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Absorption Spectra, Emission Spectra, and Magnetic Susceptibility of Chromium in Sodium-β-Alumina

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Absorption spectra, emission spectra, and magnetic susceptibility from 4.2 to 300°K have been measured for β-alumina doped with 2w/o chromium. Chromium-doped β-alumina sintered in air was found to contain only Cr(IV) even though Cr(III) was the oxidation state initially present. Heating air-sintered samples at 1200°C in 10% H_2/90% N_2 for 5 hr reduced the Cr(IV) to Cr(III). The absorption spectra for Cr(IV) and Cr(III) have been fitted to the Tanabe–Sugano diagram and *Dq* and *B* were calculated. Results are consistent with the assignment of both Cr(III) and Cr(IV) to octahedral coordination sites in β-alumina. A parallel study of chromium doped α-alumina also showed the existence of Cr(IV) and Cr(III) in that host lattice depending on the firing atmosphere.

The sinterability and ionic conductivity of β-alumina is very sensitive to impurity additions. The ionic conductivity of β-alumina can be enhanced by additions of Mg^{2+} which substitutes for Al^{3+} in the Al(2) aluminium position in the spinel block (*1*). Charge balance is achieved by incorporation of additional sodium ions in the conducting planes of β-alumina with one additional sodium ion being incorporated for each Mg^{2+} in the spinel block (*2*). Ionic conductivity can also be decreased by other metal impurity additions. Calcium (*3–6*) and yttrium (*4*) collect at the grain boundaries of a polycrystalline sinter and block intergranular conduction. Sinterability can be dramatically affected, as has been shown previously by the addition of vanadium oxides (*7*). Impurities can affect the strength of the ceramic as well, which is an important factor in battery applications (*8*).

In light of these past results on impurity addition effects upon β-alumina it is of interest to determine coordination site symmetry and oxidation states of metal impurity additions to β-alumina. It is also of interest to investigate changes in oxidation state of these impurity additions which may depend upon the preparation conditions of the β-alumina samples.

Experimental

β-Alumina doping was performed by adding chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$) to Alcoa XB-2 Super Ground β-alumina in an acetone slurry. The β-alumina plus metal nitrate was thoroughly mixed using an α-alumina mortar and pestle. The acetone was evaporated by directing a stream of compressed air into the mortar. When the powder was free of solvent further mixing was performed to break up the β-alumina lumps formed upon solvent evaporation. The β-alumina plus metal nitrate was then placed in an α-alumina crucible with cover and calcined in air at 1000°C for 24 hr to decompose the nitrate.

The calcined powder was then cold-pressed

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in a KBr pellet die using a bench laboratory press, packed in 300-mesh β-alumina and sintered in air at 1600°C for 3 hr in an Astro Industries, Inc. Model 1000A ultra-high temperature furnace. Some of the air-sintered disks were heated at 1200°C for 6 hr in a flowing stream of 10% H_2/90% N_2.

Absorption spectra were recorded by making KBr pellets (*9*) with powders of both air-fired and reductively fired samples. The KBr disks obtained were yellow-green for air and pink for H_2/N_2-fired material. Spectra were recorded from 260 to 700 nm using a Cary 15 uv/visible spectrophotometer.

Emission spectra were obtained at 77°K using a 1000-W xenon lamp and monochromator to produce 365 nm exciting radiation. Emission was scanned from 9000 to 25,000 cm^{-1} using a Perkin–Elmer Model 98 prism monochromator and an RCA 7102 photocube cooled with dry ice. Spectra were recorded on a Rikadenki B-161 chart recorder and were corrected for phototube and monochromator spectral response.

Magnetic susceptibility measurements were obtained using a vibrating sample magnetometer from 4.2 to 300°K with a constant field strength of 9560 G. All samples for measurement were carefully dried for 72 h at 300°C. Dopant concentration analysis necessary for the calculation of μ_{eff} was carried out by spectrophotometry and atomic absorption. In addition, all samples for magnetic susceptibility measurements were checked for ferromagnetic behavior by examining the susceptibility versus field strength. No ferromagnetic effects were found at 300°K.

All materials used were examined by X-ray powder diffraction for the presence of second phases, but none were found.

Absorption Spectra

Chromium is well known to prefer octahedral coordination in spinels (*10*). Initial attempts to obtain absorption spectra of chromium-doped β-alumina photographically in the range 400 to 700 nm using air-sintered disks were unsuccessful. This was puzzling since previous workers had studied chromium in spinels and had obtained absorption bands in that spectral region (*11–13*).

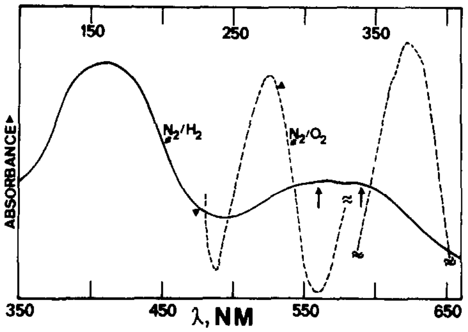

FIG. 1. Absorption spectra of 2w/o chromium-doped β-alumina for oxidizing and reducing conditions. Spectra obtained from a KBr pellet at room temperature.

The spectrum (Fig. 1) of an air-fired sample was obtained from a KBr pellet and consisted of two absorptions at high energy (275 and 371 nm). The positions of the absorption bands could not be correlated with Cr(III) in octahedral coordination using the Tanabe–Sugano diagram for a d^3 ion, and the bands do not agree with previous workers (*11–13*) studying Cr(III). Therefore, it was hypothesized that in air-fired samples chromium was being oxidized to Cr(IV) in β-alumina. Dq and B were calculated (Table I) using the experimental transition energies and equations for energy levels in octahedral complexes (*14*). The experimental results were fitted to the Tanabe–Sugano diagram for a d^2 ion using the calculated values of Dq and B. The results of these calculations are consistent with the experimentally observed absorption spectrum of air-fired chromium-doped β-alumina and support the hypothesis of oxidation of chromium to Cr(IV) with air-sintering.

Absorption spectra for reductively fired samples were obtained and values of Dq and B were calculated as before. As can be seen from Fig. 1 the band positions (410 and 565 nm) have shifted significantly from air-fired samples. Based on previous work (*11–13*) these

TABLE I

EXPERIMENTAL AND CALCULATED ABSORPTION BAND POSITIONS FOR CHROMIUM-DOPED β-ALUMINA AND α-ALUMINA

Firing atmosphere	Host lattice	Band positions, expeirmental[a]		Band positions, calculated	*Dq*	*B*
N_2/O_2	α-Al_2O_3	27,300	$^3T_{2g}(F) \leftarrow {}^3T_{1g}(F)$	27,586	2896	731
		36,600	$^3T_{1g}(P) \leftarrow$	36,550		
		—	$^3T_{1g}(F) \leftarrow$	57,018		
H_2/N_2	α-Al_2O_3	18,510	$^4T_{2g}(F) \leftarrow {}^4A_{2g}(F)$	18,750	1851	625
		25,000	$^4T_{1g}(F) \leftarrow$	25,000		
		—	$^4T_{1g}(P) \leftarrow$	40,000		
N_2/O_2	β-Alumina	26,880	$^3T_{2g}(F) \leftarrow {}^3T_{1g}(F)$	26,561	2856	744
		36,360	$^3T_{1g}(P) \leftarrow$	36,208		
		—	$^3A_{2g}(F) \leftarrow$	55,552		
H_2/N_2	β-Alumina	17,700	$^4T_{2g}(F) \leftarrow {}^4A_{2g}(F)$	17,520	1770	657
		24,390	$^4T_{1g}(F) \leftarrow$	24,309		
		—	$^4T_{1g}(P) \leftarrow$	37,230		

[a] ±100 cm^{-1}.

positions are now what would be expected for Cr(III) in octahedral coordination in a spinel. The values of *Dq* and *B* are reasonable for octahedrally coordinated Cr(III).

Antoine has also studied chromium-doped β-alumina using absorption spectroscopy (*15*) and Boilot *et al.* have studied it with electron paramagnetic resonance (*16*). The absorption spectrum was obtained by using small single crystals fabricated by fusing a mixture of $NaAlO_2$–Al_2O_3 plus sufficient Cr_2O_3 to give a final chromium concentration of 0.94 w/o for Antoine's high doping level with a β-alumina formula of $Na_2O.7.8Al_2O_3$. Antoine reported only the presence of Cr(III) in his β-alumina crystals. The result of finding only Cr(III) was due to the preparation method (*17*). Fusion of powders was performed by RF heating with the powders contain in a graphite crucible. Graphite crucibles undergo some oxidation during heating and provide an atmosphere of CO/CO_2. This is a sufficiently reducing atmosphere to prevent chromium oxidation to Cr(IV). Antoine's results and the results presented here are in full agreement for Cr(III).

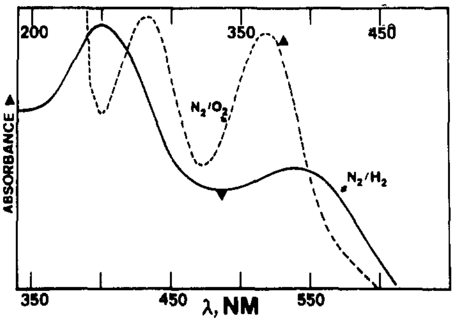

FIG. 2. Absorption spectra of 2w/o chromium-doped α-alumina for oxidizing and reducing conditions. Spectra taken as in Fig. 1.

The behavior of chromium in α-alumina was investigated by preparing a batch of α-alumina doped with 2w/o chromium. Coprecipitation of aluminium and chromium nitrates was carried out in aqueous ammonia and the resulting gel was calcined at 1200°C for 6 hr in air (*18*). The resulting powder was yellow-green in color. The absorption spectrum was obtained from a KBr pellet and is shown in Fig. 2. The absorptions are at high energy similar to β-alumina air-fired samples. *Dq* and *B* were calculated and results are given in Table I. Heating the air-fired material in 10% H_2/90% N_2 at 1200°C for 5 hr resulted in a pink powder. An absorption spectrum was taken and band positions agreed with those of chromium-doped β-alumina prepared similarly. *Dq* and *B* were calculated and the results (Table I) are in full agreement with other studies of Cr(III) in α-alumina (*13*).

Magnetic Susceptibility

Magnetic measurements on 3*d* transition metals are quite sensitive to oxidation state changes. As can be seen in Figs. 3 and 4, μ_{eff} is much greater in hydrogen-fired samples compared to air-fired samples. This is consistent with the increase of one *d*-electron when Cr(IV) is reduced to Cr(III), i.e., from a d^2 to a d^3 ion.

Figure 3 contains a plot of the predicted behavior of an ion with a $^3T_{1g}$ ground state in perfect octahedral symmetry and is not expected to follow the Curie–Weiss law, which states that μ_{eff} is independent of temperature (*19*). Cr(IV) has a $^3T_{1g}$ ground state but, as is evident, magnetic susceptibility versus temperature for both α-alumina and β-alumina host lattices does not follow the predicted behavior. The very marked deviation can be accounted for by the less than ideal octahedral site symmetry in both hosts. Deviations from Curie–Weiss behavior are expected because of spin–orbit coupling from the degenerate ground state levels to higher excited levels. Lowering of site symmetry from perfectly octahedral lifts the degeneracy of the ground state and destroys spin–orbit coupling effects. This causes ions with *T* ground states in low symmetry environments to actually obey the Curie–Weiss law (*20*) and show little change in μ_{eff} with increasing temperature, in agreement with observation (above kT/λ = 0.25).

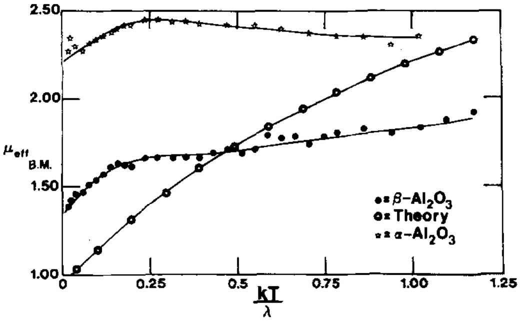

FIG. 3. Temperature dependence of the magnetic moment for chromium-doped samples from 4.2 to 300°K. Samples prepared under oxidizing conditions.

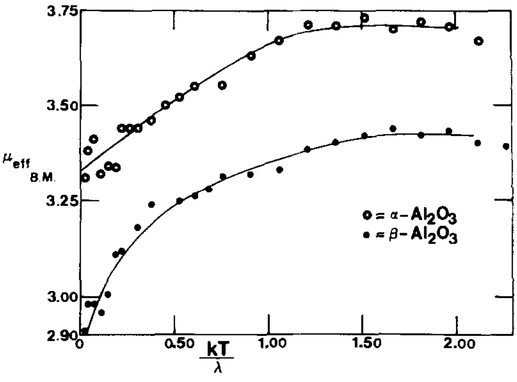

FIG. 4. Temperature dependence of the magnetic moment for chromium-doped samples from 4.2 to 300°K. Samples prepared under reducing conditions.

The decrease in magnetic moment for reduced samples at low temperatures is probably the result of some chromium–chromium or chromium–host lattice impurity exchange effects. At low temperatures such effects become important and are often observed in dilute paramagnetic systems. The moment does become constant within measurement errors above 100°K ($kT/\lambda \geqslant 0.75$). This Curie–Weiss behavior is as expected for an ion with $^4A_{2g}$ ground state symmetry (*21*).

If the assumption is made that the low site symmetries have destroyed spin–orbit coupling effects by removing ground state orbital degeneracies for Cr(III) and Cr(IV), the magnetic moments (Figs. 3 and 4) of air- and hydrogen-fired samples are low compared to the expected spin-only values of 2.83 B.M. for a d^2 system and 3.87 B.M. for a d^3 system. The moments for α-alumina are reasonably close to the expected values, but those for β-alumina are quite low.

The moment for air-fired chromium doped β-alumina is near 1.73 B.M., which is the moment for a d^1 system. Without further data one could propose that Cr(V) is present in air-fired material rather than Cr(IV). However, absorption spectrum for air-fired chromium-doped β-alumina rules out the presence of Cr(V). A d^1 system would have only a single absorption band, which is definitely not in agreement with the experimental observations.

Although the magnetic measurements deviate somewhat from the predicted, the relative increase in the moment from d^2 to d^3 configurations is expcted to be

$$3.87 \text{ B.M. } (d^3) - 2.83 \text{ B.M. } (d^2) = 1.04 \text{ B.M.} = \Delta\mu_{\text{eff}},$$

using spin-only moments. The observed $\Delta\mu_{\text{eff}}$ for β-alumina was 1.57 B.M. and that for α-alumina was 1.36 B.M. These $\Delta\mu_{\text{eff}}$ are sufficient for a one-electron reduction but are too small for a two-electron reduction, i.e. from a d^1 to a d^3 configuration. In the latter case

$$3.87 \text{ B.M. } (d^3) - 1.73 \text{ B.M. } (d^1) = 2.14 \text{ B.M.},$$

which is considerably greater than observed.

Emission Spectrum

The emission spectrum of air-fired chromium-containing β-alumina is presented in Fig. 5. The spectrum, composed of a broad emission, is qualitatively similar to that obtained by other workers (*11*, *12*, *22*). The quantitative emission features of chromium fired in air are different from that of H_2/N_2-fired (Fig. 5) material. Jaffe (*22*) found essentially identical emission spectra for chromium in β-$LiAl_5O_8$ with varying firing atmosphere. This invariance in emission spectrum with firing atmosphere was not found for β-alumina, although the difference was not large.

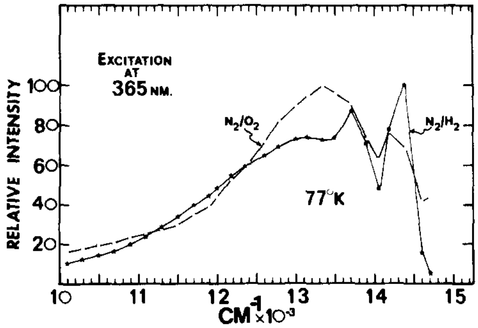

Fig. 5. Emission spectra for 2w/o chromium-doped β-alumina for samples prepared under oxidizing and reducing conditions.

It has been reported that Cr(III) fluorescence arises from the transition $^4A_{2g}(^4F) \leftarrow {}^4T_{2g}(^4F)$ and is in the region of 13,000 to 15,000 cm^{-1} (*23*). The observed emission for H_2/N_2-fired samples (Fig. 5) is in agreement with this energy region. The corresponding absorption $^4T_{2g}(^4F) \leftarrow {}^4A_{2g}(^4F)$ is centered at 17,700 cm^{-1}, indicating a reasonable Stokes' shift of ~4000 cm^{-1}.

There is also evidence in Fig. 5 for the sharp phosphorescence lines from the $^4A_{2g}(^4F) \leftarrow {}^2T_{1g}(^2G)$ and $^4A_{2g}(F) \leftarrow {}^2E_g(^2G)$ transitions at 13,700 and 14,400 cm^{-1}. This observation also is in agreement with Schläfer *et al.* (*23*).

The Cr(IV) emission is also centered at about 13,500 cm^{-1}. By analogy with Cr(III) the emission transition may be $^3T_{1g}(^3F) \leftarrow {}^3T_{2g}(^3F)$. However, the absorption line is observed at about 26,800 cm^{-1}, which would indicate a large Stokes' shift. However, the combination of very low site symmetry in the Al(1) site (*17*) plus lattice polarization due to the high charge on Cr(IV) might result in such a large shift.

One of the difficulties in interpreting the emission spectra results is that extremely little has been published on Cr(IV) spectra (*24*). The emission results do not provide conclusive evidence for the presence of Cr(IV), but the spectra of samples fired under oxidizing conditions were never identical to spectra of samples fired under reducing conditions. An examination of the Tanabe–Sugano diagram for d^2 and d^3 ions does indicate that the levels arising for the two cases are very similar in their energy relationship to the ground state. The factors of low site symmetry, high lattice polarization, and differences in internulcear separation between Cr(IV) excited and ground states all probably contribute to the observed absorption and emission spectra.

Conclusion

The absorption spectra indicate most strongly that Cr(IV) exists in and is the predominant oxidation state present upon air-sintering of chromium-doped β-alumina. This is also true for α-alumina prepared as described in the Experimental section. The magnetic susceptibility measurements clearly indicate an oxidation state change from air- to reductively fired samples. The change in the magnetic moment is in reasonable agreement with the predicted change of moment using spin-only values from a d^2 to a d^3 configuration. Emission spectra are quite similar in appearance for both firing conditions but could be expected to be so from an examination of the Tanabe–Sugano diagram. The emission was never identical for the two firing conditions. Finally, it should be noted that the conductivity of air-fired chromium-doped β-alumina should decrease if Cr(IV) is present because of the possibility of sodium loss from β-alumina for charge balance. A conductivity decrease for this material has been previously reported (7).

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