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1 **Electron paramagnetic resonance spectral studies of Australian sapphires**

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11
12 **Abstract**

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14 EPR study of two Australian sapphire samples confirms the presence of Cr(III) in
15 four different octahedral sites. The g (1.98) value is identical but D values differ for the
16 samples. The EPR spectra indicates that blue sapphire contains more quantity of
17 chromium than the green sapphire. No Fe(III) impurity in the EPR spectrum was
18 observed.

19 Key words: *sapphire*, EPR Spectra, octahedral symmetry.

20
21 **1. Introduction**

22 Sapphire is a high band gap (~ 9 eV) insulator. It has been considered a material
23 of technological interest for diverse applications such as solid state lasers, UV windows,
24 fusion energy devices and dielectric substrate for silicon-on-sapphire structures [1-2].
25 Corundum is essentially pure Al_2O_3 . However, minor amounts of other ions such as iron,
26 titanium, chromium and manganese enter into corundum structure. Red corundum is
27 called ruby, while all other gem quality forms of corundum are called sapphires. The
28 varying minute amounts of these ions present in the mineral causes change in colour in
29 the mineral. Typically, sapphires appear as blue stones, ranging from very pale blue to
30 deep indigo, due to the presence of small amounts of titanium and iron within the crystal
31 structure. The most valued shade of blue is the medium-deep cornflower blue. Sapphires
32 also occur in other natural colors and tints including colorless, gray, yellow, pale pink,

33 orange, green, violet and brown. These different colours are caused by different kinds of
34 impurities within the crystal.

35

36 The biggest source of sapphires worldwide is Australia, especially New South
37 Wales and Queensland. In the corundum, oxygen ions are arranged in approximately
38 hexagonal package. Between the oxygen layers there are sites for cations such as iron,
39 titanium, chromium and manganese octahedrally coordinated by six oxygen ions [3]. The
40 cations present in the mineral and their concentration, distribution with the structure
41 significantly influence the optical, electrical and magnetic properties including colour.

42 On natural sapphire containing iron, optical absorption, EPR and IR spectra with
43 regard to the exchange-coupled pairs of iron impurities in their ferric and ferrous states
44 have been reported. Also the sapphire color has been interpreted as a function of
45 $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios and of the presence of their pairs in the stone [4]. Radiation and spectral
46 characteristics of sapphire crystals produced by various methods have been studied [5].
47 Although some investigations have been carried out on sapphire, the electronic structure,
48 EPR studies of chromium in various sites in sapphire from New South Wales has not
49 been investigated.

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51 In this study, both electronic and EPR spectroscopy has been applied to
52 the characterization of chromium and to see the distribution of cations in sapphire. The
53 present work was prompted to examine the spectroscopic characterization of chromium in
54 sapphire from Tenterfield, New South Wales as this type of approach has not been
55 attempted previously.

56

57 **2. Experimental**

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59 EPR spectra of the samples in powder form were recorded at room temperature (RT)
60 on a Varian E-112 EPR spectrometer operating at X - band frequencies ($\nu = 9.40824$
61 GHz for blue sapphire and 9.41354 GHz for green sapphire mineral samples) having 100
62 kHz field modulation and phase sensitive detection to obtain first derivative spectra. 1.00

63 mW microwave power and 0.25 mT modulation amplitude is employed for both the
64 sapphires. DPPH with a g value of 2.0036 is used for g factor calculations.

65

66 3. Theory

67 Cr^{3+} has the electronic configuration $[\text{Ar}] 3d^3$, where $[\text{Ar}]$ stands for the closed argon
68 shell. The three d electrons give rise to the free ion terms ^4F , ^4P , ^2G , ^2H and a number of
69 other doublet terms. Among these, ^4F term is the ground state. These terms, in an
70 octahedral crystal field, split as follows:

$$71 \quad ^4\text{F} \rightarrow ^4\text{A}_{2g}(\text{F}), ^4\text{T}_{1g}(\text{F}), ^4\text{T}_{2g}(\text{F})$$

$$72 \quad ^4\text{P} \rightarrow ^4\text{T}_{1g}(\text{P})$$

$$73 \quad ^2\text{G} \rightarrow ^2\text{A}_{1g}(\text{G}), ^2\text{T}_{1g}(\text{G}), ^2\text{T}_{2g}(\text{G}), ^2\text{E}_g(\text{G})$$

$$74 \quad ^2\text{H} \rightarrow ^2\text{E}_g(\text{H}), ^2\text{T}_{1g}(\text{H}), ^2\text{T}_{2g}(\text{H})$$

75 The strong field electronic configurations for the ground state and their terms are given as
76 follows:

$$77 \quad (t_{2g})^3 (e_g)^0: ^4\text{A}_{2g}(\text{F}), ^2\text{E}_g(\text{G}), ^2\text{T}_{1g}(\text{G}), ^2\text{T}_{2g}(\text{G})$$

$$78 \quad (t_{2g})^2 (e_g)^1: ^4\text{T}_{1g}(\text{F}), ^4\text{T}_{2g}(\text{F}), ^2\text{T}_{2g}(\text{H})$$

$$79 \quad (t_{2g})^1 (e_g)^2: ^4\text{T}_{1g}(\text{P})$$

80 In both fields, $^4\text{A}_{2g}(\text{F})$ represents the ground state. Thus, one can expect three spin
81 allowed transitions from $^4\text{A}_{2g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{F})$, $^4\text{A}_{2g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{F})$ and $^4\text{A}_{2g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{P})$, in
82 addition to other spin-forbidden transitions. Generally, $^4\text{A}_{2g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{P})$ occurs in the
83 UV-Vis region.

84 4. Results and analysis

85 4.1 EPR studies

86 The sapphire minerals originated from Tenterfield, New South Wales are blue and green
87 in colour and are used in the present study. The comparison between EPR spectra of both
88 coloured samples reveal some characteristic similarities.

89 Cr(III) being a d^3 ion, the ground state is four fold spin degenerate with $M_S =$
90 $+3/2, +1/2, -1/2$ and $-3/2$. In the cubic field no splitting of these levels takes place and
91 therefore the magnetic field leads to an equidistant splitting. This gives rise to only one
92 single line in the EPR spectrum. In non-cubic fields the degeneracy is partially lifted and
93 one can observe three resonances corresponding to the transitions $|3/2\rangle \leftrightarrow |1/2\rangle$, $|1/2\rangle$
94 $\leftrightarrow |1/2\rangle$ and $|1/2\rangle \leftrightarrow |3/2\rangle$ at $g\beta B - 2D$, $g\beta B$ and $g\beta B + 2D$ respectively. Where D is
95 zero field splitting parameter. In a powder spectrum, mainly the perpendicular component
96 is visible. If all the three transitions are observed, similar to Cr^{3+} in other compounds [6],
97 the separation between the extreme sets of lines [$g\beta B + 2D - (g\beta B - 2D)$] is $4D$.
98 However if $D = 0$, one can observe a single line at $g \sim 1.98$. On the other hand, if D is
99 very large compared to microwave frequency, a single line occurs around $g = 4.0$ [7].

100 Fig.1 shows the EPR spectrum of blue sapphire, recorded at room temperature
101 (RT) from 0 to 500 mT (Fig. 1A) and 150 to 650 mT (Fig.1B). The EPR spectrum of
102 green sapphire recorded at RT is shown in Fig 2 . It is seen from the figures that several
103 resonances are present. For easy analysis of the spectrum, they are marked by a, b, c, d,
104 e, a_1 , b_1 , c_1 , d_1 . The center line (marked by e in blue sapphire and e^1 in green sapphire) has
105 a g value 2.002, which is same in both the spectra of stones. This can be attributed to the
106 main transition $|1/2\rangle \leftrightarrow |1/2\rangle$ of Cr(III) ion. On either side of this centerline, one can
107 notice four types of resonances, one for each Cr^{3+} ion having same g value (g value is
108 probably not very sensitive to the environment) but different D values. By assuming 'a'
109 (in Fig.1A) and ' a_1 ' (in Fig. 1B) are one set of components and assuming the separation is
110 equal to $4D$, the calculated value of D is 132 mT. In the case of green sapphire is 130 mT

111 On similar lines, assuming 'b' and ' b_1 ' as one set, 'c' and ' c_1 ' other set and 'd' and
112 ' d_1 ' another set, the calculated values of D are 114 mT, 94 mT and 35 mT respectively.
113 Following similar procedure the D values evaluated for green sapphire for other sites are
114 105, 65 and 34 mT respectively. As the lines are almost equally spaced on either side of
115 the central resonance (marked by 'e' and ' e^1 '), E can be assumed to be zero. These
116 results are suggesting that in blue and green sapphires there may be four different Cr^{3+}
117 octahedral sites. Due to the low abundance of ^{53}Cr , hyperfine lines from this nucleus are
118 not noticed. The strong lines marked by 'a' and 'c' in blue and ' a^1 ' and ' c^1 ' are very

119 broad and more intense suggesting high concentration of chromium in those sites. Hence,
120 one can say that the sample is ordered in nature allowing to determine the D values for
121 four types of chromium impurities. From the EPR spectra of both minerals, it is well
122 known that the intensities of resonance lines in blue sapphire is more than that of green
123 sapphire. Also in both the stones the D value for site I and site IV is identical where as
124 for site II and III it differs. It may be an indicate that blue sapphire contains more quantity
125 of chromium than green. We could not notice any Fe(III) impurity in the EPR spectrum.
126 The D values along with g value obtained for both the stones are presented in Table 1.

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Table 1
EPR parameters for blue and green sapphire samples

Sample	g value	Zero field splitting parameter (D) mT			
		Site I	Site II	Site III	Site IV
Blue sapphire	1.98	130	105	65	34
Green Sapphire	1.98	132	114	94	35

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Optical absorption spectra of both the samples are recorded even at liquid nitrogen temperature but we could not get good spectra. Thus optical absorption spectral results are not incorporated in the communication.

136 **Conclusions**

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- From the EPR spectra it is observed that the blue sapphire contains more quantity of chromium than green. We could not observe any Fe(III) impurity in the EPR spectrum.
- In blue and green sapphires there are four different Cr³⁺ octahedral sites.
- The EPR resonance line intensities in blue sapphire is greater than that of green sapphire.

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147 • g value is same for both the sapphires. D values are different .Also in both the
148 stones the D value for site I and site IV is identical where as for site II and III it
149 differs.

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151 • The EPR results conclusively prove that chromium is present in both the
152 sapphires in distorted octahedral environment.

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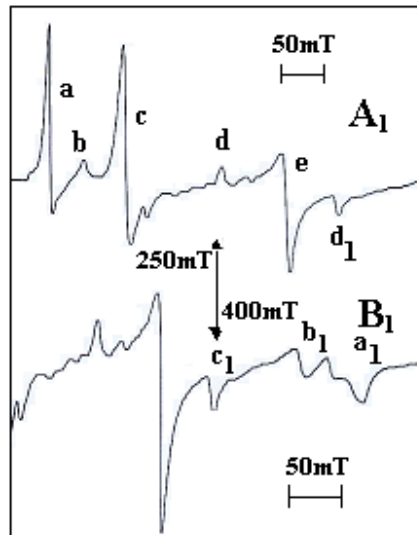


Fig.2 EPR spectrum of green sapphire at room temperature ($\nu = 9.41354$ GHz)

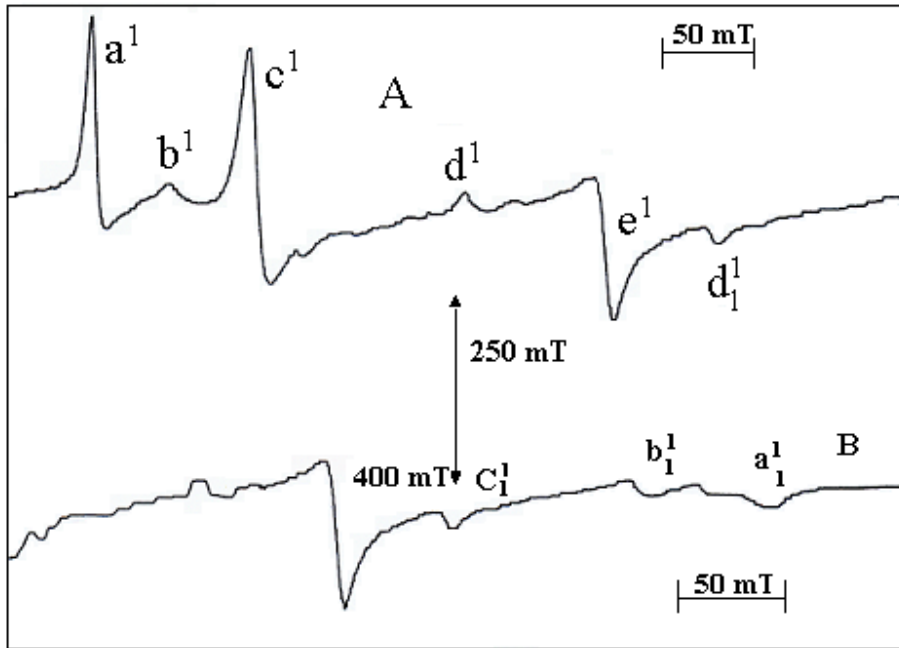
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Fig.1 EPR spectrum of blue sapphire at room temperature ($\nu = 9.40824$ GHz)