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High energy transmission of Al_2O_3 doped with light transition metals

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The transmission of transparent colored ceramics based on Al_2O_3 doped with light transition metals is measured in the visible and infrared range. To clarify the role of the dopands we perform *ab initio* calculations. We discuss the electronic structure and present optical spectra obtained in the independent particle approximation. We argue that the gross spectral features of Co- and Ni-doped Al_2O_3 samples are described by our model, while the validity of the approach is limited for Cr-doped Al_2O_3 . © 2012 American Institute of Physics. [doi:10.1063/1.3679746]

Coarse-grained ($>15\ \mu\text{m}$) translucent polycrystalline alumina was discovered in the 1960s.¹ It shows a high total transmittance (direct and diffuse transmitted light) but a low in-line transmittance (direct transmitted light), because of the scattering at the grain-boundaries related to the birefringence of alumina. Recently, it has been shown that a reduction in the grain size ($<1\ \mu\text{m}$) will increase the in-line transmission significantly, which was explained quantitatively by applying the Rayleigh-Gans-Debye light scattering theories.²

The transparent fine grained polycrystalline and dense sintered alumina is a promising replacement for sapphire as it combines improved mechanical properties (Vickers hardness $>20\ \text{GPa}$ (HV 10), four point flexural strength $>600\ \text{MPa}$ (Ref. 3)) with a comparatively economic ceramic processing method requiring lower temperatures and offering a wider range of sizes and shapes of the final product. Possible applications are described in detail in Ref. 5. In addition, the processing method also simplifies the incorporation of optically active dopants and opens new possibilities for the microstructural design of optical materials, such as displays,⁴ scintillators,⁶ optical filters, and resistant windows.⁷ In this context, *ab initio* electronic structure calculations are useful to understand the incorporation of different ions into the corundum lattice^{8,9} and to adjust the absorption of specific wavelengths in the visible and near-infrared spectral range.

A defect avoiding gel casting process¹⁰ was used to mould ceramic powder, starting with TM-DAR alumina (Boehringer Ingelheim Chemicals, Tokyo, Japan) with a $\sim 200\ \text{nm}$ average particle size and a purity $>99.99\%$ Al_2O_3 . Aqueous slurries with solid loading of $\sim 72\ \text{wt. \%}$ were prepared at pH4 (adjusted by HNO_3) and with an additive of $0.03\ \text{wt. \%}$ MgO (applied as a result of preoptimization of doping for this Al_2O_3 powder). A monomer initiator system was added to gelate the slurry after casting into glass moulds and the demoulded wet bodies were immersed with the different

dissolved nitrate solutions of Co, Cr, Fe, and Ni. The resulting concentrations of the ions in corundum were $<1\ \text{wt. \%}$.

The compacts were dried on air and the polymer was removed by annealing at 800°C . The bodies were presintered to a relative density of $96\%–98\%$ at $1200–1270^\circ\text{C}$ on air for 2 h with a constant heating rate of 2°C/h . Finally, the presintered bodies were hot isostatically pressed for 15 h at 1200°C under an argon gas pressure of $200\ \text{MPa}$. The detailed procedure for fabricating coloured transparent corundum is described in a European patent application.¹¹ The in-line transmission of polished discs with $3\ \text{cm}$ diameter and $\sim 0.8\ \text{mm}$ thickness was measured by a CARY4000 spectrophotometer (Varian, Australia) for the visible range and a Spectrum400 MIR/NIR (Perkin-Elmer, USA) for the infrared range.

For our first principles calculations we use the WIEN2k package, a full-potential linearised augmented plane wave code within density functional theory.¹² It allows us to optimise the atomic positions in doped Al_2O_3 with very high precision.^{13,14} We employ the optimized crystal structures from Ref. 13 and parametrize the exchange correlation functional in the generalized gradient approximation, using the Perdew-Burke-Ernzerhof scheme.¹⁵ The charge density is represented by more than 10 000 plane waves in each case and the plane wave cutoff is set to be $R_{\text{mt}}K_{\text{max}} = 7$. We employ a k-mesh of 60 points in the irreducible wedge of the Brillouin zone, where we have checked the convergence with respect to the plane wave cutoff and the fineness of the k-mesh. While the O $2s$, Al $2p$, and Co/Cr/Fe/Ni $3s$, $3p$ orbitals are treated as semi-core states, the valence states comprise O $2p$, $3s$, Al $3s$, Al $3p$ and Co/Cr/Fe/Ni $3d$, $4s$, $4p$ orbitals.

The lattice constants and positional parameters of sapphire are used as starting point of the structural optimization. For minimizing the required computation time one employs the primitive trigonal representation of the crystal structure. In a first step, the unit cell volume is optimised by evaluating the total energy of different sets of lattice constants by means of the third order Birch–Murnaghan equation of state. Afterwards, the internal atomic coordinates are relaxed until the forces have decayed below a $1\ \text{mRy/a.u.}$ threshold. We have compared the structural relaxation for two cells: A small

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FIG. 1. DOS and transmission of Co- and Fe-doped Al_2O_3 .

cell with 1 impurity atom, 3 Al atoms, and 6 O atoms and a large cell ($2 \times 2 \times 2$ supercell) with 1 impurity atom, 31 Al atoms, and 48 O atoms, which also was used by Gaudry and co-workers.⁹ These authors have reported that the impurity effects on the crystal structure are very local in nature. We confirm their results and conclude that already the small cell is sufficient to describe the relaxation induced by a Cr/Fe/Co/Ni impurity in Al_2O_3 .

The optical spectra are calculated within the random phase approximation. Thereby the dielectric function is given by the independent particle approximation:

$$\epsilon(\mathbf{q}, \omega) = 1 + \frac{2V(\mathbf{q})}{\Omega_c} \sum_{\mathbf{k}} \frac{f(\epsilon_{\mathbf{k}+\mathbf{q}}) - f(\epsilon_{\mathbf{k}})}{\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}} - \omega},$$

where $V(\mathbf{q})$ is the Hartree part of the Coulomb interaction, f is the Fermi distribution function, and Ω_c is the volume of the unit cell. The single particle Kohn-Sham energies are denoted by ϵ . Local field effects are neglected. For optical spectroscopy we can set $\mathbf{q} \rightarrow 0$. The reflectivity then is given by

$$R_{ii}(\omega) = \frac{(n_{ii}(\omega) - 1)^2 + k_{ii}^2(\omega)}{(n_{ii}(\omega) + 1)^2 + k_{ii}^2(\omega)},$$

where $n_{ii}(\omega) = \sqrt{(|\epsilon_{ii}(\omega)| + \text{Re } \epsilon_{ii}(\omega))/2}$ denotes the refractive index and $k_{ii}(\omega) = \sqrt{(|\epsilon_{ii}(\omega)| - \text{Re } \epsilon_{ii}(\omega))/2}$ the extinction coefficient. Beyond, $i = x, y, z$ labels the three cartesian axes. Introducing the absorption coefficient

$$A_{ii}(\omega) = \frac{2\omega k_{ii}(\omega)}{c},$$

the transmission is given by $T = 1 - R$ and the damping $D = \exp(-dA)$, with the effective thickness d of the samples. For further details see Ref. 16.

The occupied states of corundum Al_2O_3 form a 6.5 eV broad structure with dominant O $2p$ character, compare Figure 3 in Ref. 13. Some minor Al admixtures are due to the covalent part of the Al–O bonding. Applying the generalized gradient approximation, the energetic gap to the unoccupied states amounts to 6.0 eV. The transition metal doping results in sharp intra-gap states. Since the transition metal atoms substitute Al atoms they adopt a $3+$ configuration. Moreover, the

crystal symmetry leads to a distinct e_g – t_{2g} splitting. For all the impurities under investigation we have checked for magnetic ordering.

For Co doping, see the left-hand side of Fig. 1, we do not observe magnetic ordering. Moreover, the additional Co states form two new electronic bands below and above the Fermi level, separated by an energy gap of about 1.8 eV. The gap between the host states and the occupied dopand states amounts to about 1 eV. The onset of absorption, therefore, is expected to appear near 700 nm. The optical spectrum, see the right-hand side of Fig. 1, shows high transmission at long wavelengths, consistent with the low reflectivity of a semiconductor. Close to 350 nm and 700 nm there are distinct dips in the transmission, which correspond to optical transitions. The sharp drop at short wavelengths is an artefact of the high energy cutoff used in the calculation. The absorption coefficient shows a sharp, though tiny, absorption edge near 700 nm (transition between the Co $3d$ e_g and t_{2g} states, which are subject to a finite hybridization) and a broad absorption structure due to transitions between the host and the Co states. Thus, the experimental transmission peak at about 500 nm is nicely reproduced.

For Fe doping, see the left-hand side of Fig. 1, we again find no magnetic ordering. The density of states (DOS) is similar to the Co case. However, the system is slightly more metallic. The Fe e_g states show up 2 eV above the Fermi level, and the energy gap between the host states and the Fe t_{2g} states amounts to ~ 1.5 eV. In the optical spectrum on the left-hand side of Fig. 2 tiny structures are visible at 200 nm and 300 nm, which the experiment does not resolve. We obtain almost identical experimental and theoretical results for pure sapphire and for the Rayleigh-Gans-Debye approximation² of the maximal transmission of polycrystalline corundum sapphire (right-hand side of Fig. 2). The latter approximation accounts for the scattering at the crystallites, where the maximal transmission depends on the thickness (0.8 mm), the average size of the grains ($0.6 \mu\text{m}$), and the average effective birefringence (0.005 (Ref. 2)). The surface reflection has been subtracted.

For Cr doping, we obtain a ferromagnetic order with a local moment of $2.5\mu_B$ within the Cr muffin-tin spheres. We

FIG. 2. Transmission of Fe-doped and pure Al_2O_3 .

find that this solution is insulating with a bandgap of about 2.5 eV for the spin majority states and 5 eV for the spin minority states, see the left-hand side of Fig. 3. Accordingly, two dips in the transmission are visible at about 250 nm and 500 nm. In the damped transmission only the pronounced edge at 250 nm gives a significant contribution, whereas the experimental transmission has two clear edges at about 350 nm and 500 nm. The fact that there is a second edge in the experimental spectrum which is not reproduced by the theory indicates that the independent particle approximation entering the calculations is not valid in the Cr case. Multi-orbital effects are known to be important for V_2O_3 ,¹⁸ and here can play a role due to the d^3 configuration of the Cr^{3+} ions.

For Ni doping, we find a ferromagnetic state, with partially occupied spin majority and minority bands at the Fermi level, see the left-hand side of Fig. 3. There is an energy gap of about 1 eV (4.5 eV) between the occupied (unoccupied) host states and the Ni states. We note that we have neglected the intraband optical transitions between the Ni states at the Fermi level. The transmission decreases from long wavelengths to a broad dip around 650 nm, a pronounced maximum, and a sharp dip at 450 nm. The transition between the Ni and the unoccupied host states shows

up at a short wavelength of some 275 nm. The experimental absorption peak near 550 nm is well reproduced by the calculation.

In conclusion, we have discussed a set of first principles electronic structure calculations for transparent colored ceramics based on Al_2O_3 . The materials are obtained by replacing part of the Al atoms in sapphire by transition metals (Cr, Fe, Co, Ni). We find that the electronic structure in each case shows sharp dopant states. For Cr, Fe, and Co doping, the valence band is formed by the $3d\ t_{2g}$ states, while the $3d\ e_g$ states are located in the optically active energy range. On the contrary, the $3d\ e_g$ states are partially occupied for Ni doping. Tiny structures in the theoretical Fe spectrum cannot be resolved by the experiment. On the other hand, the theoretical spectra of the Co- and Ni-doped compounds resemble the experiment. Since only minor absorption edges are not resolved, we conclude that our structure model is valid, i.e., the Co/Ni atoms substitute Al atoms. In contrast, important spectral features of the Cr-doped samples are not reproduced within the independent particle approximation, which is in agreement with previous findings.¹⁷

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FIG. 3. DOS and transmission of Cr- and Ni-doped Al_2O_3 .

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