

# Ti(III) in synthetic pyrope: A single-crystal electron paramagnetic resonance study

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**Abstract:** Electron paramagnetic resonance measurements were undertaken on a synthetic Ti-bearing pyrope single crystal of approximate composition  $\text{Mg}_{3.01(2)}\text{Al}_{1.93(2)}\text{Ti}_{0.04(1)}\text{Si}_{3.00(2)}\text{O}_{12}$  in order to further (Geiger *et al.*, 2000) characterize the oxidation state of titanium. The crystal was synthesized hydrothermally at high pressure and temperature and starting with  $\text{Ti}_2\text{O}_3$ . The angular dependence of the observed EPR spectrum can uniquely be interpreted as being due to an electron centre with spin 1/2 on a site of  $\bar{3}$  point symmetry. It is proposed, based on the composition of the pyrope and its known structure, that the EPR spectrum results from a small concentration of Ti(III) on the octahedral 16a site. Based on previously published optical absorption measurements and microprobe analysis, most of the octahedral Ti should be in the oxidation state (IV).

**Key-words:** synthetic pyrope, titanium, EPR.

## Introduction

The common oxidation state of Ti in natural silicates and oxides is as Ti(IV). The more reduced state Ti(III) has been identified in lunar minerals and glasses and synthetic Ti(III)-containing phases are known, but its existence in minerals found in near surface Earth conditions is matter of some debate. Burns (1993) summarizes the state of affairs. Ti(III) has been proposed to occur in zoisite, mica and pyroxene, for example. Another silicate that has received much attention with regard to Ti is garnet. There have been several studies made on natural Ca-rich titanium-containing garnets (*i.e.* melanites and schorlomites) in which Ti(III) has been inferred (Manning, 1967; Manning & Harris, 1970; Amthauer *et al.*, 1977; Schwartz *et al.*, 1980; Kühberger *et al.*, 1989). In the case of synthetic garnets, Ti(III) has been proposed to have been found in Ti-andradites (Kühberger *et al.*, 1989) and Ti-pyrope (Khomenko *et al.*, 1994). In some of these studies, the findings are based on indirect arguments, whereby the garnet composition and oxidation state of Ti were determined by combined chemical and Mössbauer analyses and stoichiometric considerations. Thus any conclusions are problematic, because in Ca-rich garnets other transition metal cations such as Fe and Mn can also be present and they can occur in both the (II) and (III) oxidation states. Furthermore, the presence of (OH<sup>-</sup>) groups makes the assumption of strict garnet stoichiometry tenuous, as does the presence of Ti(IV) on the octahedral site, for example (*i.e.* 8 cations and 12 oxygens in the formula unit).

More direct experimental evidence on the oxidation state

of Ti can be obtained from single-crystal optical absorption spectroscopic measurements. Ti(III) has the 3d<sup>1</sup> electronic state and should have d-d absorption band(s) in the UV/VIS region. Several such studies suggest the presence of octahedral Ti(III) in synthetic pyrope (Khomenko *et al.*, 1994) and natural andradite crystals (Manning, 1967; Manning & Harris, 1970). However, optical absorption measurements also have some inherent uncertainty because the assignment of possible Ti(III) d-d absorption bands is done empirically and absorption features can arise from a number of factors (*i.e.* other transition-metal elements, charge-transfer processes, *etc.*). Indeed, the issue of Ti(III)-Ti(IV) intervalence charge transfer in silicates is a rather controversial matter (Burns, 1993). Electron paramagnetic resonance (EPR) spectroscopy is an excellent method to address the question of Ti in materials, because only Ti(III) and not Ti(IV) is active. It can also determine on which site Ti(III) is incorporated, if single-crystal measurements can be made. There has, however, to the best of our knowledge, been no single-crystal EPR investigation made on garnet with respect to Ti. Therefore, we have undertaken an EPR study of a well-characterized synthetic Ti-bearing pyrope single crystal in order to address the issue of the oxidation state of Ti.

## Experimental

The synthetic pyrope crystal (sample K012) used for study is described in Stahl (1998) and Geiger *et al.* (2000). The sample was synthesized from an oxide mixture of MgO-

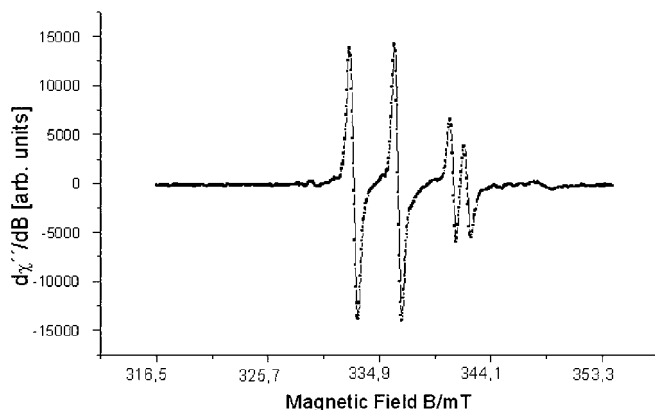


Fig. 1. Single-crystal EPR spectrum of Ti-bearing pyrope (sample K012) at room temperature. The spectrum was taken at 9.238 GHz using 100 kHz modulation frequency and 0.25 mT modulation amplitude.

$\text{Al}_2\text{O}_3\text{-SiO}_2\text{-Ti}_2\text{O}_3$  corresponding to the composition 97 mole%  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ -3 mole%  $\text{Mg}_3\text{Ti}_2\text{Si}_3\text{O}_{12}$ . The purity of the commercially purchased oxides was 99.99%, except for  $\text{Ti}_2\text{O}_3$ , which had a purity of 99%. The oxides were homogenized and mixed using doubly distilled water in an agate mortar to produce a fine mixture. A 5 mm diameter and 8 mm long Au capsule with a wall thickness of about 0.5 mm was filled with about 7  $\mu\text{l}$  doubly distilled  $\text{H}_2\text{O}$  and about 100 mg of the oxide starting material. At the bottom of the capsule a small amount of Ti-metal powder was introduced to act as a reducing agent. The capsule-sealing method and the general construction of the salt-based high-pressure cell are that described in Cemic *et al.* (1990). The synthesis was undertaken at 25 kbar and 950 °C for 17 hours in a piston-cylinder device in order to optimize the size and quality of the single crystals (Geiger *et al.*, 1991). More information on the synthesis methods and a description of the microprobe analyses and optical absorption and IR measurements that were made on resulting single crystals are found in Stahl (1998) and Geiger *et al.* (2000).

The EPR measurements were performed at room and at low temperatures using an 'Oxford ESR 900 A' cryostat. The spectra were measured with a 'Varian X-band' spectrometer and 100 kHz modulation. The external magnetic field,  $\mathbf{B}$ , could be varied between 0 and 1 T and was monitored by a Gauss meter (Bruker BH 15). At room temperature the resonance frequency is about 9.51 GHz and at low temperature about 9.24 GHz. The exact frequencies were measured with a frequency counter ('HP 5340') and are given in the figures. In order to determine the angular dependence of the EPR signal, the crystal was oriented by X-ray methods and mounted on a quartz fibre. In this way, the pyrope crystal could be rotated around its threefold axis from 30 to 150° in steps of 8°.

## Results

The high-pressure synthesis experiment produced single crystals with a range of sizes with some up to about 2 mm in

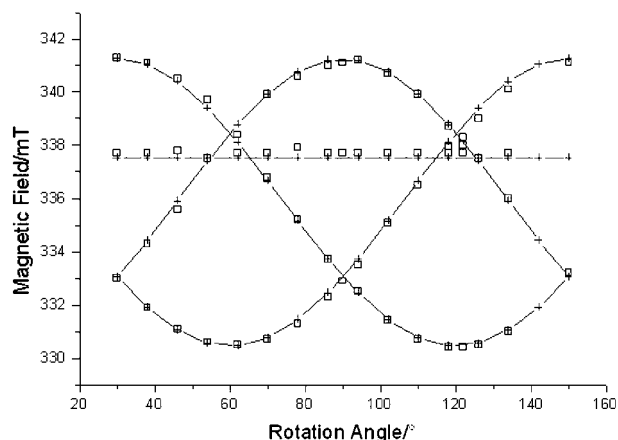


Fig. 2. Experimental (open squares) and fitted (crosses) magnetic resonance fields of the observed EPR spectrum. The microwave frequency was 9.238 GHz. The best fit was obtained with  $S=1/2$  and  $g_{xx} = 1.9342(0.0002)$ ,  $g_{yy} = 1.9342(0.0002)$ ,  $g_{zz} = 2.0181(0.0003)$ .

diameter. The crystals are subhedral to euhedral in nature, often with well developed {110} faces. All are colourless. Electron microprobe analyses give the composition  $\text{Mg}_{3.01(2)}\text{Al}_{1.93(2)}\text{Ti}_{0.04(1)}\text{Si}_{3.00(2)}\text{O}_{12}$  based on eight cations and twelve oxygens in the formula unit (Stahl, 1998; Geiger *et al.*, 2000). No compositional zoning was determined from line traverses made with the microprobe. The optical absorption measurements did not reveal the presence of any absorption bands in the UV/VIS region. Single-crystal IR spectra indicate the presence of  $\text{OH}^-$  groups occurring in more than one substitution mechanism (Geiger *et al.*, 2000). The single-crystal EPR spectrum with  $\bar{3}$  perpendicular to  $\mathbf{B}$  is shown in Fig. 1 and the angular dependence of the four components in Fig. 2. The pattern is highly symmetric and reiterates every 60°. This suggests that all lines belong to one EPR centre.

## Discussion

In the initial stages of this study, the spectrum could not be conclusively attributed to Ti(III), because the characteristic hyperfine pattern for the odd numbered isotopes,  $^{47}\text{Ti}$  and  $^{49}\text{Ti}$ , were neither detectable at room temperature nor at low temperatures. This is probably, however, due to the low intensities of their hyperfine lines. It was then considered, if the spectrum could arise from an electron centre. However, the resonance magnetic fields vary from 330 to 341 mT and such a large variation is not characteristic of electron centres. For example, in fluoroapatite the magnetic resonance field of the electron centres varies approximately within  $3 \times 10^{-4}$  T and that of the hole centres is within  $30 \times 10^{-4}$  T (Piper *et al.*, 1965). Therefore, we propose that the observed EPR must be due to a paramagnetic ion having an electron spin  $S = 1/2$ . Considering the high purity oxides used for the synthesis of the pyrope crystal, only Ti(III) comes into question.

Crystallographically equivalent sites are often magnetically inequivalent depending on the symmetry operations of the space group. In pyrope, space group  $Ia\bar{3}d$ , the most

likely site for Ti is on the octahedral 16a site of point symmetry  $\bar{3}$ , and we examine this possibility here. The 16a sites in the unit cell are magnetically equivalent in twos because of the inversion centre. Therefore eight EPR transitions, *i.e.* eight EPR signals, are to be expected in a spectrum with an arbitrary orientation of **B** with respect to the crystal axes. The eight signals will degenerate further, if the crystal is oriented. For example, with  $\bar{3}$  perpendicular to **B** a maximum of four signals will appear. Each signal represents four crystallographically equivalent sites. They are magnetically equivalent, *i.e.* not discernible in EPR, because there exists at least one symmetry operation in  $Ia\bar{3}d$  that transforms **B** to all four sites without changing its orientation. One signal must be angular independent, whereas the other three signals should exhibit an angular dependence that is repeated every 60° (Fig. 2). The EPR angular dependence is described by the spin Hamiltonian,  $H = \beta\mathbf{B}\mathbf{g}\mathbf{S}$ , with  $S = 1/2$ , and where **g** is a second-rank tensor. Its numerical value depends on the spin-orbit coupling, the crystal-field symmetry and the chemical bonding of the paramagnetic ion under investigation. Because Ti(III) is a  $3d^1$  ion with  $S = 1/2$ , the best interpretation of the data is that the EPR is caused by Ti(III) at the 16a site.

Geiger *et al.* (2000) argued that the pyrope sample studied herein contained mainly octahedral Ti(IV) and not Ti(III), because a single-crystal electronic absorption spectrum did not reveal any absorption bands. Thus, the concentration of Ti(III) must be very low. In principal, it is possible to determine the number of Ti(III) spins by EPR. However, no reliable standards are available that would allow one to determine the concentration of Ti(III) in the sample investigated here. Khomenko *et al.* (1994), in their study of synthetic Ti-containing pyrope, observed two absorption bands at 22,300  $\text{cm}^{-1}$  and 16,100  $\text{cm}^{-1}$  that they assigned to octahedral Ti(III). One electronic transition is expected for a perfect octahedron. Hence, they proposed that the two bands arise from electronic  ${}^2T_{2g} \rightarrow {}^2E_g$  transitions with a Jahn-Teller split  ${}^2E_g$ -state. Their analysis was based on comparisons with other spectra of oxides and silicates. Two electronic d-d bands are observed for octahedral Ti(III) in other silicates and oxides with a crystal field splitting parameter of  $\Delta_o$  between 19,200  $\text{cm}^{-1}$  and 22,500  $\text{cm}^{-1}$ .

The pyrope synthesis was undertaken starting with Ti metal and  $\text{Ti}_2\text{O}_3$  and, if chemical equilibrium prevailed in capsule, the Ti/ $\text{Ti}_2\text{O}_3$  buffer must have defined the oxygen fugacity. However, the presence of Ti(IV) in the garnet supports the observation that the Ti metal was oxidized and that higher oxygen fugacities prevailed at some time during the synthesis. Thus, the oxygen fugacity during the synthesis was changing and octahedral Ti(IV) became stable. It constitutes the major oxidation state of Ti in the pyrope. We consider the EPR results the best evidence to date relating to the presence of Ti(III) in garnet. Further EPR studies should be undertaken on other garnet compositions in order to determine more rigorously the oxidation state of Ti in them.

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