ELECTRONICALLY CONDUCTIVE PEROVSKITE TYPE MATERIALS

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Abstract: Since oxide materials with exceptional electronic properties recently found their application in semiconductor technology, materials research has got important stimulation. New preparative techniques offer the possibility to integrate materials, whose utilisation for a long time was considered to be confined to the ceramics world. This contribution will give a review on a group of electronically conductive oxides with perovskite structure. A short introduction into the crystallography is followed by an overview of theoretical models of band type conduction and polaronic conduction. General considerations for the formation of bands are discussed and the conditions for itinerant or localised electrons are outlined. Examples are given to illustrate these concepts.

Elektronsko prevodni perovskitni materiali

Ključne besede: materiali tipa perovskite, materiali prevodni elektronsko, materiali oksidni, prevodnost elektronska, prevodnost ionska, prevodnost protonska, prevodnost polaronska, prevodnost tipa pas, polaroni, tehnologija polprevodnikov, oblikovanje pasov, strukture pasovne, odvisnost temperaturna

Povzetek: Uporaba oksidnih materialov z izjemnimi elektronskimi lastnostmi v polprevodniški tehnologiji je dodatno vzpodbudilo raziskovanje na področju materialov. Nove tehnike priprave so omogočile izdelavo komponent, v katerih so kombinirani oksidni materiali z različnimi karakteristikami. V prispevku obravnavamo skupino elektronsko prevodnih oksidov s perovskitno strukturo. Po kratkem uvodu, ki obravnava kristalografijo teh materialov, nadaljujemo s pregledom teoretičnih modelov pasovnega in polaronskega prevajanja. Obravnavamo splošne pogoje za tvorbo prevodnih pasov kakor tudi pogoje za pojav lokaliziranih elektronov. Z nekaj primeri tudi podpremo opisane koncepte.

1. INTRODUCTION

Perovskites represent a very common type of ternary compounds with the general formula ABO_3. They exhibit a wide range of interesting electrical and magnetic properties, which depend primarily on the character of the d-electrons of the metal cation at the B-site. Most ABO_3 compounds are semiconductors or insulators. However a few of them show metal-like electronic conductivity, while others are good ionic conductors. Similar is the range of magnetic properties including the interesting effect of giant magnetoresistance. The source of electric conductivity in some cases is the electronic structure and the formation of bands like in $SrRuO_3$ or $LaNiO_3$. Such compounds theoretically can be treated as "metals". Due to the temperature dependence of spin and valence states and coupling of the electronic orbitals non-metal to metal transitions or semiconductor to metal transitions can be observed.

Another reason for conductivity may be the formation of polarons as charge carriers. Polarons are electrons, partially localised by the polarisation of the lattice. The transport of a polaron in an electric field needs the hopping over an energy barrier located between neighbouring cations of the same species with different valence state. The preparation and modification of such mixed valence compounds can be done by doping with heterovalent cations (examples will be given). In other cases the mixed valence is caused intrinsically by oxygen deficiency. The temperature characteristics of such polaron conductors is similar to semiconductors because of the activated charge transport.

Just to complete this overview it has to be mentioned that also ionic conductivity occurs in perovskite type oxides as oxide ion conduction (e.g. $LaAlO_3$ and $CaTiO_3$) or as proton conduction (e.g. doped $SrZrO_3$). The effect depends strongly on the concentration and distribution of vacancies in the lattice. Ionic conductivity is combined in some cases with a certain electronic conductivity. For some applications e.g. electrode materials for solid oxide fuel cells (SOFC) such a mixed ionic and electronic conductivity is highly appreciated.

Principal investigations and the theoretical treatment of these types of conductors have been done years and decades ago. The application of these materials however is just on the start. Nowadays conductive perovskites are under investigation as electrode material as well as solid electrolyte for solid oxide fuel cells (SOFC), to replace noble metal electrodes or as sensor material. As thin films these compounds have raised attention as buffer layers or even electrodes for ferroelectric /1/ or superconductive /2/ thin films. New preparative techniques such as pulsed laser deposition, magnetron sputtering or chemical solution deposition are vital for extending the field of application.

2. STRUCTURAL CONSIDERATIONS

Particular for the crystallography of ABX_3 perovskites is the combination of cations of different size. The bigger A-cation, similar in size to the anion X, forms together with this anion a close packed cubic structure. There the A-cation is twelve-fold co-ordinated. The smaller B-cation occupies octahedrally co-ordinated interstices in that structure entirely formed by the anions. By this way, octahedra containing B-cations are linked at their corners to form a three-dimensional framework (fig. 1).
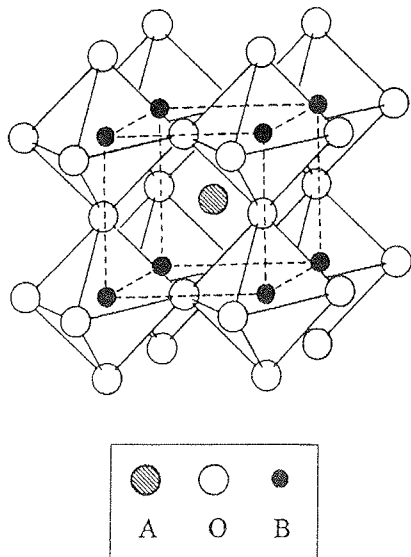

◍	◯	●
A	O	B

Fig. 1:   Unit cell of an ideal perovskite ABO_3.

The stability of the perovskite structure is primarily derived from the electrostatic energy achieved by the twelve-fold co-ordination of the A-cation. These sites are formed by the corner sharing octahedra containing the B-cation. Thus the first prerequisite of a stable perovskite is the existence of a rigid octahedral framework, which, in turn, requires the preference of the B-cation for an octahedral co-ordination. Moreover a high effective charge is favourable. Since any A-cation must occupy the relatively large interstices created by these corner sharing octahedra, a second prerequisite is the appropriate size of the A-cation. If the A-cation is too large, the B-X bond length cannot be optimised, thus hexagonal stacking with face sharing octahedra becomes competitive /3,4/. If the A-cation is too small, A-X bonding stabilises structures with a lower anionic co-ordination around the A-cation. It should be noted that the ionic radii strongly influence the bonding between the ions and by that way also the band structure.

Goldschmidt /5/ defined a very useful relationship for the stability of perovskites containing a tolerance factor t.

$$R_A + R_X = t\sqrt{2}(R_B + R_X) \qquad (1)$$

R_A, R_B and R_X are the empirical ionic radii of the respective ions. The perovskite structure occurs only for values of $0.8 < t < 1.1$. The ideal close packing with cubic structure corresponds to $t = 1$. In most cases however orthorhombic and rhombohedral distortions occur, but also tetragonal, triclinic and monoclinic structures are found. Small values for t ($t < 0.8$) correspond to a comparable size of A-and B-cations and lead to more close packed structures like ilmenite. For $t > 1$ the space available for the B-cation in its oxygen cage becomes so large that a displacement is possible. This is the origin of the ferroelectric effect of $BaTiO_3$.

The valences of the A- and B-cation can be chosen nearly arbitrarily as long as they sum up to six. Thus perovskites can be classified as I-V-perovskites (e.g. $KNbO_3$), II-IV-perovskites (e.g. $BaTiO_3$) and III-III-perovskites (e.g. $LaCoO_3$). Even ReO_3 can be treated as perovskite with Re^{6+} as B-cation and a vacancy as "A-cation". Because of the different size of the cations, an inversion, i.e. an exchange between A- and B-cations like in spinels, is impossible. On the other hand the perovskite structure is very tolerant towards defects and so deviations from stoichiometry (oxygen excess or deficiency) can cause mixed-valence compounds. The defect distribution can be statistical or ordered, forming superstructures. Well known for such defect superstructures are the perovskite type high temperature superconductors.

3. PEROVSKITES WITH BAND STRUCTURE

Several perovskite oxides exhibit metallic conductivity. Typical examples are ReO_3, A_xWO_3, $AMoO_3$ (A = Ca, Sr, Ba), $SrVO_3$, $LaTiO_3$ and $LaNiO_3$. An early but still very valuable approach to the band structure of transition metal compounds was derived by Goodenough /6, 7, 8/. With empirically formulated criteria for the overlap of cation-cation and cation-anion-cation orbitals, Goodenough rationalises the nature of the d-electrons in transition metal compounds and the conditions for localised and itinerant electrons.

The concept is based on the transfer energy term b_{ij}, which measures the strength of the interaction between two neighbouring atoms i and j:

$$b_{ij} = \langle \Psi_i H \Psi_j \rangle \approx \varepsilon_{ij} \langle \Psi_i \Psi_j \rangle \qquad (2)$$

In this equation H is the Hamilton operator for the electronic wave functions or orbitals Ψ_i and Ψ_j of the neighbouring atoms i and j and ε_{ij} is the one-electron energy term. The expression $\langle \Psi_i \Psi_j \rangle$ is known as overlap integral. Although it is not possible to get good absolute estimates of b_{ij}, one can predict its variation in a series of isostructural compounds. In oxides with significant cation-cation interaction, b_{ij} is proportional to the reciprocal cation-cation separation. Where the cation-anion-cation interaction is important, b_{ij} is related to the covalent mixing of the cation-anion orbitals. For small values of b_{ij}, the outer d-electrons are localised, for large values of b_{ij} they are itinerant in a band and behave like in a metal. In a series of isostructural compounds, there is a critical value of the transfer energy, separating the localised from the itinerant electron regime. This critical transfer energy b_c is expressed in terms of the position of the cation in the periodic table, the principal quantum number of the d-orbital, the formal charge and the total spin of the cation.

In the case of the perovskite the B-cations are octahedrally co-ordinated by the anions. That means that d-orbitals of the B-cation are no longer degenerated but split into e_g-and t_{2g}-orbitals. This splitting has to be taken into account for estimating the overlap integrals. Figure 2 illustrates the position and the interesting electron orbitals in the perovskite structure. The B-cations are placed in the corners of a cube with the anions inbetween on the edges. To simplify at one B-cation only the e_g-orbitals and on another B-cation only the t_{2g}-orbitals are drawn. For the one anion the p-orbitals are drawn. The bonding between anion and B-cation thus can be σ- or π-type. In principle also a bonding between B-cations across the face of the cube has to be considered. Hence the following overlap integrals between neighbouring B-cations labelled 1, 2 and 3 (fig. 2) are possible:

$$\Delta\sigma_{cc} = \langle \Psi_{t2} \ \Psi_{t3} \rangle \qquad (3)$$

$$\Delta\sigma_{cac} = \langle \Psi_{e1} \ \Psi_{e2} \rangle \qquad (4)$$

$$\Delta\pi_{cac} = \langle \Psi_{t1} \ \Psi_{t2} \rangle \qquad (5)$$

$\Delta\sigma_{cc}$ is the overlap integral between the t_{2g} orbitals between the cations 2 and 3 (the label cc is for cation-cation overlap). Since the distance across the face of the cube is 5 - 6 Å the contribution of $\Delta\sigma_{cc}$ is considered negligibly small. $\Delta\sigma_{cac}$ and $\Delta\pi_{cac}$ are the corresponding overlap integrals along the edge of the cube involving the covalent bonding with the anion. These integrals determine the behaviour of the d-electrons and if they are large enough, it is appropriate to construct collective electron orbitals or bands. On the other hand, if these overlap integrals are small, the d-electrons are localised on discrete cationic sites. Therefore it is possible to define a critical overlap integral that is proportional to a critical transfer energy b_c and to distinguish between systems with localised d-electrons and such with itinerant or "band" electrons.
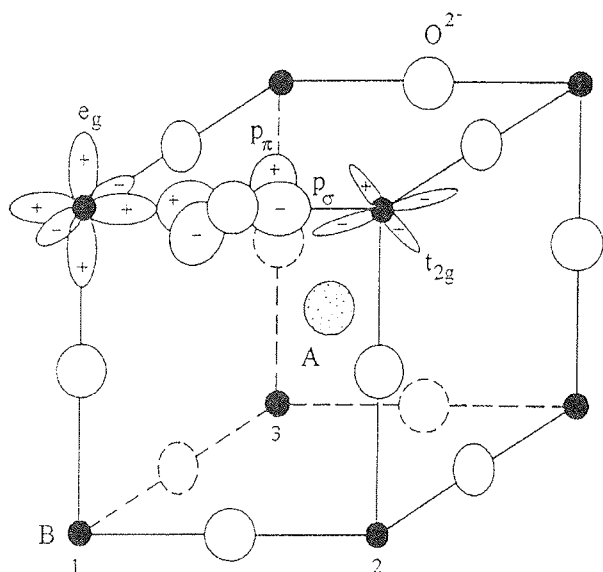
As mentioned before, bc is related to the atomic number, the formal charge, the principal quantum number of the d-electrons and the total spin of the B-cation. Applied to the $LaBO_3$-series, with B from the first period of the transition metals (Ti^{3+}, V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Ni^{3+}) it turns out that the total spin determines the electron behaviour /9/. Figure 3 contains the data for the electrical resistivity ρ and the activation energy E_a for the conductivity of these $LaBO_3$ compounds. In $LaTiO_3$ and $LaNiO_3$ (Ni in the "low-spin" configuration) the spin of the transition metal ions S is equal to 1/2 resulting in itinerant electrons and metallic behaviour (low resistivity and low activation energy). Compounds with $S \geq 1$ for the B-cations, such as V^{3+}, Cr^{3+}, Mn^{3+} and Fe^{3+} are insulators with localised electrons (high resistivity and high activation energy). A special case is found with the compound $LaCoO_3$ where the temperature dependent population of "low-spin"- and "high-spin"-states causes a transformation from an insulator (or better semiconductor) to a metallic conductor around 1200 K /10, 11/.
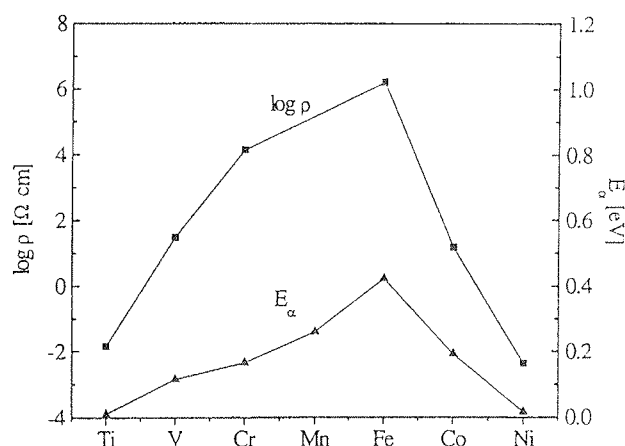

Fig. 3: Activation energy E_a and resistivity ρ at 300 K for $LaMeO_3$ compounds (from /9/).

The influence of the A-cation is demonstrated in the case of $LnTiO_3$ (Ln = La, Nd, Sm, Dy, Yb) in a work published by P. Ganguly et al. /9/. The electrical resistivities of these compounds are shown in figure 4. $LaTiO_3$ has the lowest resistivity with a weak temperature dependence according to its metallic behaviour. $NdTiO_3$ shows similar characteristics. In $SmTiO_3$ temperature dependence of the resistivity becomes pronounced but is comparable to thermal excitation energies of degenerate semiconductors. Thus it appears, that at least in the lighter rare-earth titanates exist itinerant d-electrons. With decreasing size of the rare-earth ion (Dy, Yb) a distinct increase of the resistivity is observed. This trend indicates narrowing of the d-band due to the decreasing overlap of the orbitals of the B-cation. As the electronic configuration of the Ti^{3+}-ion is $t_{2g}^1 e_g^0$, which means that only one electron occupies a t_{2g}-orbital, the bonding along Ti-O-Ti is π-type over the oxygen p-orbital. Such type of bonding would have competition from Ln-O bonding, which becomes favourable as the electron affinity of the Ln^{3+}-ion increases or its size decreases (both leads to a shorter bond length).

Fig. 2: Unit cell of a perovskite with electron orbitals. Overlap integrals can be distinguished as $\Delta\sigma_{cac}$, $\Delta\pi_{cac}$ (between cation 1 and 2 or 1 and 3) and $\Delta\sigma_{cc}$ (between cation 2 and 3).

Measurement of the Seebeck-coefficient /9/ reveals, that $LaTiO_3$ is a p-type conductor. $LaNiO_3$ is reported to be a metallic oxide with n-type conduction /12, 13, 14/. It crystallises in a rhombohedrally distorted perovskite structure where the nickel ions (Ni^{3+}) are in the low spin configuration of $t_{2g}^6 e_g^1$. According to a first approximation the conduction band is formed by the hybridisation of the e_g-orbitals of nickel and the oxygen p-orbitals. Since the t_{2g}-band is filled and the e_g electron takes place in forming the delocalised, quarter filled σ^*-band, the compound has no local components at the Ni^{3+} site and shows a temperature independent susceptibility (Pauli-paramagnetic behaviour). The Seebeck-coefficient of $LaNiO_3$ is small and negative (around -20 μV/K). Its magnitude increases linearly with temperature, thereby confirming the presence of a partially filled band /12/.

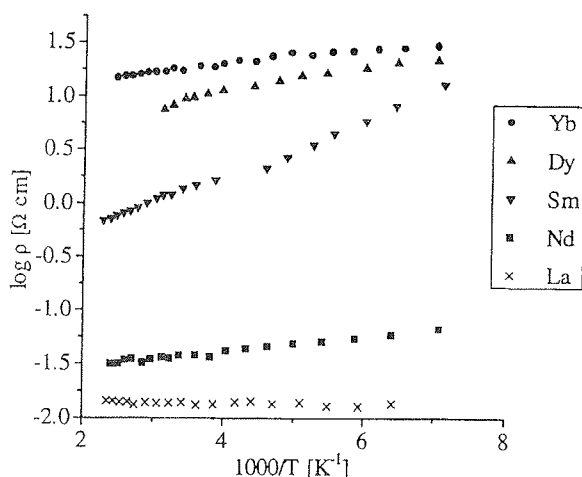*Fig. 4:* *Temperature dependence of the resistivity ρ of $LnTiO_3$ (from /9/).*

In air $LaNiO_3$ decomposes above 860°C /15, 16/ emitting oxygen and NiO. There exists a series of intergrowth phases with the general formula $(LaO)(LaNiO_3)_n$ or $La_{n+1}Ni_nO_{3n+1}$. It can be understood as a phase with n perovskite layers followed by one LaO layer with rock salt structure. For n = 1 this will end up with the compound La_2NiO_4 (and NiO). La_2NiO_4 is a two-dimensional conductor with complex electrical behaviour /17/. To overcome the problem of decomposition the perovskite can be stabilised by doping with other transition metals such as Cr, Mn, Fe or Co. For each system $LaNi_{1-x}Me_xO_3$ there exists a critical composition or x_c, where the temperature coefficient of resistivity changes its sign. Thus x_c formally defines the concentration at which a metal-semiconductor transition takes place. The best stabilisation can be achieved with Co ($x_c \approx$ 0.35-0.5) /18, 19/. The compound $LaNi_{0.6}Co_{0.4}O_3$ can be sintered in air up to 1300 °C.

4. POLARONIC CONDUCTION IN PEROVSKITES

In a polar crystal the electron-lattice interaction in many cases is so strong that a band model is not applicable. The polarisation and the decrease of the overlap integrals leads to a narrowing of the band width. To a certain extent of the electron-lattice interaction the band model is still valid, only with a higher effective mass of the electron. With increasing electron-lattice interaction the band structure breaks down and one has to consider localised electrons. Electronic conductivity in such materials is still possible but the behaviour is fundamentally different from band conductors. The charge transport is described by the polaron model. A polaron is an electron or hole which polarises its surrounding and thus gets trapped at a lattice site in an energy minimum. Through interaction with phonons the polaron can overcome this energy barrier and move in an electric field to an appropriate neighbouring lattice site, where it will be localised again for a certain time. As a consequence the charge transport is thermally activated with a low but strongly temperature dependent mobility.

A simple model compound for polaronic conduction is NiO doped with lithium /20/. The Li^+ ions occupy nickel-sites giving rise to the formation of Ni^{3+}-ions. These Ni^{3+}-ions can be regarded as holes trapped by polarisation and surrounded by Ni^{2+}-ions. The number of charge carriers is determined by the lithium concentration. Activated by phonons an electron can hop from a neighbouring Ni^{2+} to the Ni^{3+}. Thus in first order the charge transport can be treated similar to the movement of an ion into a defect. The mobility μ and hence the conductivity σ exhibit an exponential temperature dependence:

$$\sigma = \sigma_0 \exp\left(\frac{E_A}{kT}\right) \qquad (6)$$

In this expression E_A is the activation energy necessary for the hopping over the energy barrier, k is the Boltzmann-factor, T the absolute temperature. The activation energy E_A usually lies in the region of 0.2 - 0.8 eV. The forefactor σ_0 is considered temperature dependent and contains a hopping probability, which usually is taken near one.

However at low temperatures (below the Debye temperature exactly spoken) the conductivity deviates intrinsically from this purely exponential characteristics and more sophisticated models have to be applied to explain the behaviour in this region. A detailed description of polaron transport is given by Appel /21/ or Austin and Mott /22/. Generally it can be said that polaronic charge transport occurs between neighbouring ions of the same species on crystallographically equivalent sites with a valence difference of one. The conductivity characteristics is determined by the temperature dependence of the mobility whereas the number of carriers in principle remains constant. The most common way to influence the number of carriers, i.e. the ration between Me^{n+} and $Me^{(n+1)+}$ is doping with heterovalent ions.

In the case of perovskite type materials, most of the compounds assigned as "insulators" or "semiconductors" exhibit polaronic conductivity, if one of the cations is able to posses different valence states. The development of electrode materials for solid oxide fuel cells has focused on perovskite type materials based on lanthanum as A-cation and Cr, Mn, Fe, Co as B-cations with various dopants added, because of their thermal stabil-

ity and good electrical conductivity at high temperatures. The same materials can be used for temperature sensors as well /23/. For this application a high temperature coefficient of resistivity and a suitable resistivity range is important. Depending on the application one is interested either in an increase or in a decrease of the electrical conductivity. This is achieved in most cases by doping either with heterovalent ions or aliovalent ions, the latter causing simply a dilution of carriers. Due to the high tolerance of the perovskite structure towards defects, the excess or deficiency of oxygen has a considerable impact on the carrier concentration as well. Thus the oxygen partial pressure during preparation and operation is an important parameter for the electrical characteristics. The consequences of all these aspects should be demonstrated in the following examples.

$LaCoO_3$ is known to be a p-type semiconductor between 200 K and 1210 K. The relatively high conductivity of this compound is found to be due to a disproportion of high spin and low spin Co^{3+} into Co^{4+} and low spin Co^{2+} /11/. Both species in a matrix of Co^{3+} act as polarons with an activation energy of 0.35 eV /24/. The p-type conductivity is explained by the higher mobility of the "holes" (i.e. the Co^{4+}).

Addition of strontium to $LaCoO_3$ will increase the conductivity. The Sr^{2+}-ions will substitute La^{3+}-ions on A-sites. For electroneutrality reasons Co^{4+}-ions are formed, which act as additional p-type carriers. The same effect will be caused by doping with Mg^{2+}-ions for example, which occupy B-sites. This electronic charge compensation however is limited to low dopant concentrations. As the valence of +4 of cobalt is rather unstable, also ionic charge compensation can occur by the formation of oxygen vacancies:

$$2\, Co^{\bullet}{}_{Co} + O_O \rightarrow V_O^{\bullet\bullet} + 2\, Co_{Co} + 1/2\, O_2 \qquad (7)$$
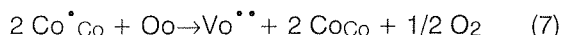
In the Kröger-Vink notation the $Co^{\bullet}{}_{Co}$ corresponds to the Co^{4+}-ion. It is eliminated by the formation of an oxygen vacancy. Thus ionic charge compensation does not contribute to the polaronic conduction and the conductivity (i.e. charge carrier concentration) exhibits a pronounced dependence on oxygen partial pressure. Contrary to $LaCoO_3$ is the behaviour of $LaMnO_3$. As the Mn^{4+}-ion is much more stable, this species already exists in undoped $LaMnO_3$ causing an oxygen excess. Even after doping with two-valent ions such as Sr^{2+}, an oxygen excess can be observed at high oxygen partial pressure /25, 26/. The excess oxygen is not found at interstitial sites but causes cation vacancies on A- and B-sites /27/.

For n-type conductivity $LaCoO_3$ has to be doped with ions with a valence of four. Examples are Th^{4+} (on A-sites) and Ti^{4+} (on B-sites). For low dopant concentrations the perovskite exhibits n-type conductivity, due to the formation of Co^{2+}. In the case of $LaCo_{1-x}Ti_xO_3$ the electronic charge compensation takes place up to $x \approx 0.2$, higher concentrations of titanium result in compounds with oxygen excess. The Seebeck coefficient however, indicating the conduction type, turns its sign already for $x \approx 0.1$. This unusual behaviour is due to the formation of Ti^{4+}-Co^{2+} clusters. In these clusters Co^{2+}-ions are bound and cannot act as donors for the polaronic conduction.

5. SUMMARY

Among perovskite type oxides electronic conduction, either as band-type or polaronic conduction, is frequently found. The differentiation between these mechanisms is done mainly by considerations about magnitude and temperature dependence of the conductivity and the charge carrier concentration. From the estimation of overlap integrals, which involves the atomic number, the formal charge, the principal quantum number of the d-electrons and the total spin of the B-cation, one can derive an approximate band-structure and roughly explain the electrical behaviour. Additional influences come from the crystal structure (ionic radii of A- and B-cation, superstructures, lattice distortions). That is why, despite of the availability of good commercial software for the calculation of band structures, the estimation and prediction of electric properties still needs a great deal of empirical assumptions and experimental efforts.

In many cases a band picture is not applicable, due to the more or less polar character of oxides. The polarisation causes a narrowing of the bands leading finally to a break down of the band structure, because of the uncertainty relation. In such a case the charge transport is described with a hopping process of an electron from a cation Me^{n+} to a cation $Me^{(n+1)+}$ over an energy barrier. Thus the conductivity is mainly influenced by the height of the energy barrier and the probability that the neighbouring cation is an appropriate one. For the great variety of semiconducting oxides the polaron model has turned out to be a good tool to explain the electrical behaviour over a wide range of temperature and conductivity values.

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