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Thermoluminescence and ESR of boron-stabilized β-dicalcium silicate

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Thermoluminescence and ESR in boron-stabilized β-dicalcium silicate have been studied before and after ultraviolet irradiation. Most of the results, apart from the electron spin resonance signals from impurity iron and manganese, can be explained on the basis of electron location on the substituent BO_4 groups replacing silicate tetrahedra, with electron capture at this centre being responsible for the thermoluminescence.

1. Introduction

Dicalcium silicate (Ca_2SiO_4, C_2S*) is one of the major components in Portland cement, and exists in several different forms. The β-form is the important cement phase where it is stabilized by a range of impurity ions. In laboratory preparations the β-form is commonly stabilized with boron(III) oxide, B_2O_3. The structure of β-dicalcium silicate has been determined [1]. It consists of SiO_4 tetrahedra linked to two types of Ca(II) ions. Ca_I is six-coordinated, Ca_{II} is eight-coordinated and the coordination is irregular in each case. Four of the Ca_I ions are alternately above and below tetrahedra in the y-direction and Ca_{II} ions are positioned between tetrahedra. As outlined in a previous article [2], electron spin resonance (ESR) and thermoluminescence (TL) spectra may provide useful information concerning electron or hole trapping defects in crystal structures. These techniques have been applied to boron-stabilized β-dicalcium silicate.

2. Experimental details

2.1. Starting material

Analytical reagent grade calcium carbonate and precipitated silica were thoroughly mixed in the correct ratio along with 0.5 wt % boron(III) oxide (% of final product). The mixture was fired at 1470 K to drive off carbon dioxide and then immediately removed from the furnace, cooled and finely ground. It was then fired at 1730 K overnight, cooled to 1370 K in the furnace, removed, and allowed to cool rapidly to ambient temperature (this helped to stabilize the β-form). It was then reground and the whole firing procedure was repeated three times. The sample was characterized by X-ray diffraction and found to be virtually pure β-C_2S. There was probably no more than a few per cent of the γ-form present. White's test [3] indicated that negligible free lime was present.

2.2. Thermoluminescence

TL work was carried out as previously described by tricalcium aluminate [2]. Ultraviolet excitation was used ($\lambda = 253.7$ nm), and traps were saturated. TL spectra were obtained from samples heated in the temperature range 300 to 570 K.

2.3. ESR spectroscopy

ESR work was carried out as previously described [2] and included spectra for unirradiated, irradiated, and annealed samples. The annealing temperatures were 360, 390, 440 and 520 K as indicated in the TL curve. A standard packing technique was used and spectra were obtained at 77 K.

3. Results

3.1. Thermoluminescence

The TL spectrum of β-C_2S is shown in Fig. 1. The spectrum is complex and consists of at least four shoulders at about 390, 400, 430 and 474 K, and a peak at about 417 K. The overall profile is a broad envelope and the spectrum is not similar to that of Fierens *et al.* [4].

3.2. ESR spectra

The ESR spectra for β-C_2S are shown in Figs 2 and 3. The spectrum from the unirradiated sample shows a group of resonance around $g = 4.2$, while the region around the free spin vlaue (3200 G) has no obvious features. The rest of the spectrum is fairly broad. Features a, b, and c (Fig. 2a) are characteristic of a rhombically distorted Fe(III) centre which has not quite reached the limit of a simple feature at $g = 4.3$. The set of three lines shown as d, e, and f are thought to be part of a sextet of features due to ^{55}Mn(II) ($I = 5/2$, giving six lines) also in a rhombic site. Unfortunately, if this is correct, much of the spectrum is hidden by the more intense Fe(III) signals.

4. Discussion

Substitution of Mn(II) ions into the calcium sites in the crystal structure already described [1] could give

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*Cement nomenclature: C = CaO, S = SiO_2.

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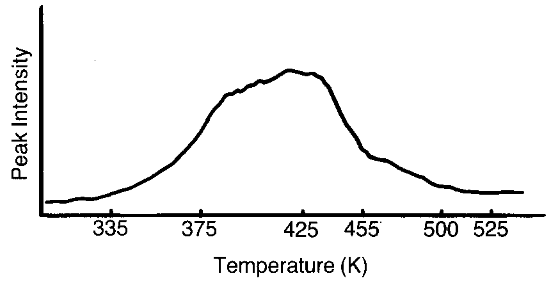

Figure 1 Thermoluminescence spectrum for boron-stabilized β-dicalcium silicate.

rise to a low-field ESR spectrum, as is seen. The SiO_4 tetrahedra are only slightly distorted and Mn(II) or Fe(III) substitution into such tetrahedra is highly unlikely because of charge and size considerations. There is only one type of SiO_4 tetrahedron in β-C_2S and, assuming only one kind of distortion, the spectrum would be rhombic and fairly simple. Lines b and c in Fig. 2a would therefore seem to be due to Fe(III) ions in such sites. Fe(III) could also substitute for calcium ions and there is evidence for this in silicates [5]. However, such substitution would be likely to produce a complex rhombic spectrum because there are two low symmetry sites. This seems unlikely here on the basis of the ESR evidence, and in addition, charge compensation would again be required. The spectrum in the "free spin" region is rather featureless and there was no indication of the presence of symmetrically coordinated Mn(II) ions. This further suggests that the broad resonances around $g = 5$ are due to Mn(II) since this ion is known to be present as a low level impurity.

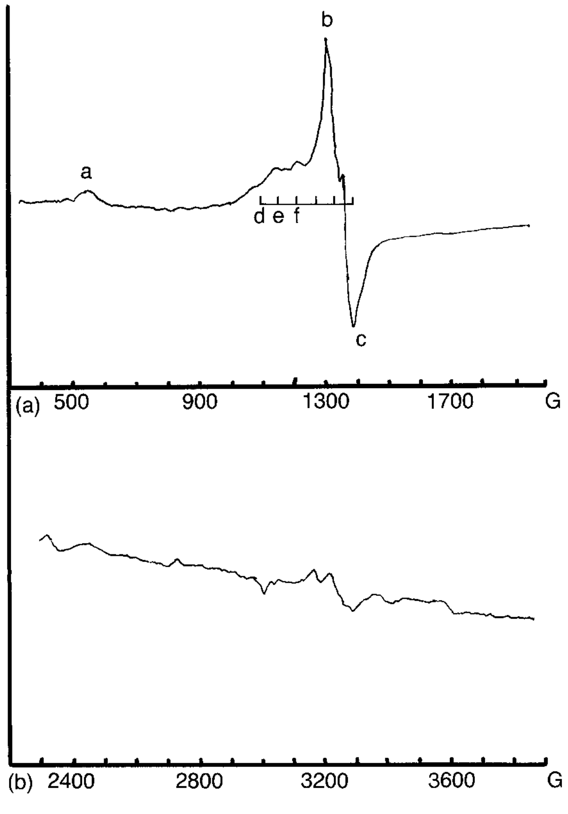

Figure 2 (a) ESR spectrum in range 300 to 1900 G (for explanation, see text). (b) ESR spectrum in range 2200 to 3900 G.

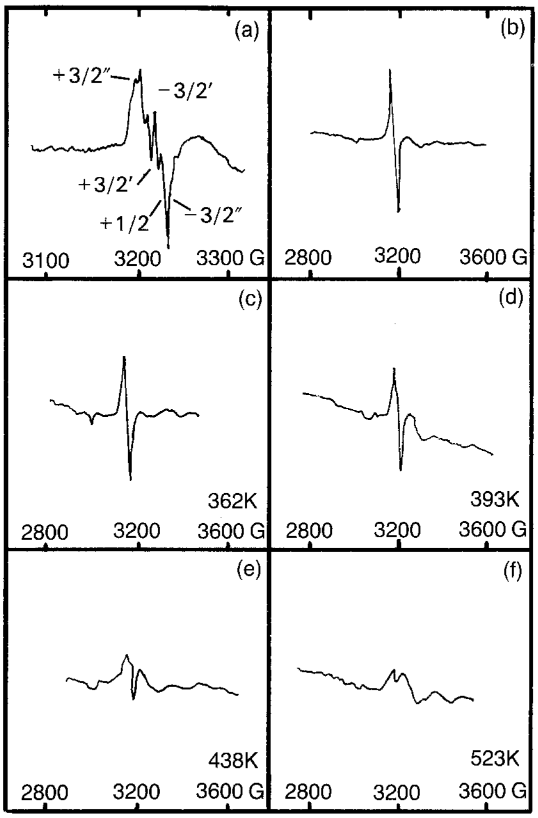

Figure 3 Changes from 2800 to 3600 G spectra with temperature.

4.1. Identification of electron trapping/donor sites

The intensities of lines around $g = 5$ did not alter on irradiation or subsequent annealing. Fe(III) ions do not therefore seem to be implicated in trapping and subsequent TL under the experimental conditions used. Therefore, electrons are probably not excited to the conduction band. No other changes were seen in this part of the spectrum. Around the free spin region, new intense sharp resonances were seen after irradiation (Figs 3a and b: note the difference in scales). These were centred around $g = 2.02$. The results of irradiation and subsequent annealing are shown in Fig. 3 and Table I. These resonances are obviously connected with the TL. No other changes were seen in this part of the spectrum. From Fig. 3 it can be seen that the lines are split into two sets of four components. Such quadruplet splittings are characteristic of a centre with nuclear spin, $I = 3/2$. They were assigned as parallel or perpendicular components as indicated on the spectrum.

The only atom present in β-C_2S which is likely to give such a spectrum is the boron atom from the stabilizer. This is likely to be present as the BO_4 group because it replaces SiO_4 [6]. Substitution of BO_4 for SiO_4 is not thought to change lattice dimensions in β-C_2S, because the RO_4 group size is probably determined by the O–O distance, not by cation size [6]. The insertion of BO_4 groups is thought to cause the introduction of extra Ca(II) ions into structural holes in

TABLE I Relative intensities (peak/peak) derived from Fig. 3

Unirradiated	Irradiated	362 K	393 K	438 K	523 K
70.0	57.5	57.5	45.5	16.5	0.0

β-C_2S. Such changes would cause distortions in the structure. ^{11}B hyperfine coupling constants for various $\geqslant$B–O$^{\cdot}$ hole centres fall in the range $A_{\parallel}$ 12 − 18 G and $A_{\perp}$ 8 − 14 G [7–10]. Our results give $A_{\parallel} \sim 12$ G and $A_{\perp} \sim 7$ G, the latter having a large error of ±2 G. Hence there can be little doubt that the centre is indeed a hole on oxygen in a BO_4 unit, with hyperfine coupling to boron.

4.2. Mechanism of trapping/thermoluminescence

The borate group is known to trap holes on irradiation [10–14]. The excess negative charge on the BO_4 group as compared with SiO_4 indicates that here the BO_4 group would donate rather than trap an electron

$$BO_4^{5-} = BO_4^{4-} + e$$

leaving behind a positive hole. The above splittings indicate that the hole is located on the oxygen atoms and not on the boron atom. It is also possible that release of electrons from BO_4 groups may cause migration of Ca^{2+} ions from nearby holes in order to retain the charge balance. The TL peaks are stable over several days at ambient temperatures indicating that this could be so.

Brief TL work on sulphate-doped β-C_2S indicated that SO_4^{2-} may be involved in the mechanism [15]. This ion could replace SiO_4 in the structure giving an excess positive charge as a result. The mechanism could then be

$$BO_4^{5-} = BO_4^{4-} + e$$

$$SO_4^{2-} + e = SO_4^{3-}$$

Examination of the ESR spectrum from a sulphate-doped β-C_2S specimen showed an extra unexplained peak in the "free-spin" region. On irradiation this peak increased somewhat. This may indicate that the reactions take place spontaneously when SO_4^{2-} ions are introduced. This mechanism is tentative and requires further study. The entire TL spectrum appears to be associated with only one acceptor:

$$e_t^- + BO_4^{2-\cdot} = h\nu + BO_4^{3-}$$

There are, however, likely to be several different stages in the overall TL process. The BO_4 groups are unlikely to be in more than one type of environment, because there is only one kind of SiO_4 tetrahedron in β-C_2S. It is more likely that the trapped electrons are present in different environments and/or are of different types, leading to a broad TL spectrum.

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