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Electron spin resonance and thermoluminescence of tricalcium aluminate, $Ca_3Al_2O_6$

MATTHEW C. BALL, CLIFFORD M. MARSH
Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire LE11 3TU, UK
MARTYN C. R. SYMONS
Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK

Electron spin resonance (ESR) spectra and thermoluminescence (TL) curves and have been obtained for tricalcium aluminate, $Ca_3Al_2O_6$. The ESR spectra and one peak in the TL spectrum can be rationalized in terms of electron trapping at Fe(III), present as impurity, in all of the possible tetrahedral sites, with holes on non-bridging oxygen atoms. Manganese(II), which is also present as an impurity, probably replaces calcium in only two out of six possible sites.

1. Introduction

Tricalcium aluminate, $Ca_3Al_2O_6$, (C_3A)*, is one of the major components of Portland cement, together with di- and tri-calcium silicates and the ferrite phase [1]. Most of the work done on these compounds and the commercial mixtures has concentrated on the reactions with water [1]. Relatively little has been done on the electronic reactivity of these compounds, even though, as insulators, their properties should be dependent on the type and concentration of impurity ions. Defect centres in such cement minerals have been shown to act as hydration sites [2–5]. Such centres may be studied by thermoluminescence (TL) and electron spin resonance (ESR) to give information concerning trapping mechanisms, and these techniques have been used indirectly in previous hydration studies [3]. As an example, there are interesting parallels between electron escape probabilities in tricalcium silicate, derived from TL, and the induction period of the hydration [3].

The present work presents ESR and TL spectra for tricalcium aluminate, discusses the identity and environments of defects responsible for the TL, and where possible proposes reaction mechanisms. The crystal structure of C_3A has been determined [6] and shown to be made up of rings of Al–O tetrahedra, with calcium ions at the centres of the rings. Some thermoluminescence curves have been published [7], but previous ESR work does not appear to have been carried out.

2. Experimental procedure

C_3A was prepared from AR calcium carbonate and AR aluminium nitrate. The correct proportions were mixed, the nitrate decomposed at red heat and the resulting mixture fired at 1650 K. Repeated firing and grinding was carried out until White's test [8] showed that no free lime was present. The firing was also followed by X-rays; the diffraction pattern of the product was in excellent agreement with that published [9].

A thin layer of sample was irradiated for 15 min (with regular agitation) using UV light (λ = 253.7 nm) to saturate all the traps, as far as possible. TL spectra were obtained using a Teledyne Isotopes TLD7300 TL dosimeter. A Stanton–Redcroft potentiometric temperature controller (Type LVP-C) was used to control the heating rates. Spectra were obtained in the temperature range 300 to 570 K.

ESR spectra were obtained using either a Varian E3 or Varian E109 spectrometer. The spectra were obtained at room temperature and 77 K for unirradiated, irradiated and heat-treated samples, using DPPH as reference standard. A technique was devised for the packing of powdered samples in the ESR tube which was found to be reproducible to ± 10% at 77 K. This permitted a semi-quantitative study of the ESR spectra.

3. Results and discussion

3.1. Thermoluminescence spectrum

The spectrum from C_3A is shown in Fig. 1. It consists of two main peaks with maxima at 407 and 453 K. A smaller peak appears at about 513 K, partially merged into the black-body background. The full resolution of this spectrum will not be discussed here; the kinetics of decay of each peak are approximately first-order [10].

3.2. ESR spectra

The spectra are shown in Figs 2 to 4. Overall, the spectrum consists of six equally spaced lines at the centre of the spectrum (ca. 3200 G), around the "free-spin" g value (= 2.0023) and a group of lines around

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*Cement nomenclature: C = CaO, A = Al_2O_3.

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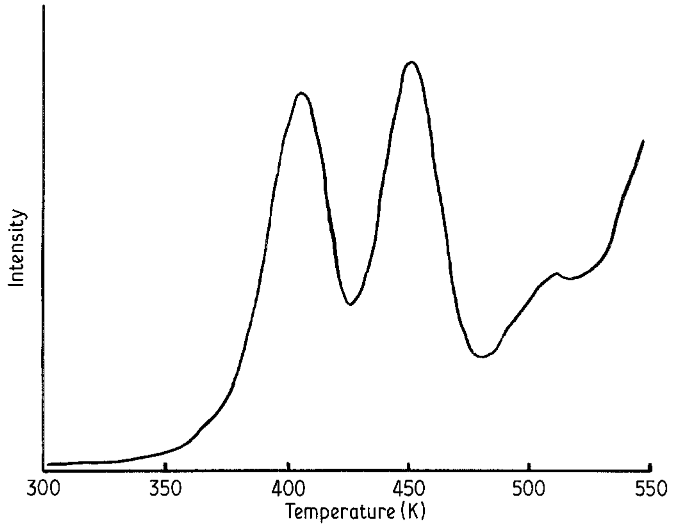


Figure 1 Thermoluminescence spectrum for tricalcium aluminate.

$g = 4.3$. The six central lines are characteristic of the high-spin, d^5, Mn(II) ion ($S = 5/2$) [11]. Lines were sharp both at 77 K and ambient temperature, the latter further indicating an S-state ion. There was no further splitting of each line at 77 K indicating the absence of detectable zero-field splitting. The hyperfine coupling constant, A, is almost isotropic at ~ 85 G. The symmetry and position of the lines indicate that the manganese ions are in reasonably symmetrical sites. However, two sets of wing lines were detected on either side of the sextet suggesting a slight distortion in the environment. An extra line at the centre of the manganese spectrum has not been identified but does not seem to be connected with the thermoluminescence.

In C_3A, Ca(II) ions occupy six different kinds of sites [6], all more or less distorted. Two of these sites, Ca_I and Ca_{II}, consist of Ca(II) octahedrally coordinated to oxygen atoms, in which the octahedron is compressed along the threefold axis. It therefore seems that Mn(II) replaces Ca(II) at these particular sites, rather than generally across all six possible positions. The ionic radius of Mn(II) is less than that of Ca(II) (0.08 nm compared with 0.099 nm) and Mn(II) could substitute in these sites. The amount of manganese in the sample is very low (not more than a few p.p.m.) and such selective substitution is reasonable.

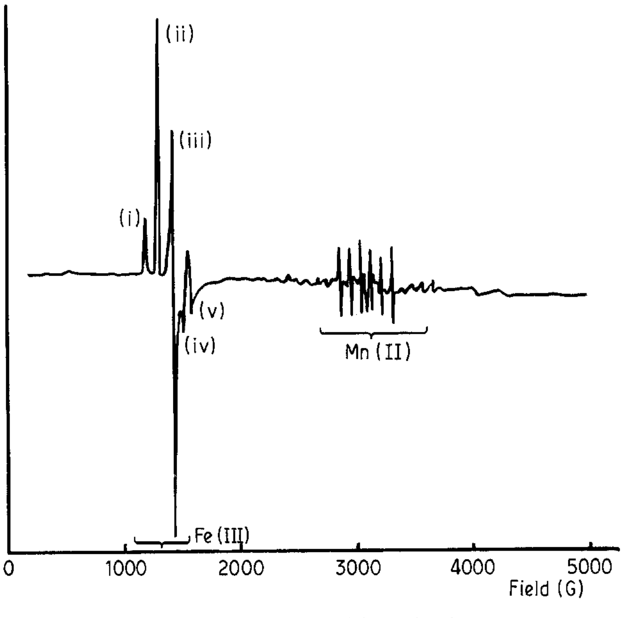


Figure 2 Full ESR spectrum for tricalcium aluminate.

The group of lines at $g = 4.3$ arises from a high-spin system, probably d^5, with a non-magnetic nucleus [12–14]. This g value is not a true g value, but represents a well-defined extremum for the limiting case of a strong rhombic distortion [15]. The Fe(III) ion is far more likely to show such a spectrum than any other transition metal ion. Analysis showed that iron was present in the starting materials, and that other possible ions were absent. The extreme sharpness of the lines at ambient temperature further indicates an S-state ion, with large zero-field splitting but little g-value variation. The spectrum at 77 K consists of two sets of parallel and perpendicular type features indicating two slightly different, distorted sites for Fe(III). These lines were assigned as shown in Table I. Line (v), which appears to be isotropic, is assigned to a third low abundant species. The overall picture from the ESR spectra indicates that Fe(III) ions are in distorted or low-symmetry environments. It is unlikely that Fe(III) is in a network-modifying environment or the lines would be unlikely to be sharp [16]. It is therefore most likely to be in a network-forming position, i.e. at the centre of a polyhedron. The ESR lines narrow slightly on cooling from ambient to 77 K, further indicating that Fe(III) is acting as a lattice-former and is subject to spin–lattice interactions.

Crystallographic evidence is very much in favour of the replacement of Al(III) ions by Fe(III) ions in C_3A [17–20]. At such a low concentration of iron (< 1000 p.p.m.), Fe(III) ions will still have a marked preference for Al(III) sites. Al(III) in C_3A is found in

TABLE I Assignments of $g = 4.3$ lines

Line	Site	Relative intensity	g value*	
(i)	B	9.5($\parallel$)	4.9	Average 4.2
(iv)	B	11.0($\perp$)	3.83	
(ii)	A	43.5($\parallel$)	4.56	Average 4.3
(iii)	A	71.5($\perp$)	4.17	
(v)	C	4.5	3.97	

*These are not true g values, but are commonly quoted for high-spin complexes.

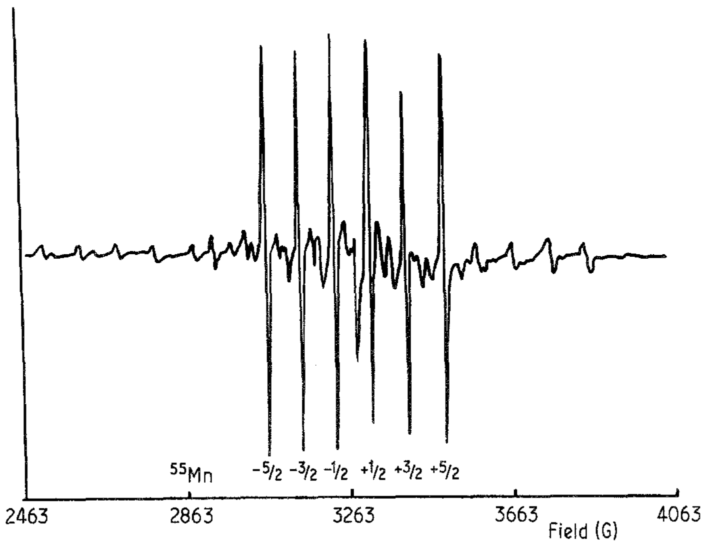


Figure 3 ESR spectrum in the range 3263 ± 800 G.

tetrahedral coordination [6], and these tetrahedra form Al_6O_{18} rings. Each tetrahedron is distorted, in two alternative ways. The ESR evidence indicates that most Fe(III) ions are in two slightly different low-symmetry environments. Substitution of the larger Fe(III) ion (ionic radius = 0.067 nm) for the smaller Al(III) ion (ionic radius = 0.050 nm) would enhance the natural distortions. This accounts well for the two major ESR signals.

It has been shown [13, 14] that for a $g = 4.2$ resonance the tetrahedral environment of the metal (M) could be of the form MA_2B_2, a C_{2v} distortion. This further correlates with the type of tetrahedra existing in C_3A since there are two bridging (A_2) and two non-bridging (B_2) oxygen atoms around each Al(III) or Fe(III) ion.

Finally, it is worth noting that the ionic radii of Fe(III) (0.067 nm) and Ca(II) (0.099 nm) are very different and hence that occupation of a Ca(II) site is unlikely. Charge compensation would also be a limiting factor in this case. Furthermore, substitution of Ca(II) by Fe(III) would probably give a more complex rhombic spectrum due to the six differently distorted Ca(II) sites.

3.3. Identification of electron trapping/donor sites

Fe(III) can act as an electron or hole trap depending upon the radiation conditions and the presence of other impurities [21, 22], but it is more likely to act as an electron trap. Mn(II) normally only acts as a poor hole trap, or is inactive [23]. It was found that the Mn(II) ESR lines did not change in intensity on UV irradiation. Annealing at the TL peak temperatures caused no changes. Thus Mn(II) is not implicated in TL processes either as a trap or a donor (in this temperature range). Results for iron are shown in Table II. On irradiation all Fe(III) lines decreased by ca. 20%. Annealing at 407 K (Peak 1 in the TL spectrum) brought all lines back to their original intensities.

TABLE II Intensity changes (δ) for the Fe(III) ESR spectra on irradiation (arbitrary units)*

Line	Unirradiated intensity	Irradiated intensity	δ(%)
(i)	12.8	8.5	20
(ii)	64.5	41.0	22
(iii)	100.0	65.8	21
(iv)	12.5	8.3	20
(v)	7.0	4.7	20

*The relative unirradiated intensities differ slightly from those in Fig. 1: this indicates the slight variability found within a range of samples.

The processes involved are of the type

$Fe^{3+} + e = Fe^{2+}$ Absorption of radiation

$Fe^{2+} = Fe^{3+} + e$ Luminescence at 407 K

Hole movements could be involved, but with UV exitation, electron movements are more likely [24]. Since Line (v) behaves in the same way as others this centre must closely resemble the other two, being connected with Fe(III) in Al(III) sites and is not due to Fe(III) in a different environment (e.g. Ca(II) sites).

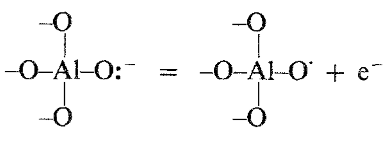
There were no other changes anywhere else in the ESR spectra, either on irradiation or annealing.

Lead was present in the starting materials, and a sample of C_3A was doped with lead. TL and ESR results indicated that lead was not implicated in any charge-transfer process. It was not possible, therefore, to correlate the thermoluminescence peak at 453 K with any trapping site.

3.4. Mechanism of trapping/thermoluminescence

For the 407 K TL peak the mechanism has been established for the iron centres. Possible electron donor centres include the following:

(a) an Al–O centre, namely



$$-O-\overset{-O}{\underset{-O}{Al}}-O{:}^{-} = -O-\overset{-O}{\underset{-O}{Al}}-O^{\cdot} + e^{-}$$

Such a structure contains two bridging and two non-bridging oxygen atoms. This type of centre is well known, being characterised by six lines from hyperfine coupling to ^{27}Al. No features of the type expected were observed on irradiation.

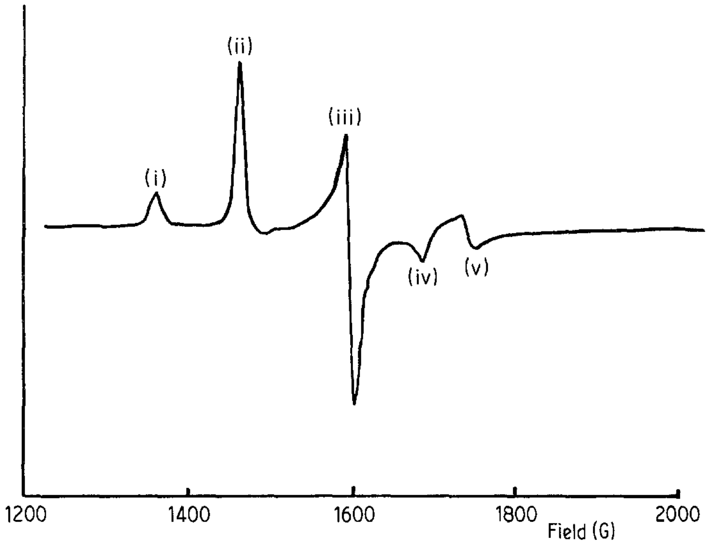


Figure 4 ESR spectrum in the range 1600 ± 400 G.

(b) It remains possible that Al–O centres are formed, but that they are so close to iron that spin–spin interactions broaden the ESR features for Al–$O^{\cdot -}$. This mechanism is consistent with the ESR data and with the C_3A structure. The O–Al–O–Fe–O ring structure would make it easy for –Al–$O^{\cdot}$ to "see" Fe(III). The overall effect is electron trapping by Fe(III), leaving a hole on a non-bridging oxygen atom.

(c) If there are excess oxide ions (O^{2-}) present, these might act as donors, giving $O^{\cdot -}$ radicals. The ESR spectra for $O^{\cdot -}$ can be very broad if the environment does not provide a strong crystal-field splitting of the 2p orbitals. Unfortunately, we can do no more than speculate at this stage.

Acknowledgement

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