NOTES

The Ce³⁺ Ion in Strontium Titanate (SrTiO₃): Optical Absorption and Photoelectrochemistry

The presence of $Ce^{3+}(4f^1)$ in $SrTiO_3$ results in a broad optical absorption in the visible region. This is ascribed to a charge-transfer transition from Ce^{3+} to Ti^{4+}. This material is not successful as an anode in photoelectrochemical cells. The reasons for this are discussed.

1. Introduction

Recently we have discussed the coloration of titanates with transition-metal ions in view of their applicability in photoelectrochemical cells for conversion of solar energy (1–3). The coloration was ascribed to charge-transfer transitions in which an electron is transferred from the transition-metal ion to the empty $3d$ orbitals of the Ti^{4+} ion. In $SrTiO_3$ and TiO_2 these orbitals constitute the conduction band. It was shown that under certain conditions visible-light irradiation of anodes in photoelectrochemical cells consisting of transition-metal-ion-doped titanates yields photocurrents. In this way the production of hydrogen from water by solar irradiation might be possible.

An important condition for the occurrence of photocurrents in these cells is the requirement that the electron and the hole created upon irradiation are both mobile. The electron is brought into the conduction band, where its mobility will be high enough. The hole remains on the transition-metal ion, where it will be rather localized (1, 3, 4). In order to explain the presence of photocurrents under visible-light irradiation in, for example, Cr^{3+}-doped titanates, it has been suggested that the hole tunnels to the valence band.

In this note we report on the effects obtained by doping titanates with the Ce^{3+} ion (electron configuration $4f^1$). This ion was selected because it is well known that its $4f$ electron can easily be excited to higher energy levels (5). In this way we aimed to obtain Ce^{3+}–Ti^{4+} charge-transfer transitions in the visible. At the same time, it seemed interesting to know whether irradiation into such an absorption band would yield photocurrents in a photoelectrochemical cell.

2. Experimental

The compound $CeAlO_3$ was prepared from the binary oxides by firing in a N_2/H_2 mixture. Surface-doped anodes consisting of a $SrTiO_3$ single crystal with a $CeAlO_3$ dopant were prepared as described elsewhere (6). A powder sample of composition $Sr_{0.995}Ce_{0.005}Ti_{0.995}Al_{0.005}O_3$ was prepared by firing the perovskites $SrTiO_3$ and $CeAlO_3$ at 1450°C in a nitrogen atmosphere. The color of this sample was orange. All samples were checked by X-ray powder analysis. Reflection spectra were measured on a Perkin–Elmer spectrometer EPS-3T. Photoelectrochemical measurements were performed as described in Ref. (6).

3. Results

The optical-absorption edge of pure $SrTiO_3$ is at about 380 nm. The Ce^{3+} ion was introduced by doping $SrTiO_3$ with $CeAlO_3$

390

in order to maintain the trivalent valency of the Ce^{3+} ion by charge compensation with the Al^{3+} ion ($Sr^{2+} + Ti^{4+} \rightarrow Ce^{3+} + Al^{3+}$). The reflection spectrum of samples $SrTiO_3 : CeAlO_3$ showed an additional absorption in the visible region extending down to 600 nm (Fig. 1). This spectrum shows a strong analogy with that of, for example, Cr^{3+}-doped titanates as far as its spectral extension is concerned (1). The intensity of the absorption induced by the Ce^{3+} ion is weaker than that induced by the Cr^{3+} ion.

A surface-doped photoanode $SrTiO_3$: $CeAlO_3$ was used in a photoelectrochemical cell. Photocurrents were only observed under band-gap excitation of the $SrTiO_3$ host lattice ($\lambda < 380$ nm). No photocurrents were observed under visible light excitation.

4. Discussion

4.1. Optical Absorption

The additional absorption band in the visible region cannot be ascribed to the Ce^{3+} ion because it is not present in the pure $CeAlO_3$. It is also absent in undoped $SrTiO_3$ prepared under the same conditions as the doped samples. We, therefore, ascribe this absorption to a charge-transfer transition in which an electron is transferred from the Ce^{3+} ion to the Ti^{4+} ion, i.e., from the $4f$ orbital to the titanate conduction band. A similar absorption band has been reported by Paul (7) for cerium-and-titanium-codoped glasses of composition $Na_2O–Al_2O_3–B_2O_3–SiO_2$. Here the charge-transfer transition is situated at higher energies: The maximum of the absorption is at about 30,000 cm^{-1}.

In view of the nature of the allowed optical transitions of trivalent lanthanide ions in oxides (see, e.g. (8)), not only the Ce^{3+}, but also Tb^{3+} ($4f^8$) ion is expected to give such a charge-transfer transition.

These have been discussed many years ago in order to explain the absence of Tb^{3+} luminescence in Tb^{3+}-activated vanadates, niobates and tungstate (9, 10). The vanadate, niobate, and tungstate groups are very similar to the titanate group, since the transition-metal ions have lost all their d electrons. Tb^{3+}-activated materials of this type show absorption in the ultraviolet region. This absorption has been ascribed to a $Tb^{3+}–V^{5+}(Nb^{5+}, W^{6+})$ charge-transfer transition. From the excited charge-transfer state nonradiative return to the ground state is possible.

Note the similarity between the behavior of Ce^{3+} and Cr^{3+} in $SrTiO_3$. Both give charge-transfer absorption in the visible. The lower intensity in the case of the Ce^{3+} ion can be ascribed to the fact that the $4f$ electrons are more shielded than the $3d$ electrons. The Cr^{3+} ion, finally, also has a quenching influence on the luminescence of vanadate, niobate, and tungstate groups (11).

4.2. Photoelectrochemistry

The results of the photoelectrochemical measurements are in agreement with models which have been proposed to explain the results on photoelectrochemical cells with anodes consisting of transition-metal-ion doped titanates. Holes created upon band-gap excitation will easily be trapped by the Ce^{3+} ions. This will decrease their mobility. In this way the low efficiency for band-gap excitation in the case of the doped material compared with the undoped material is easily understood. The absence of photocurrents under visible light excitation points to a very low mobility of the hole remaining on the cerium ion. Tunneling to the valence band does not seem to occur although the energy level scheme cannot be strongly different from that of Cr^{3+} in $SrTiO_3$, where tunneling seems to occur. It should be realized, however, that the hole in the $4f$ orbital of the
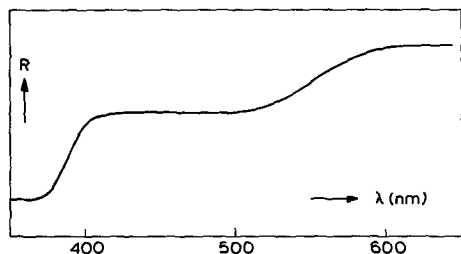
FIG. 1. Diffuse reflection spectrum of $SrTiO_3$: $CeAlO_3$ (0.5 mole%).

cerium ion will be considerably more localized than a hole in the $3d$ orbital of a transition-metal ion. The fact that Cr substitutes for Ti, but Ce substitutes for Sr also results in a lower tunneling probability for the Ce case, since the valence band is constituted from the oxygen $2p$ orbitals, and the Ce–O distance (12-coordination) is larger than the Cr–O distance (6-coordination). Finally we note that the application of hydroquinone did also not yield photocurrents under visible-light excitation, which confirms the model proposed above.

References

1. G. BLASSE, P. H. M. DE KORTE, AND A. MACKOR, J. Inorg. Nucl. Chem., in press.

2. G. BLASSE AND G. J. DIRKSEN, Chem. Phys. Lett. 77, 9 (1981).

3. P. H. M. DE KORTE, L. G. J. DE HAART, R. U. E. 'T LAM, AND G. BLASSE, Solid State Commun., in press.

4. G. CAMPET, M. P. DARE-EDWOODS, A. HAMNETT, AND J. B. GOODENOUGH, Nouv. J. Chimie 4, 501 (1980).

5. G. BLASSE AND A. BRIL, J. Chem. Phys. 47, 5139 (1967).

6. P. H. M. DE KORTE, R. U. E. 'T LAM, J. SCHOONMAN, AND G. BLASSE, J. Inorg. Nucl. Chem., in press.

7. A. PAUL, Phys. Chem. Glasses 17, 7 (1976).

8. G. BLASSE, in "Handbook on the Physics and Chemistry of Rare Earths" (K. A. Gschneidner, Jr., and L. Eyring, Eds.), Vol. 4, Chap. 34, North-Holland, Amsterdam (1979).

9. G. BLASSE AND A. BRIL, Philips Res. Rep. 22, 481 (1967); J. Lumin. 3, 109 (1970).

10. R. G. DeLOSH, T. Y. TIEN, E. F. GIBBINS, P. J. ZACMANIDES, AND H. L. STADLER, J. Chem. Phys. 53, 681 (1970).

11. G. BLASSE, J. Inorg. Nucl. Chem. 29, 1817 (1967).

G. BLASSE AND G. J. DIRKSEN

Physical Laboratory, State University
P.O. Box 80.000
3508 TA Utrecht
The Netherlands