of hopping charges to the ionic environment, i.e. during the hopping process neighbouring ions are rearranging almost immediately. Observed and expected mean jump frequencies agree satisfactorily.

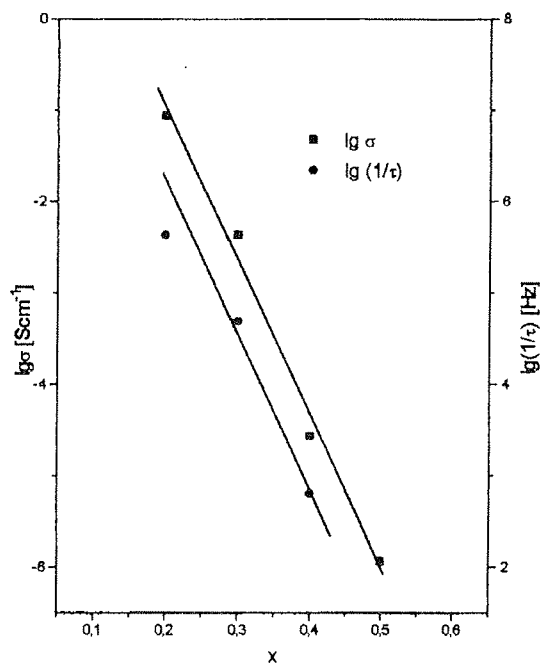


Fig. 9: Composition dependence of mean jumping frequency compared with composition dependence of the conductivity σ of $\text{LaTi}_x\text{Co}_{1-x}\text{O}_3$

HOPPING IN SPINELS

A more detailed interpretation taking into account the different atomistic structure of the materials with regard to application still remains to be discussed. Because of the inverse spinel structure of NiMn_2O_4 (degree of inversion 70-90% [2]) in connection with disproportion, the octahedral cation chains contain Mn^{3+} in a matrix of Mn^{4+} ions, corresponding to an electron majority. Undoped NiMn_2O_4 shows a negative Seebeck coefficient [15].

However, the Seebeck coefficient does not depend exclusively on the excess charge density but also on the relative mobilities of the hopping charges. So for undoped stoichiometric materials with equal positive and negative charge densities, the sign of the Seebeck coefficient is determined by the ratio of mobilities. This seems to be the case with undoped LaCoO_3 [16].

To understand the different conductivity response upon doping we start the discussion from a more or less

hypothetical intrinsic situation. In this situation the densities are given by the equilibrium of disproportion, the corresponding energies we estimate to be about 1 eV. Now, doping of spinels in the range $0,1 < x < 0,5$ causes no appreciable change as observed e.g. in ZnNiMnO_4 or $\text{Cu}_x\text{Ni}_{1-x}\text{Mn}_2\text{O}_4$ or even in the non-stoichiometric compound $\text{Ni}_x\text{Mn}_{2-x}\text{O}_4$ /17, 18, 19/.

The reason, why spinels doping in the range $x = 0$ to about 0,5 is not very effective seems to be simply given by the native high degree of polaronic disorder provoked by inversion. Observed conductivity changes range within one order of magnitude, the activation energies remain approximately constant. The weak density dependence of conductivity is usually approximated by the jump probability product $c(1-c)$.

HOPPING IN PEROVSKITES

A quite different situation of polaronic disorder is found in perovskites. Doping with donors or acceptors below $x = 0,1$ causes a quite normal i.e. linear conductivity increase with x (see Th^{4+} and Sr^{2+} doping in LaCoO_3 , /16/). The same holds for Ti^{4+} doping, but above the limit $x = 0,1$ there is an exponential-like decrease with increasing x .

To explain the crucial exponential-like decrease (fig.4) we assume, that the probability factor $c(1-c)$ is inadequate and has to be improved by statistical methods. There are two statistical approaches, a random liquid model leading to a probability given by $\text{cexp}(-c)$ /20, 21/ and a solid state model leading to a binominal distribution probability /22, 23/, which itself is the precursor of the Gaussian function $\text{exp}(-c^2)$. For small c values the first model would give on expansion the product $c(1-c)$.

According to the binominal distribution, the probability of finding no or one acceptor ion in the second nearest shell around a donor ion or vice versa, is given in table 1. For high x values a pronounced decrease of donor-acceptor pairs (conducting polarons) is calculated.

Table 1: Composition of second shell

x	no acceptor [%]	one acceptor [%]
0.01	88.64	10.74
0.05	54.04	34.13
0.10	28.24	37.66
0.20	6.87	20.62
0.30	1.38	7.12
0.40	0.22	1.74
0.50	0.02	0.29

Both models supply probability functions with an initial increase and a following exponential-like decrease of conducting $\text{Co}^{3+}/\text{Co}^{2+}$ or blocking $\text{Ti}^{4+}/\text{Co}^{2+}$ and

$\text{Al}^{3+}/\text{Co}^{3+}$ pairs. As no irregularities in the susceptibility behaviour are observed /10/, we exclude super-exchange hopping via oxygen ions to one of the 6 nearest neighbours. Hence a hopping process to one of the 12 second nearest neighbours over a distance of about 6 Å remains to be operative. This is in contrast to hopping in spinels over distances of about 3 Å to one of the 4 octahedral neighbours.

CONCLUSIONS

Comparing the electrical properties of doped manganites and cobaltites, one can state that small polaron hopping is operative in both kinds of materials. However, there are essential differences upon doping concentration, arising from the different structures. In the perovskite case there is no inversion provoking high native disorder, so that doping is much more effective than in the spinel case. Hence for a quantitative description of the hopping probability one needs a better statistical approach. Because of the exponential decrease of DC conductivity with increasing Ti doping, the higher activation energies and the much better thermal stability, perovskites could be used for NTC applications up to 500°C. Al doped cobaltites do not meet all of these requirements.

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