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# Luminescence and photoconductivity in magnesium aluminum spinel

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Ultraviolet-light excitation of thermochemically reduced $MgAl_2O_4$ single crystals below room temperature produces a luminescence band with a peak at 2.69 eV. The excitation spectrum of the 2.69-eV band coincides with the broad *F*-center absorption band at 5.30 eV. The 2.69-eV band is also emitted in uv-stimulated glow peaks which occur at 95 and 265 K. A photoconductivity maximum is observed at 5.39 eV at temperatures above 160 K, but the band is readily bleached by uv light.

## I. INTRODUCTION

Magnesium aluminum spinel ($MgAl_2O_4$) is an oxide with important optical and electrical applications. Many of its properties are intermediate between those of its constituent oxides, but its relatively complex crystal structure has made the study of defects considerably more difficult than for either $\alpha$-$Al_2O_3$ or MgO. Consequently, although much is now known about anion vacancy (*F*-type) centers and cation vacancy (*V*-type) centers in both MgO and $\alpha$-$Al_2O_3$, relatively little is known about these centers in $MgAl_2O_4$. Part of the problem is that synthetic crystals of spinel are usually nonstoichiometric and the existence of two kinds of cations with different charge states allow for many possible defect configurations, especially antisite defects. Another problem has been that the usual experimental techniques such as photoluminescence, electron spin resonance, and photoconductivity have so far not proved very productive. The optical properties of defect centers in insulators are of renewed interest because of the advent of color center lasers. Because of the potential for high thermal stability, thermochemically reduced materials are of particular interest in this regard.

An optical-absorption band at 5.3 eV (234 nm) which can be produced by irradiation with electrons[1] or neutrons,[2] or by thermochemical reduction[3] has been assigned with some confidence to the *F* center (an oxygen vacancy with two electrons). Optical bleaching of this band causes it to decrease, while a band at 4.75 eV (261 nm) develops which has been assigned to the $F^+$ center[1] (an oxygen vacancy containing one electron). A similar photochromic effect is observed in both MgO (Ref. 4) and $\alpha$-$Al_2O_3$ (Ref. 5). In these materials confirming evidence for the process comes from photoconductivity[6,7] measurements. In the case of spinel, however, no photoconductivity or luminescence has so far been reported from *F* centers even in thermochemically reduced samples.

The effect of x and $\gamma$ rays on spinel has been studied in detail by White *et al.*[8,9] In particular, a careful analysis was made of possible charge trapping sites involved in thermally stimulated processes occurring above room temperature.[10] Woosley *et al.*[11] have reported a comprehensive study of the photoelectric effect and photoconductivity in untreated, particle-irradiated, and $\gamma$-irradiated spinel. They concluded that no photoconductivity could be attributed to the *F* center in their samples.

The anion-cation separation is comparable in $MgAl_2O_4$, $\alpha$-$Al_2O_3$, and MgO, although the *F*-center site symmetry is different in each material. In MgO an oxygen vacancy site has octahedral, $O_h$, symmetry, whereas in $\alpha$-$Al_2O_3$ an oxygen vacancy site is surrounded by four $Al^{3+}$ ions in $C_2$ symmetry. Despite the different site symmetry, *F* centers in both materials have somewhat similar properties. In spinel there is one kind of oxygen vacancy site in the perfect lattice, in which the vacancy is surrounded by three $Al^{3+}$ ions and one $Mg^{2+}$ ion. There seems to be no obvious reason why the optical properties of *F* centers in $MgAl_2O_4$ should be significantly different from those in $\alpha$-$Al_2O_3$ or MgO, apart from the lack of stoichiometry of the samples.

We report here a study of photoluminescence, thermoluminescence, and photoconductivity produced by optical excitation of the 5.3-eV absorption band in thermochemically reduced spinel. The measurements were made over the temperature range 80—300 K. The results suggest that the *F* center in spinel may luminesce and produce photoconductivity, although much less efficiently than in other oxides such as MgO.

## II. EXPERIMENTAL DETAILS

Most of the samples used were provided by J. H. Crawford. They were cut from a boule grown by Union Carbide Corporation and chemical analysis showed that Fe and Cu were the most abundant impurities (76 and 22 ppm, respectively), with Cr, V, Ni, and Mn also present in concentrations of a few ppm.[10] The thermochemically reduced sample was prepared by heating close to 2000 °C in an atmosphere of aluminum vapor.[3] The sample was 0.074 cm thick and had an optical density of 3.7 at 5.3 eV. Taking the oscillator strength of the *F*-center absorption as $\sim 1$ and the half-width of the band as $\sim 1$ eV, we estimate using Smakula's equation that the sample contained $\sim 10^{18}$ *F* centers $cm^{-3}$.

Photoluminescence was excited using light from a 60-W deuterium lamp, with particular wavelengths being selected by thin-film interference filters. Luminescence was dispersed by a 0.3-m McPherson grating monochromator and detected by a thermoelectrically cooled RCA model no. C31034 photomultiplier tube. For measuring excitation spectra, the light from the deuterium lamp was dispersed by the McPherson monochromator before falling on the sample. Stray light was reduced by inserting a suitable sharp-cut filter in front of the photomultiplier. The sample was supported in the exchange gas space of an Oxford Instruments variable-temperature cryostat system. In order to make photoconductivity measurements the usual sample holder was replaced by one in which the sample was held between a semitransparent front electrode and a high-impedance back electrode made of copper foil. The front electrode consisted of a spring-mounted fine phosphor-bronze gauze, which was separated from the sample by a thin sapphire plate. This plate effectively "blocked" the front electrode. The rear electrode could be blocked in the same way. Photocurrents were excited with the same optical system used for the luminescence measurements and were detected using a Cary model no. 401 vibrating reed electrometer. Sapphire insulation was used throughout for the high-impedance electrode. Thermoluminescence measurements were made using the same cryostat system. The spectral dependence of the thermoluminescence was measured by rapidly scanning the monochromator in both directions once the luminescence intensity was close to a maximum.

## III. RESULTS

### A. Photoluminescence

Photoluminescence was excited in thermochemically reduced $MgAl_2O_4$ with light from a deuterium lamp, used in conjunction with an intereference filter with peak transmission at 225 nm. The resulting luminescence band is shown in Fig. 1, in which the data have been corrected for the spectral dependence of the detection system. At 95 K the peak of the luminescence is at 2.69 eV (461 nm), but there is a clearly resolved shoulder at 2.95 eV (420 nm). As the temperature increased above 140 K, the peak of the band shifted to lower energy and by 250 K was located at 2.58 eV (480 nm) (Fig. 1 ). A detailed plot of the peak energy versus temperature is shown in Fig. 2. The high-energy side band became less clear as the temperature increased and by 250 K was not resolved (Fig. 1). The whole band became narrower as the temperature was raised, so that at 95 K the half-width was 0.66 eV, whereas at 250 K the half-width was 0.51 eV. The relative intensity of the luminescence increased between 95—140 K, but then decreased again as the temperature was further raised to 300 K (Fig. 2).

Figure 3 shows the excitation spectrum of the 2.69-eV luminescence at 160 K, which is the temperature region where the luminescence intensity is highest. Figure 3 shows that the excitation spectrum has a peak at 5.3 eV, is slightly skewed towards high energy, and has a half-width of $\sim 1.0$ eV. There is a small secondary maximum at $\sim 4.45$eV, but this is only $\sim$ 7% of the main peak. No difference was observed in the excitation spectrum for luminescence anywhere in the 2.69-eV band.

The 2.69-eV luminescence intensity decayed rapidly once the excitation was removed. The lifetime was less than $\sim 1$ ms, which was the time constant of the detection system. There was no evidence of the long lifetime observed for $F$-center luminescence in some samples of thermochemically reduced MgO (Ref. 12) and $\alpha$-$Al_2O_3$ (Ref. 13). Although the luminescence was readily detected, it was only about one tenth as intense as the 2.3-eV $F$ center luminescence in a comparably-sized MgO sample which contained approximately the same concentration of $F$ centers and which was excited with the same optical system. The 2.69-eV band could also be excited very weakly in some as-received samples.

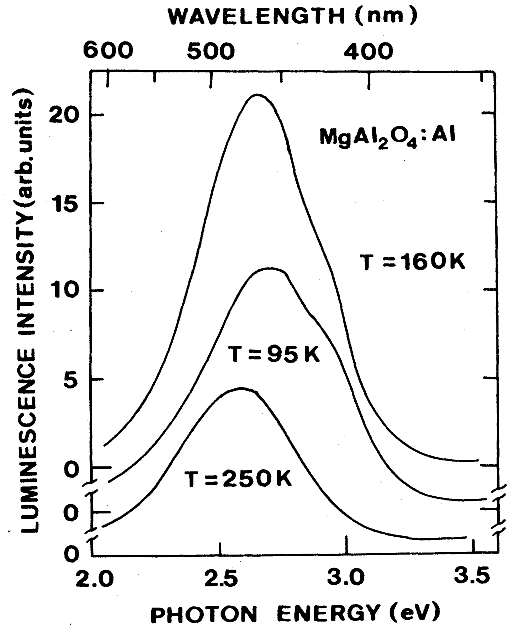

FIG. 1. Photoluminescence spectra excited in thermochemically reduced $MgAl_2O_4$ by 225-nm (5.4-eV) light.

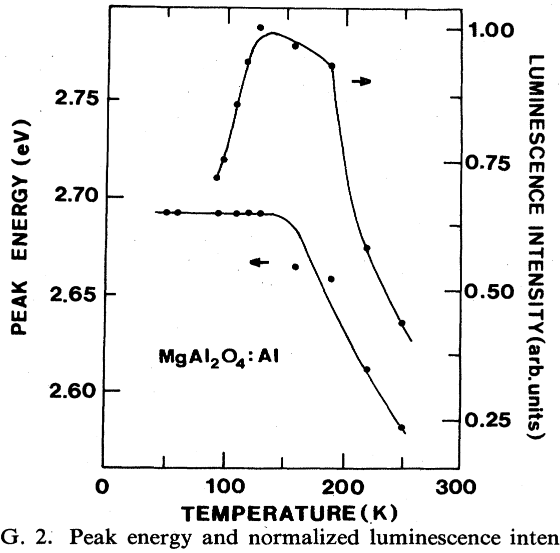

FIG. 2. Peak energy and normalized luminescence intensity of the 2.69-eV band in thermochemically reduced $MgAl_2O_4$ as a function of temperature.

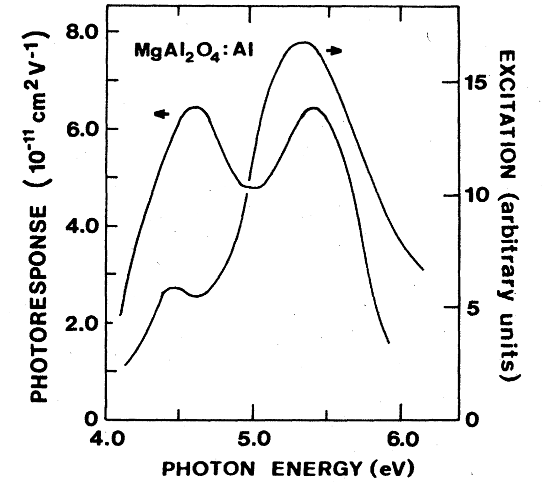

FIG. 3. Excitation spectra of the 2.69-eV luminescence band and the photoresponse of thermochemically reduced $MgAl_2O_4$. The photoresponse is shown for $T=216$ K and the luminescence excitation curve is shown for $T=160$ K.

### B. Thermoluminescence

Figure 4 shows the thermoluminescence (TL) glow curve for the same sample used in the photoluminescence experiments (Fig. 1). In TL experiment the sample was cooled to liquid-nitrogen temperature, illuminated for a few minutes with unfiltered light from a deuterium lamp, and then heated to room temperature at $\sim 0.1$ K $s^{-1}$. Figure 4 shows that there are TL peaks at 95 and 265 K, with the latter peak considerably weaker than the first. No TL was detected from an as-received sample under similar conditions. The spectral dependence of the emission at 95 and 265 K is shown in Fig. 5. At 95 K the emission consists of a band with a main peak at 2.68 eV and with a half-width of $\sim$0.65eV. A shoulder is visible at $\sim$2.95 eV. At 265 K the peak shifts to 2.57 eV and the half-width narrows to 0.52 eV. The bands in Fig. 5 are clearly similar to the photoluminescence curves shown in Fig. 1.

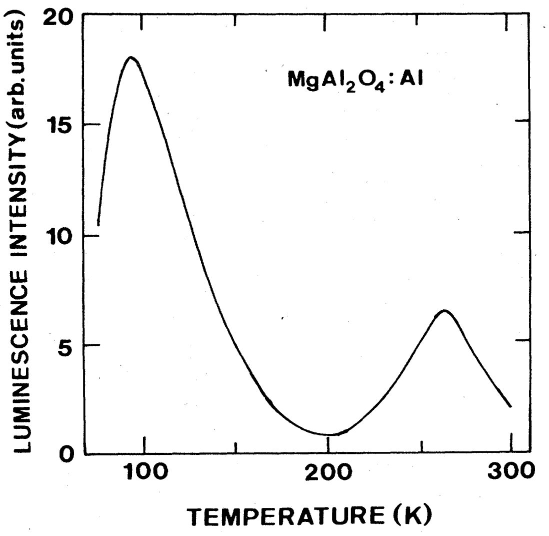

FIG. 4. Thermoluminescence glow curve for thermochemically reduced $MgAl_2O_4$. The sample was illuminated at 80 K for several minutes with unfiltered light from a deuterium lamp before heating.

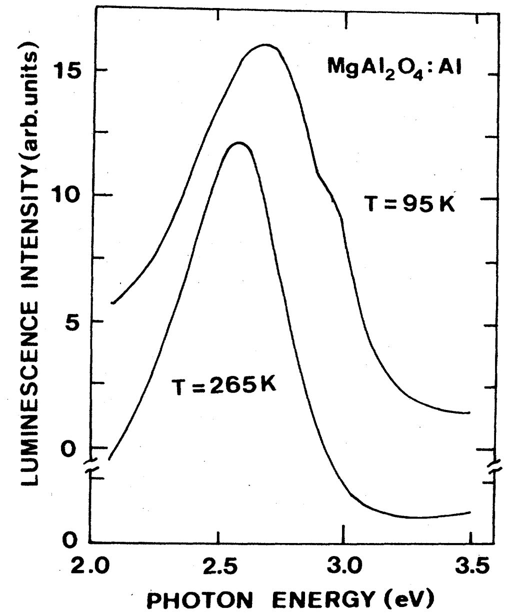

FIG. 5. Thermoluminescence emission spectra at each of the glow peaks shown in Fig. 4.

### C. Photoconductivity

As long as the mean charge-carrier range $\omega_0 V/d$ in the direction of the applied electric field $V/d$ is smaller than the thickness of the sample, $d$, the photoresponse of an insulating material sandwiched between two plane-parallel electrodes, is given by[14]

$$\eta\omega_0=(I/N)(d^2/|e|V)\ , \qquad (1)$$

where $\eta$ is the free electron yield per incident photon, $\omega_0$ is the mean range per unit applied electric field, $I$ is the photocurrent, $N$ is the incident photon flux, and $|e|$ is the magnitude of the charge on an electron. Equation (1) shows that the photoresponse at a certain wavelength depends not only on the probability of a photon producing a free charge carrier but also on the distance that the charge carrier moves in the direction of the field before becoming trapped. The photocurrent is, therefore, sensitive to the distribution of effective traps in the sample and can be affected by altering this distribution, even if the quantum yield remains unchanged.

Figure 3 shows the photoresponse at 216 K of the same sample that was used for the luminescence measurements. At this temperature the photoresponse consists of two peaks, one at 5.39 eV and the other at 4.59 eV. There was no measurable photoresponse over the same energy range for an as-received sample. The intensity of the 4.59-eV peak was approximately independent of temperature over the range 80—300 K and was not affected by prolonged exposure of the crystal to the incident light. The peak at

5.39 eV, however, was only apparent between 190—250 K and was very sensitive to bleaching by the incident light. For example, when the spectrum was scanned from low to high photon energy, i.e., if the 4.59-eV band was excited first, the 5.39-eV band was not apparent. It was then necessary to reverse the direction of the applied electric field and to scan the spectrum from high to low photon energy to produce the 5.39-eV band. Although this behavior is particularly pronounced in $MgAl_2O_4$, similar bleaching effects are observed in the photoresponse of $F$ centers in other oxides. This will be discussed further in Sec. IV.

## IV. DISCUSSION

In Sec. III we presented photoluminescence, thermoluminescence, and photoconductivity results for $MgAl_2O_4$, which taken as a whole, are similar to results for other thermochemically reduced oxides, particularly MgO. The 5.30-eV absorption band of the $F$ center in $MgAl_2O_4$ occurs between that for MgO (5.0 eV) and that for $\alpha$-$Al_2O_3$ (6.1 eV). It is tempting therefore to assign tentatively the 2.69-eV luminescence band, which falls between $F$-center emission bands in MgO (2.3 eV) and $\alpha$-$Al_2O_3$ (3.0 eV) to luminescence from $F$ centers in $MgAl_2O_4$. This assignment is supported by the facts that the excitation spectrum of the 2.69-eV band (Fig. 2) peaks at $\sim 5.3$ eV and has a half-width of $\sim 1.0$ eV, which are characteristic of the $F$-center absorption band. The results indicate, however, that the quantum efficiency of the 2.69-eV band in our sample is less than one-tenth that of the 2.3-eV $F$-center luminescence in thermochemically reduced MgO. The reason for such a low efficiency for an $F$-center luminescence is difficult to explain without information about the local environment and electronic structure of the center. However, the expected large nonstoichiometry in synthetic $MgAl_2O_4$ crystals, which can be as high as 30%, suggests that it might be due to the fact that some $F$ centers may be in unusual environments. For example, some oxygen vacancies may be surrounded by four $Al^{3+}$ ions, while others may be surrounded by two $Al^{3+}$ ions and two $Mg^{2+}$ ions. It is possible that only those $F$ centers in a particular configuration decay radiatively. We note that $F$ centers in other complex crystal structures such as $KMgF_3$ also do not decay radiatively or decay radiatively with a very low quantum efficiency for reasons which are not yet completely known. Because of the uncertainties, we emphasize that the assignment of the 2.69-eV band to $F$-center luminescence is tentative. The resolved structure on the high-energy side of the 2.69-eV band does not appear to be a phonon sideband. If the 2.69-eV luminescence does indeed come from $F$ centers, the structure could be a result of a low site symmetry, which could raise the degeneracy of $p$-like excited states. The position of the structure would thus indicate a splitting of $\sim 0.2$ eV. Splitting of this magnitude has been deduced for the $p$-like emitting state of the $F$ center in $\alpha$-$Al_2O_3$ (Ref. 13), although in this case no resolved structure was observed. The shift of the peak position of the 2.69-eV band to lower energy as the temperature is increased is observed in the luminescence of most anion vacancies. The shift is due partly to the thermal expansion of the lattice with increasing temperature.

The increase in magnitude of the 2.69-eV band as the temperature increased to 160 K, followed by a decrease in magnitude as the temperature increased further is similar to the behavior of the 2.3-eV band in MgO (Ref. 15). In a simple three-level model in which an electron in the excited state of an $F$ center can either decay radiatively to the ground state or escape into the conduction band, a decrease in luminescence intensity with increasing temperature is expected to be accompanied by a corresponding increase in photoconductivity.[16] This behavior is apparent in spinel above 160 K. The behavior of the photoconductivity is unusual, however, and deserves further comment.

The peak of the photoconductivity band at 5.39 eV is $\sim 0.1$ eV higher in energy than the $F$-center absorption band. However, the absorption band is quite broad ($\sim 1.0$ eV) and skewed to high energy, which suggests that it might consist of several components due to the low symmetry of the oxygen-vacancy site, as discussed above in relation to the luminescence. In this case photoconductivity might be found only on the high-energy side of the absorption band. Because of the point-by-point measurement technique used by Woosley *et al.*[11] the precise locations of the photoconductivity peaks they reported are somewhat uncertain. Peaks were reported at 3.75, 4.0, 4.25, 4.5, 5.0, and 5.5 eV in $\gamma$- and electron-irradiated samples, and at 4.5, 5.0, and 5.5 eV in neutron-irradiated samples. None of these bands coincides with the two bands shown in Fig. 3. The 4.59-eV (276-nm) band in spinel is close in energy, however, to a band found in thermochemically reduced MgO. This band has not yet been identified,[6] but is possibly due to an electron trap such as Fe.

The magnitude of the photoresponse per absorbed photon at 5.39 eV is comparable to that of $F$ centers in other high-resistivity materials. In spinel the photoresponse was $\sim 6.5\times 10^{-11}$ $cm^2 V^{-1}$. For $F$ centers in electron-irradiated CaO (Ref. 17) and SrO (Ref. 18) the values were $\sim 1.5\times 10^{-10}$ and $\sim 4\times 10^{-10}$ $cm^2 V^{-1}$, respectively. The bleaching effect observed in the 5.39-eV band has also been seen in MgO (Ref. 6), CaO (Ref. 17), and SrO (Ref. 18). In each case it was necessary to irradiate the sample with $\gamma$ rays or ultraviolet light to maximize the photoresponse. The usual explanation for this behavior is that the irradiation fills traps which would otherwise reduce the range of the free charge carriers. We have also found it difficult to observe the photoresponse of $F$ centers in thermochemically reduced MgO, especially when the concentrations were high.[19] Recent results[20] indicate that the charge-trapping mechanisms in thermochemically reduced MgO and by analogy other oxides are quite complex. The behavior of the 5.39-eV photoresponse band in spinel is, therefore, unusual but not atypical of behavior seen in other oxides containing $F$ centers.

The thermoluminescence glow curve of spinel (Fig. 4) is similar to that seen in thermochemically reduced MgO (Ref. 15) and CaO (Ref. 21). In all cases there is a peak near room temperature and a peak below 100 K. The higher-temperature peak in MgO and CaO is due to release of electrons from substitutional $H^{2-}$ ions and their subsequent capture into the excited states of *F* centers. The hydrogen originates as dampness in the starting materials from which the crystals are grown. A TL peak at 260 K is also seen in some samples of $\alpha$-$Al_2O_3$ (Ref. 7), and this has also been tentatively assigned to release of electrons from $H^{2-}$ ions. We would expect thermochemical reduction of $MgAl_2O_4$ to produce substitutional $H^-$ ions in addition to *F* centers, just as in the case of MgO. By analogy to the behavior of both MgO and $\alpha$-$Al_2O_3$ we therefore suggest that the 260 K TL peak in spinel is due to release of electrons from $H^{2-}$ ions. The lower temperature peaks in MgO and CaO have not been identified. Just as in the case of spinel, however, these peaks are introduced by thermochemical reduction and are not present in the original material.

## V. CONCLUSIONS

In Sec. IV we showed that the optical behavior of thermochemically reduced $MgAl_2O_4$ is generally similar to that of other oxides. This discussion suggests that the 2.69-eV photoluminescence band is possibly due to a low-quantum-efficiency process involving *F* centers and that the 5.39-eV photoresponse band is due to electrons which are thermally excited into the conduction band from an excited state of the *F* center. The charge-trapping mechanisms seem very efficient, however, so that the photoresponse is easily bleached. We note that the fact that the 2.69-eV band was excited in some as-received samples does not rule out the possibility of it being due to *F* centers, because crystals of oxides are often partially reduced during growth.[7] Alternatively it could be argued that the 2.69-eV band is due to emission from a chemical impurity which has an excitation spectrum similar to the *F*-center absorption spectrum. Iron group ions would seem to be the most likely candidates but we can rule out $Cr^{3+}$ and $V^{3+}$, which emit at 1.8 eV (Ref. 22) and 2.38 eV (Ref. 23), respectively. $Mn^{2+}$ on tetrahedral sites emits at 2.38 eV (Ref. 24). $Fe^{2+}$ is unlikely to be found in our crystals for the reasons discussed by White *et al.*[9] but $Fe^{3+}$ on tetrahedral sites could be involved, although White *et al.*[9] suggest that these ions are also not observed in the as-received samples. $Fe^{3+}$ on octahedral sites absorbs at 4.8 eV, but no absorption band is observed at this energy in our samples. Finally the 2.69-eV band could be an emission from Cu ions, which as far as we can tell has not been reported in the literature for an $MgAl_2O_4$ host. We note, however, that in MgO substitutional Cu ions produce optical-absorption bands of about equal intensity at 5.5 and 4.5 eV, with half-widths of ~0.6 eV at room temperature. Excitation of these crystals with ultraviolet light produces a weak luminescence band at 3.0 eV with a half-width of ~1.3 eV. In untreated samples of the $MgAl_2O_4$ used here the only absorption bands visible occurred at 4.8 and 6.4 eV and these have been assigned to $Fe^{3+}$ (Ref. 3).

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