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► **To cite this version:**

R. Cox. CHEMICAL REACTIONS AND MASS TRANSPORT PROCESSES IN DONOR AND ACCEPTOR DOPED Al₂O₃ CRYSTALS. *Journal de Physique Colloques*, 1973, 34 (C9), pp.C9-333-C9-335. 10.1051/jphyscol:1973958 . jpa-00215433

HAL Id: jpa-00215433

<https://hal.science/jpa-00215433>

Submitted on 4 Feb 2008

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CHEMICAL REACTIONS AND MASS TRANSPORT PROCESSES IN DONOR AND ACCEPTOR DOPED Al_2O_3 CRYSTALS

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Résumé. — La résonance paramagnétique électronique et l'absorption optique ont été étudiées pour des monocristaux de Al_2O_3 dopés avec l'impureté de type donneur Ti ou l'impureté de type accepteur Mg. Ces études fournissent des renseignements utiles concernant les propriétés chimiques des défauts ponctuels et les mécanismes de transport de masse dans cet oxyde.

Abstract. — Information about the chemical and transport properties of point defects in Al_2O_3 is given by ESR and optical spectroscopic studies of the oxidation and reduction of crystals which have been doped with the donor impurity titanium or the acceptor impurity magnesium.

Much information about the chemical and transport properties of point defects in alpha Al_2O_3 can be obtained by spectroscopic studies (electron spin resonance and optical absorption measurements) of single crystals which have been doped with titanium or magnesium. We have observed that the charge state of the impurity defects present in these crystals can be varied by heating in oxidising or reducing atmospheres; these changes are necessarily accompanied by the diffusion of compensating, intrinsic defects into or out of the crystal. The observed phenomena are explained by the very general theory of the thermochemical properties of binary compounds containing donor or acceptor impurities, which has been given by Kröger and Vink [1].

This theory shows that any donor or acceptor impurity can (in principle) be incorporated in the lattice either as a neutral defect without compensation or as a charged defect with compensation by an intrinsic defect of opposite kind. When the crystal is brought to equilibrium with the vapour of its constituent elements, the degree of compensation which occurs depends on the partial pressures of those constituents. Among ionic compounds, Al_2O_3 appears to provide a rare example where, for both donor and acceptor impurities, transitions between compensated and uncompensated incorporation occur at readily achievable vapour pressures and where enough spectroscopic information is currently available to identify the occurrence of such transitions. The results described here are based on studies of crystals grown by the Verneuil process from alumina powders doped with quantities of order 100-1 000 ppm of either TiO_2 or MgO . In substitution for aluminium, the tetravalent metal titanium is a donor, whereas the divalent metal magnesium is an acceptor.

Several authors have shown that titanium may be present in Al_2O_3 crystals as either Ti^{3+} or Ti^{4+} ions [2], [3], [4]. If the crystals are reduced in hydrogen at about 2000 K, the predominant charge state is Ti^{3+} . This ion has a single 3d electron outside a closed shell, argon-type core: it may be identified by its ESR spectrum or by its optical absorption, which gives the crystal a pink colour. When Ti doped crystals are heated in air (that is in an oxygen pressure of 0.2 bar) at 2 000 K, they become colourless, showing that Ti^{3+} has been converted to the optically inactive (and diamagnetic) closed shell ion Ti^{4+} . In the language and notation used by Kröger and Vink [1], one would say that the oxidation process has caused a neutral donor $\text{Ti}_{\text{Al}}^{\times}$ to give up its electron, leaving the positively ionised donor $\text{Ti}_{\text{Al}}^{\cdot}$ (here we use a cross, meaning no charge, and a dot, meaning a single, positive charge, to indicate the effective charge of the impurity defect with respect to the site it occupies, which is given as a subscript).

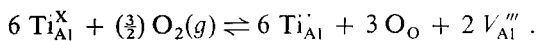
The ionised donor must be compensated by a negatively charged intrinsic defect, that is, by a negatively ionised intrinsic acceptor. In any ionic compound, the (simplest) intrinsic acceptors are the interstitial anion and the cation vacancy. We note that both these defects represent an excess of the non-metallic constituent element of the crystal; this explains why compensation of a donor impurity is favoured by heating in a high pressure of this constituent, which, in our case, is oxygen.

When the electronic charge distribution is in thermal equilibrium, the acceptor defects in oxidised Ti : Al_2O_3 are in a charge state which can not be detected by ESR or optical spectroscopy. We have shown that they may be converted to an observable charge state by gamma irradiating the crystal at room tem-

perature [4], [5]. Such an irradiation ionises the lattice, producing free electrons and free holes; the electrons become trapped by Ti^{4+} , forming Ti^{3+} , leaving the equivalent number of holes free to be trapped by the ionised acceptor. One then observes the presence of a paramagnetic colour centre which we identify as being a hole trapped by the cation vacancy. This identification is based on the properties of the centre's ESR spectrum, which have been discussed elsewhere [5]; the centre may also be identified by its broad optical absorption band, which peaks near 4 000 Å, giving the irradiated crystals a dark brown colour.

Gamma irradiation produces only a metastable redistribution of the electronic charge: the trapped electrons and holes recombine progressively at 300°-400 °C. In connection with the present discussion, the important result of the irradiation studies is to show that the intrinsic defect in oxidised Ti : Al_2O_3 is the cation vacancy, which is present in the fully ionised state V_{Al}''' when the electronic distribution is in thermal equilibrium. (Here V means vacuum and each prime designates an effective negative charge; in a real charge notation, this defect is $V_{Al^{3+}}$.)

Thus, one can represent the oxidation of Ti doped Al_2O_3 by the following chemical reaction :



Successive heat treatments show that this reaction is reversible.

Application of the mass-action law to the reaction shows immediately that high oxygen pressures drive its equilibrium towards the compensated state, whereas low oxygen pressures (or high aluminium pressures) induce the uncompensated state. The graphical methods of Brouwer [6] and Kröger and Vink [1] can be used to derive the functional dependence of the various defect concentrations on oxygen partial pressure. The detailed analysis shows that the cation vacancy concentration in Ti doped Al_2O_3 is much higher than it would be in a pure crystal at the same oxygen pressure. That is, the presence of a donor impurity enhances the incorporation of excess oxygen in the crystal; one may interpret this by saying that Ti^{3+} provides the electrons which are required for the incorporation of gaseous oxygen as O^{2-} ions.

Crystals which have been doped with Mg have chemical properties which are the opposite of those of Ti doped crystals. For Al_2O_3 : Mg, low oxygen pressures favour the compensated state. Samples which have been reduced in hydrogen, or merely in commercial argon (oxygen pressure of order 10^{-4} - 10^{-5} bar), are colourless and give no ESR spectra. Such samples contain only the closed shell impurity defect Mg_{Al}' , that is, Mg^{2+} on an Al^{3+} site. Its negative effective charge must be compensated by the positive charge of an ionised, intrinsic donor.

(Here, we refer to argon reduced samples; in hydrogen reduced samples the compensatory defect may be OH^- ions on anion sites.) The intrinsic donor might be either the interstitial cation or the anion vacancy. Unfortunately, gamma irradiation of Mg doped crystals has not yet provided the type of information which it gave in the case of Ti doped Al_2O_3 : it does not appear to generate any ESR spectrum which could be attributed to an electron trapped by an interstitial cation or an anion vacancy.

If Mg doped crystals are heated in air at 2 000 K and cooled rapidly, they have an intense grey-purple colour. In correlation with the appearance of this colour, one observes an ESR spectrum which can be attributed to a hole trapped by Mg^{2+} , that is to the neutral defect Mg_{Al}^x . The hole is trapped on an oxygen ion next to the impurity; it has a broad optical band peaking near 4 900 Å, which is responsible for the coloration.

We have previously observed the neutral acceptor Mg_{Al}^x in a metastable state (annealing rapidly at -30 °C) after low temperature gamma irradiation of doubly doped samples containing Mg^{2+} and Ti^{4+} ions [5]. In the singly doped crystals discussed here, the neutral acceptors are perfectly stable. This means that the compensating defects have been removed from the crystal by the oxidation treatment. The process is exactly the opposite of that described above for Ti : Al_2O_3 , where compensating defects are removed by reduction. That the impurity defect changes charge state by trapping a hole on a neighbouring anion instead of by becoming a 3 + ion does not change the nature of the chemical processes. However, the binding energy of a hole localised beside Mg^{2+} is rather less than that of an electron localised in Ti^{3+} ; thus there will be more thermal ionisation at high temperature in Mg : Al_2O_3 than in Ti : Al_2O_3 . (Thermal ionisation is negligible for Mg_{Al}^x at room temperature, even though magnesium is a relatively good acceptor impurity: acceptor levels in highly insulating oxides lie at depths of order 1 eV within the forbidden gap.)

In order to be able to write a reversible chemical reaction to represent the oxidation-reduction of Mg : Al_2O_3 , we need to know the identity of the intrinsic donor which compensates Mg^{2+} in the reduced crystals. The only information we have at present concerning this defect comes from comparison of the rates of the oxidation and reduction reactions in Mg and Ti doped samples.

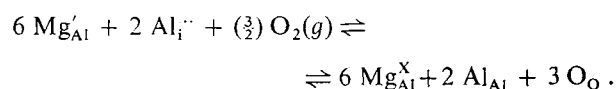
These reactions involve the appearance or disappearance of an excess of oxygen in the interior of the crystal and therefore require the transport of mass between the interior and the surface. (In addition, since the defects probably diffuse as charged defects, the reactions also require the movement of free electrons or free holes. However, we would expect that free carriers are sufficiently mobile not to control the reaction rates.) In both Ti : Al_2O_3 and Mg : Al_2O_3

it is the rate of these mass transport processes which limits the rate of oxidation or reduction. Evidence for this was first given for Ti : Al₂O₃ by Jones *et al.* [3]. They showed that the oxidation or reduction starts at the surface and progresses gradually into the sample, the limit of progression being marked by a front between coloured and uncoloured regions. This would not occur if the rate of the colour change were limited by the rate of some localised reaction step (e. g. an ionisation process or a surface reaction) for, in that case, the whole crystal would gradually change colour as a single block. Jones *et al.* [3] were able to measure the diffusion coefficient for the mobile defect in these crystals by measuring the rate of progression of the colour boundary. We have observed that exactly the same effect occurs during heat treatment of Mg : Al₂O₃; the colour change starts at the surface and progresses into the bulk of the crystal. However, in the acceptor doped crystals, the colour boundary moves at a remarkably rapid rate at quite low temperatures.

For Mg doped samples of dimensions 1 × 1 × 1 cm³, equilibrium with the vapour is achieved in less than an hour at only 1000 K. This temperature is less than half the melting point (2 300 K). To oxidise or reduce a similar sized sample of Ti doped Al₂O₃ in the same time, one must go to temperatures exceeding 2 000 K [3]. This very great difference between the properties of acceptor and donor doped crystals leads us to suggest that the intrinsic defect in the reduced Mg doped crystals is the interstitial cation, and not the anion vacancy. General experience with the diffusion properties of other ionic crystals indicates that small interstitial cations have much higher mobility than vacancy defects. Thus, mass is transported with great ease in the acceptor doped Al₂O₃ crystals by inward or outward movement of the interstitials. By contrast, the donor doped samples contain a high concentration of cation vacancies,

which depress the interstitial concentration via the equilibrium of the Frenkel defect generation mechanism $\text{Al}_{\text{Al}} \rightleftharpoons \text{Al}_i^{\prime\prime} + V_{\text{Al}}^{\prime\prime\prime}$. (This maintains the product of the concentrations of vacancies and interstitials at a constant value for a given temperature in all Al₂O₃ samples.) Thus, in Ti doped Al₂O₃, mass is transported by only a very small concentration of interstitial cations or by the cation vacancies, which are no doubt much less mobile. In either case, the diffusion rate will be relatively low.

If, as seems probable, the donor defect in Mg : Al₂O₃ is the interstitial cation, the oxidation and reduction of Mg doped samples will be represented by the following reaction :



This may be combined with the reaction $\text{Mg}^{\text{X}}_{\text{Al}} \rightleftharpoons \text{Mg}'_{\text{Al}} + p^{\cdot}$ to take account of the thermal ionisation of the acceptor. As before, graphical methods may be used to derive the functional dependence of the defect concentrations on oxygen pressure. The resultant graphs are mirror images of those obtained for Al₂O₃ : Ti, with the compensated situation now occurring at low oxygen pressures instead of high oxygen pressures.

Taken together, the results for Mg and Ti doped Al₂O₃ suggest that the most common intrinsic defects in this oxide are the cation vacancy and the interstitial cation. This agrees with recent suggestions based on electrical conductivity measurements [8] that the predominant disorder in pure Al₂O₃ is Frenkel disorder in the cation lattice. We note that the present work indicates that the ionic conductivity of Al₂O₃ should be strongly dependent on oxygen pressure if the crystal contains a high concentration of a donor or an acceptor impurity.

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