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Charge-Transfer Transitions in Mixed Metal Oxides: Their Consequences and Influence on Physical Properties

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Charge-Transfer Transitions in Mixed Metal Oxides: Their Consequences and Influence on Physical Properties

Charge-transfer transitions can be observed in the optical spectra of many mixed metal oxides. Attention is drawn to the fact that their occurrence is even more frequent than sometimes thought. It is shown that their influence on physical properties can be large. Examples are taken from the fields of luminescence and photoelectrochemistry.

INTRODUCTION

Because they determine the color of many compounds, charge-transfer (CT) transitions are known to every chemist. Well-known examples in the field of inorganic chemistry are the compounds $KMnO_4$ and $K_2Cr_2O_7$. The strong optical absorption of these compounds in the visible region is due to an electron which is promoted from the highest-filled molecular orbital (localized on the oxygens) to the lowest-empty molecular orbital (consisting of a 3d orbital of the transition-metal ion). Transitions of this type can be observed in many complexes consisting of a highly charged cation surrounded by a number of anions. Jørgensen's work should be especially mentioned in this context.[1,2]

Another type of transition giving rise to strong optical absorption is the intervalence charge-transfer transition, in which an electron jumps between two ions of the same element, but with different charge. A very recent review has been given.[3] As a special case of this type we may consider charge-transfer transitions between ions of different metals. The situation here is considerably less clear than in the foregoing cases. The "donating" cation should have readily excitable electrons of its own, and the electron affinity

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of the "accepting" cation should be large. Examples of such combinations are:

(i) Tl^+–Ir^{4+}. The introduction of Tl^+ in Cs_2IrCl_6 produces an extra absorption band which has been ascribed to charge transfer from the 6s level of Tl^+ to the $5d(t_{2g})$ level of Ir^{4+}.[4]

(ii) Ag^+–Cr^{6+}. The brick-red color of Ag_2CrO_4 (compare the yellow K_2CrO_4) has been ascribed to charge transfer from the 4d level of Ag^+ to the empty 3d(e) level of Cr^{6+}.[5]

(iii) Bi^{3+}–V^{5+}. The absorption and emission band observed at low energies in the system $(Y,Bi)VO_4$ has been ascribed to charge transfer between the 6s level of Bi^{3+} and the 3d(e) level of V^{5+} because neither $BiPO_4$ nor YVO_4 shows this transition in its spectra.[6]

In this Comment we shall stress the importance of these charge-transfer states for certain physical properties of various kinds. We shall not enter into the problem of the real physical nature of these transitions. In the case of the CT transitions between oxygen ions and highly charged, closed-shell transition-metal ions, this problem has been solved by Ziegler *et al.*[7] These authors showed that the amount of charge transfer is very small. Population analysis shows that electronic excitation consists of a rearrangement of electron density both at the ligand and at the metal instead of a buildup of charge on the metal at the expense of the ligands.

Robbins and Day[8] have questioned the assignment of charge transfer between different metal ions in Ag_2CrO_4. Undoubtedly the picture given above is an oversimplification. The role of the anion orbitals must also be taken into account. It is not excluded that in the future the word "charge-transfer transitions" will only indicate a certain type of optical transition. The amount of charge transfer involved may be very small, however.

The intention of this Comment is to stimulate further work on the nature of this type of transition because of its influence on physical properties.

CHARGE TRANSFER BETWEEN Cr^{3+} AND Ti^{4+}, Nb^{5+}, W^{6+}

The presence of the Cr^{3+} ion in mixed metal oxides results always in coloration of the host lattice. Usually this is due to the well-known crystal-field transitions within the $3d^3$ configuration of the Cr^{3+} ion. Although its color is extreme, ruby (Al_2O_3–Cr) has become the best-known and most intensely studied example.

In compounds containing ions like Ti^{4+}, Nb^{5+} or W^{6+}, however, the presence of slight amounts of Cr^{3+} induces strong and broad absorption bands

in the visible region. As a consequence, such compounds are yellow to brownish. Perhaps the first report was that by Kröger.[9] He found that low Cr^{3+} concentrations color $CaWO_4$ strongly yellow and quench the blue tungstate luminescence dramatically. The phenomenon was later investigated by us.[10] The yellow color was ascribed to a charge-transfer transition between Cr^{3+} and W^{6+}. The luminescence quenching is due to energy transfer from the excited tungstate group without Cr^{3+} neighbors to a tungstate group with a Cr^{3+} neighbor. This transfer is partly radiative and very efficient in view of the high oscillator strength of the Cr^{3+}–W^{6+} charge-transfer transition. The phenomenon was quite general; in the case of $Mg_4Nb_2O_9$–Cr^{3+} the transferred excitation energy was emitted by the Cr^{3+} ion via the $^4T_2$–$^4A_2$ transition.

Whereas in this example the charge-transfer transition is not favorable for a physical property (viz., luminescence), it has recently been shown that this transition can be used to sensitize certain materials for solar energy conversion. Titanates like TiO_2 and $SrTiO_3$ can be used as anodes in a photoelectrochemical cell where they convert (ultraviolet) radiation into hydrogen. What happens in principle is that the radiation creates electrons and holes in the semiconducting titanates. These are separated due to band bending in the semiconductor at the interface with the electrolyte (Figure 1). The holes oxidize water to O_2 while the electrons migrate through the ti-

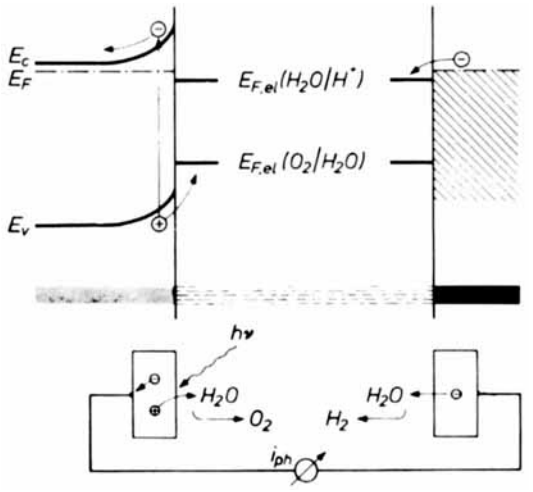

FIGURE 1 Schematic representation of the photoelectrolysis of water. Photoholes migrate to the semiconductor surface (oxygen formation). Hydrogen formation occurs at the hatched counter electrode (platinum). E_v: top valence band, E_c: bottom conduction band, E_F: Fermi level in semiconductor, $E_{F,el}$: relevant redox levels. After R. Memming, Philips Tech. Rev. **38**, 160 (1978/9).

tanate to a counter electrode where they reduce water to H_2. For a more sophisticated treatment the reader is referred to recent reviews.[11] What is of importance here is the fact that these titanates are white and do not absorb visible radiation. For solar energy conversion it is necessary to have optical absorption in the visible region. In this way photoelectrochemical water decomposition may become possible with the advantage that solar energy is converted and stored (as hydrogen) in one step.

There are several ways to sensitize the titanates for visible light irradiation. One is doping with the Cr^{3+} ion.[12] (An example has been given in Figure 2.) There has been some discussion about the origin of the visible ab-

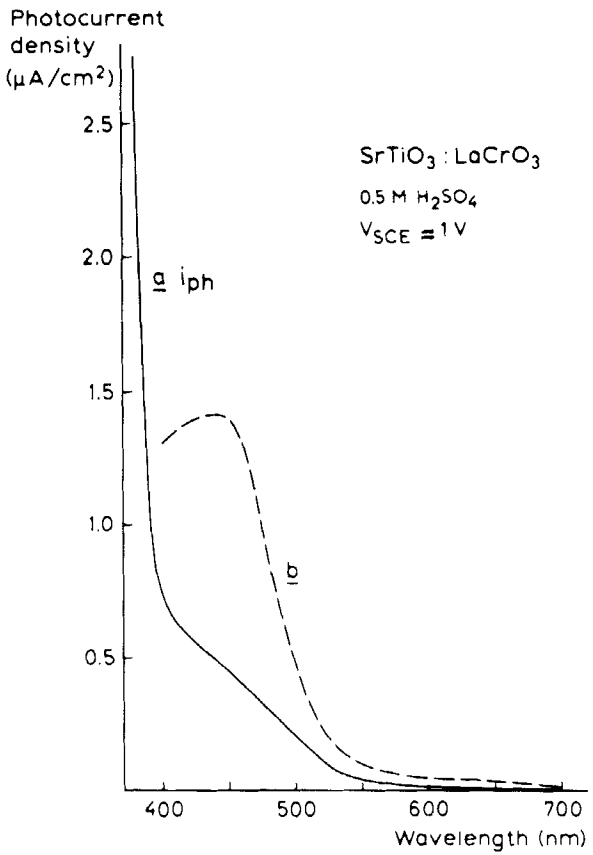

FIGURE 2 (a) Photocurrent vs wavelength of the irradiating light for a photoelectrochemical cell for water photoelectrolysis using $SrTiO_3 : LaCrO_3$ as photoanode. (b) Optical absorption spectrum of the Cr^{3+} ion in $SrTiO_3 : LaCrO_3$. After A. Mackor and G. Blasse, Chem. Phys. Lett. 77, 6 (1981).

sorption due to Cr^{3+} in titanates. But there seems to be not much doubt that this transition is in principle a Cr^{3+}–Ti^{4+} charge-transfer transition.[13,14]

It is interesting to compare isomorphous $SrZrO_3$–Cr^{3+} and $SrTiO_3$–Cr^{3+}.[13] The host lattice $SrZrO_3$ has its optical bandgap at about 46 000 cm^{-1}. In the visible region $SrZrO_3$–Cr^{3+} shows the usual Cr^{3+} crystal-field transitions. The host lattice $SrTiO_3$ has its optical bandgap at about 26 000 cm^{-1}. The introduction of Cr^{3+} results in a very broad band (>16 000 cm^{-1}). If the host lattice is changed, this broad band "follows" the host lattice absorption. For example, $MgTiO_3$ has its gap at 36 000 cm^{-1}. In $MgTiO_3$–Cr the Cr^{3+}–Ti^{4+} charge transfer is above 28 000 cm^{-1}.

There seems to be one essential difference between a CT transition of this type in $CaWO_4$–Cr and in $SrTiO_3$–Cr. In the former case the charge transfer can be schematized as $Cr^{3+} + W^{6+} \rightarrow Cr^{4+} + W^{5+}$. The electron in the 5d orbital of tungsten will be localized in $CaWO_4$ (with isolated WO_4^{2-} groups). In $SrTiO_3$, however, we have $Cr^{3+} + Ti^{4+} \rightarrow Cr^{4+} + Ti^{3+}$. The electron in the 3d orbital of titanium will be strongly delocalized, since the titanium 3d orbitals constitute the conduction band of $SrTiO_3$. For the utilization of these CT absorptions in photoelectrochemistry it is essential that the hole on the chromium, i.e., the Cr^{4+} state, be mobile. This point is under discussion in the literature, but not relevant to this Comment. Here we wish to consider what is to be expected if other transition-metal ions are used as electron donors instead of the Cr^{3+} ion.

CHARGE TRANSFER BETWEEN OTHER TRANSITION METAL IONS AND Ti^{4+}, Nb^{5+}, W^{6+}

The position of the CT absorption band under discussion will depend upon the ionization potential of the donating transition metal ion. In such a simple approach crystal-field and polarization effects are neglected. The transition-metal elements with a lower fourth ionization potential than chromium are vanadium and titanium. In fact the V^{3+} ion in $SrTiO_3$ yields an additional absorption which extends over the whole visible region.[15] The Ti^{3+} ion lies formally in the conduction band and is not discussed here. The other transition-metal ions were found to give less coloration of $SrTiO_3$ than Cr^{3+}, in agreement with the higher fourth ionization potential.[13]

The M^{4+} transition-metal ions are expected to give even less effect due to their higher (fifth) ionization potential. In particular, a comparison of Mn^{4+} and Cr^{3+} is interesting in view of their isoelectronic configuration. For $SrTiO_3$–Mn^{4+} we were able to observe the $^4A_2 \rightarrow {}^4T_2$ and $^4T_1$ crystal-field transitions in the visible and no strong Mn^{4+}–Ti^{4+} charge-transfer transition was found.

With this knowledge it is interesting to reconsider the photochromism of transition-metal doped $SrTiO_3$.[16] We restrict ourselves to the case of $SrTiO_3$–Fe,Mo. In the "dark" there is practically no visible absorption. In a small area (390–430 nm) below the bandgap of $SrTiO_3$ there is an additional absorption band. Since the dark state of $SrTiO_3$–Fe,Mo contains Fe^{3+} and Mo^{6+} according to ESR measurements, this additional absorption is ascribed to Fe^{3+}–Ti^{4+} charge transfer, following the arguments given above. The electron donated by Fe^{3+} to the conduction band is trapped by Mo^{6+}, so that the excited state is in fact $Fe^{4+} + Mo^{5+}$. The decay time of this state is about 1 min.[16] It gives rise to strong absorption in the visible, causing the photochromism of $SrTiO_3$–Fe,Mo. The Fe^{4+} ion gives two strong absorption bands at 415 and 505 nm. These bands cannot be ascribed to Fe^{4+}–Ti^{4+} charge transfer, since this transition is expected at higher energies than the Fe^{3+}–Ti^{4+} charge transfer; rather they are ascribed to electron capture by the Fe^{4+} ion, i.e., to $Fe^{4+} + O^{2-} \rightarrow Fe^{3+} + O^-$ charge transfer, where O^- represents a hole in the valence band of $SrTiO_3$. For higher-charged transition-metal ions the present considerations should be applied with care, because $M^{n+} + Ti^{4+} \rightarrow M^{(n+1)} + Ti^{3+}$ charge transfer may be less favorable than $M^{n+} + O^{2-} \rightarrow M^{(n-1)+} + O^-$ charge transfer.

Considerations of this type are well known from the field of electrical conductivity.[17] The introduction of nickel in MgO yields n-type conductivity according to $Ni^{2+} + Mg^{2+} \rightarrow Ni^{3+} + Mg^+$, where Mg^+ represents an electron in the conduction band and Ni^{3+} a hole localized on Ni^{2+}. By contrast, Fe^{3+} yields p-type conductivity: $Fe^{3+} + O^{2-} \rightarrow Fe^{2+} + O^-$, where O^- represents a hole in the valence band of MgO.

Let us now turn to the case where a divalent transition-metal ion is the donating species. $SrTiO_3$ is not a very suitable lattice for this purpose, because it will not accept these ions without charge compensation. We have studied Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} in $MgTi_2O_5$.[18] Diffuse reflection spectra are given in Figure 3. The undoped $MgTi_2O_5$ shows its optical bandgap at about 320 nm (O^{2-}–Ti^{4+} charge transfer). The introduction of divalent transition metal ions changes the spectrum drastically. Only Co^{2+} and Ni^{2+} are expected to show spin-allowed crystal-field transitions in the visible. These are in fact observed (see Figure 3): $^4T_1 \rightarrow {}^4T_1$ (P) for Co^{2+} at 590 nm, and $^3A_2 \rightarrow {}^3T_1$ (P) for Ni^{2+} at 450 nm.

The interesting observation is the presence of a broad, intense absorption region covering a part of (Mn^{2+}, Co^{2+}, Ni^{2+}) or even the whole visible region (Fe^{2+}). These absorptions are ascribed to M^{2+}–Ti^{4+} charge transfer. The onset of this absorption increases in the series Fe^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, in good agreement with the increasing third ionization potential. These potentials are lower than the fourth ionization potentials, so that the divalent

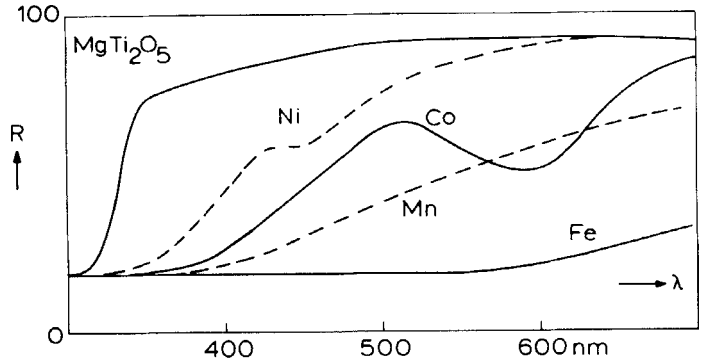

FIGURE 3 Diffuse reflection spectra of $MgTi_2O_5$ and $Mg_{0.99}Me_{0.01}Ti_2O_5$ (Me = Mn, Fe, Co, Ni). After Ref. 18.

transition metal ion gives a much more extended absorption area (relative to the gap of the host lattice) than the trivalent ions.

Charge-transfer transitions with the divalent ions as electron-donating species have been observed many times before, although they were not always ascribed to charge transfer. Perhaps most well-known is the blue color of sapphire (Al_2O_3–Fe, Ti) which has been assigned to Fe^{2+}–Ti^{4+} charge transfer. The broad absorption band peaks at about 15 000 cm^{-1}.[19] In this case the charge transfer occurs really in an isolated pair of ions, in contrast to the titanate systems discussed above.

Absorptions of this type have also been observed in the work of Reinen on $La_2Ni_{0.4}Mg_{0.6}TiO_6$ and of Kasper on Co^{2+}- and Ni^{2+}-doped pseudobrookites (see discussion in Refs. 13 and 18) and are in fact very general.

In the case of $MgTi_2O_5$–Fe^{3+} the Fe^{3+}–Ti^{4+} charge transfer occurs at much higher energies than the Fe^{2+}–Ti^{4+} charge transfer mentioned above. This is expected. As in $SrTiO_3$–Fe^{3+}, it occurs as a narrow additional absorption region.[18]

These arguments lead to the search of new semiconductors for water photoelectrolysis with visible light. As an example let us consider $NiNb_2O_6$.[20] This compound has columbite structure with zigzag chains of NiO_6^{10-} and NbO_6^{7-} octahedra. The optical band edge is situated at about 28 000 cm^{-1}, which is at much lower energy than the gap of the isomorphous $MgNb_2O_6$, which is at 36 000 cm^{-1} (O^{2-}–Nb^{5+} charge transfer). The optical bandgap of $NiNb_2O_6$ is ascribed to Ni^{2+}–Nb^{5+} charge transfer. Irradiation into this gap yields in fact water photoelectrolysis. The electron is mobile in the conduction band (mainly niobium 4d orbitals) and the hole appears to be mobile in the narrow Ni^{2+} ($3d^8$) band. As in the case of NiO,

the activation energy for hopping in this band is obviously low. In the case of $CoNb_2O_6$ no photocurrents were observed: the hole is probably trapped as low-spin Co^{3+}, as has also been suggested for CoO.

Water photoelectrolysis by visible light has also been reported for $FeTiO_3$[21] and $FeNbO_4$.[22] The visible absorption of $FeTiO_3$ is due to Fe^{2+}–Ti^{4+} charge transfer and its edge corresponds with the values given above. The optical edge of $FeNbO_4$ is at too low energies to be ascribed to Fe^{3+}–Nb^{5+} charge transfer. In this case O^{2-}–Fe^{3+} charge transfer seems to be more appropriate.[20]

Nowhere did we use the typical transition metal properties of the electron-donating species considered above. Therefore our discussion should have a rather general value as will be shown next.

CHARGE TRANSFER BETWEEN TRIVALENT LANTHANIDE IONS AND Ti^{4+}, Nb^{5+}, W^{6+}

Some of the trivalent lanthanide ions can easily lose an electron. Common examples are Ce^{3+} and Tb^{3+}. In the ultraviolet region their spectra show intense 4f → 5d transitions. However, charge-transfer transitions to ions like Ti^{4+}, Nb^{5+}, W^{6+} are also possible. An early example has been given by Paul[23] for Ce^{3+}–Ti^{4+} charge transfer in borosilicate glasses. The absorption maximum was at about 30 000 cm^{-1}.

The Ce^{3+} ion in $SrTiO_3$ exhibits additional optical absorption down to 600 nm.[24] This transition has also been ascribed to Ce^{3+}–Ti^{4+} charge transfer. This way of doping $SrTiO_3$ does not lead to water photoelectrolysis under visible irradiation. This is probably due to the strongly localized nature of the hole on the cerium ion (i.e., Ce^{4+}).

Transitions of this type play also an important role in the field of luminescence. It has been found that Tb^{3+} and Ce^{3+} do not luminesce efficiently in vanadate, niobate and tungstate lattices, whereas ions like Eu^{3+}, Sm^{3+} and Dy^{3+} do. This has been ascribed to the presence of a charge-transfer excited state of the type Tb^{4+}–V^{4+}. It is assumed that nonradiative decay of this excited CT state to the ground state is possible. In those exceptional cases where this charge-transfer state is at very high energies, luminescence from Tb^{3+} and Ce^{3+} has been observed. Two examples are $CaSO_4$–V^{5+}, Tb^{3+} and $YTaO_4$–Tb^{3+}.[25] The former example is interesting because the ions participating in the charge-transfer transition occur in pairs in a host lattice which does not itself participate.

Undoubtedly, the literature contains more examples of this type of charge transfer transition. Here we want to turn to still other electron-donating ions.

CHARGE TRANSFER BETWEEN OTHER IONS AND Ti^{4+}, Nb^{5+}, W^{6+}

The first ion to be discussed here is Bi^{3+} ($6s^2$). Its charge-transfer transitions to ions like Ti^{4+}, Nb^{5+} and W^{6+} have been mentioned in the Introduction and we refrain from further discussion.

Not much work has been performed on other systems. However, many other charge-transfer transitions of the type under discussion are possible. We shall mention a few examples here. The first deals with double tungstates of Cu^+ and the lanthanides: $CuLn(WO_4)_2$.[26] These crystallize in two structure types, viz., scheelitelike for Ln = La–Dy and wolframitelike for Ln = Ho–Lu. The former are red-orange, the latter almost black. It seems obvious to ascribe the red color to a Cu^+–W^{6+} charge transfer, which is in fact expected to be at much lower energies than the O^{2-}–W^{6+} charge transfer. The almost black color of the wolframitelike compounds may be due to a similar CT transition. It cannot be excluded, however, that the black color is related to a deviation from stoichiometry. In connection with Cu^+ it is interesting to note that Na_2WO_4 has the O^{2-}–W^{6+} charge transfer at very high energies (40000 cm^{-1}, Ref. 27), whereas the isomorphous Ag_2WO_4 is yellow.[28]

As a matter of fact, the accepting ions do not necessarily belong to the group of ions considered in this paper. For example, many cases of photoinduced electron transfer have been observed in solution, where they usually are studied in connection with luminescence quenching. We mention two cases by way of illustration. The Ce^{3+} luminescence in sulfate solution is quenched by Cu^{2+}, Fe^{3+}, Cr^{3+}, Tl^{3+} and Eu^{3+}.[29] In the case of Cu^{2+} photoinduced electron transfer has been observed and ascribed to the following mechanism:

$$Ce^{3+} \xrightarrow{h\nu} (Ce^{3+})^* \xrightarrow{Cu^{2+}} Ce^{4+} + Cu^+.$$

Also intermolecular charge transfer is the predominant mechanism[30] for the quenching of the luminescence of uranyl solutions by metal ions. This illustrates that charge transfer is a very general phenomenon which plays an important role in different fields.

INTERVALENCE CHARGE TRANSFER

Finally we would like to mention two examples of physical properties in which intervalence charge transfer plays a role. This type of charge transfer has been dealt with extensively in a recent summer school.[3]

Krol *et al.*[31] have shown that the luminescence of uranates is quenched by killer centers which consist of U^{5+} and the surrounding U^{6+} ions. The luminescence properties of uranates which contain UO_6^{6-} octahedra are determined by migration of the excitation energy through the crystal lattice, even at very low temperatures. Uranate centers near defects act as traps for the migrating energy. It is from these traps that the emission originates. When the temperature is raised the traps get emptied and the excitation energy reaches killer sites. These are the sites where the excitation energy is lost nonradiatively. In the case of uranates the nature of these killer centers has been solved. Uranates are usually oxygen deficient and contain a small amount of U^{5+}. Due to the presence of U^{5+} in a U^{6+} compound there is a strong absorption in the near infrared which can be ascribed to an intervalence charge-transfer transition between U^{5+} and U^{6+}. There is enough spectral overlap between the intrinsic uranate emission and the intervalence charge-transfer absorption to account for efficient energy transfer to these killer centers.

In those uranates where the U^{5+} concentration is high, the luminescence efficiency is low (e.g., $MgUO_4$). In those U^{6+} compounds where the oxygen deficiency is negligible, for example, in uranyl compounds, the killer concentration is very low and efficient luminescence is observed up to room temperature (e.g., $Cs_2UO_2Cl_4$).

The other example originates from the absorption spectra of WO_3 and MoO_3.[32] Consider WO_3. At room temperature the optical bandgap is situated at 22 200 cm^{-1} (O^{2-}–W^{6+} charge transfer). The charge carriers are large polarons and consequently the near-infrared spectral region shows free-carrier absorption. In a low-temperature modification of WO_3, however, the edge shifts to 25 600 cm^{-1}, the free-carrier absorption vanishes and a distinct peak appears in the near-infrared spectral region (around 6000 cm^{-1}). This phenomenon is due to strong electron–phonon coupling. Charge carriers are trapped at tungsten positions corresponding to the formation of W^{5+} and consequent polarization of the surrounding structure (small polaron formation). This near-infrared absorption can be considered as an intervalence charge transfer between W^{5+} and W^{6+}. The introduction of H stabilizes the W^{5+} state: $H^0 + W^{6+} \rightarrow H^+ + W^{5+}$ and the W^{5+}–W^{6+} intervalence charge transfer is now at about 10 000 cm^{-1}. Further, the optical transition Mo^{5+} to W^{6+} was found at about 7500 cm^{-1}. For $MoO_{2.99}$ a

Mo^{5+}–Mo^{6+} absorption has been observed at about 10000 cm^{-1}. These values are not strikingly different from those observed for the U^{5+}–U^{6+} system in the uranates.

CONCLUSIONS

Many physical phenomena in mixed metal oxides and other systems are related to or strongly influenced by charge-transfer transitions. Here we have stressed those transitions in which two metal ions seem to play a role. A further investigation of the nature of these transitions seems to be required. Further, their influence should by no means be underestimated. A related problem has been discussed some years ago by McGlynn,[33] who proposed another type of charge-transfer transition.

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