

ABSORPTION SPECTRA OF Ti^{3+} IN TITANITE

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Optical and ESR absorption studies are reported on titanite. The optical absorption spectrum of titanite has a broad, asymmetric and typical peak at 13700cm^{-1} and is attributed to ${}^2B_2 \rightarrow {}^2B_1$ transition of Ti^{3+} in a tetragonally distorted octahedron. Relatively weak absorption at 7140cm^{-1} and 16130cm^{-1} are assigned to ${}^3E'$ and 2A_1 states respectively. The tetragonal field parameters are found to be $Ds = -1367\text{cm}^{-1}$ and $Dt = 608\text{cm}^{-1}$. From the ESR spectrum of the sample, the g -factors are measured to be $g_{||} = 1.957$ and $g_{\perp} = 1.926$. Correlating the ESR results ($g_{||}$) with the optical measurements (13700cm^{-1}) we get a covalent factor of 0.51. It is concluded that Ti^{3+} in titanite is sited in a tetragonally distorted octahedron.

Keywords : Titanite-- Ti^{3+} ; EPR Spectrum; Optical Absorption Spectra

INTRODUCTION

THE titanium complexes have been creating great interest since titanium (III) showed its own characteristic behaviour irrespective of the ion being substituted as an impurity or existing in concentrated form. ESR and optical studies are reported on many natural and grown titanium complexes (Dionne, 1964; and Burns & Huggins, 1973) to indicate that such a behaviour arises due to the fact that Ti^{3+} site undergoes a natural distortion. In the present investigation, the authors studied titanite and found that its ESR and optical absorption could be attributed to Ti^{3+} in a distorted octahedron and not to Ti^{4+} (Hunt *et al.*, 1973).

Titanite (or sphene, $Ca TiO SiO_4$) is a widespread accessory mineral in igneous and metamorphic rock. Its structure consists of infinite parallel chains of corner-sharing TiO_6 octahedra crosslinked by SiO_4 tetrahedra. Natural titanites incorporate Ti, Al, Fe etc., as octahedral cations (Higgins & Ribbe, 1976). While the oxygen atoms surrounding the Ti atoms form nearly regular octahedra, Ti atoms are displaced from geometric centres. The larger Ti^{3+} ions (of 0.76\AA) might force localized distortions (Speer & Gibbs, 1976) and experience a strong C_{4v} distortion over O_h field in titanite.

EXPERIMENTAL

The purple coloured sample, made available by M/s Minerals Unlimited, U. S. A., is reported to be collected from Baja California, Mexico. For the powder sample, ESR spectra were recorded at room and liquid nitrogen temperatures on a Jeol

X-Band spectrometer and optical absorption spectrum was recorded on a DMR-21 spectrophotometer in the range 350-1500nm. Nujol mull spectra of the sample were also recorded in the region of 300-3300nm on Carl-Zeiss and Perkin-Elmer spectrophotometers and the measured band positions by the different instruments are found to be the same. Mössbauer measurements of the sample were made using a Co-57 (Rh) source, but no specific features could be observed for the Fe site in the sample.

Chemical analysis reported on the sample from Baja California, Mexico by Higgins and Ribbe (1976) reveals that the sample contains $TiO_2 = 38.80$ per cent but rare earths are not detected. Semiquantitative analysis by spectrochemical method as described by Reddy and Sarma (1982) was carried out to estimate minor and trace elements of iron group transition metals in the present sample. The sample is found to contain $V = 0.02$, $Fe = 0.1$, $Mn = 0.01$ and $Cr = 0.01$ per cent. Thus the sample contains titanium in a higher concentration than any other transition metal and optical absorption of the sample is attributed to titanium only. During the present studies, the optical and ESR spectra provided evidence for attributing the observed absorption to Ti^{3+} in a distorted octahedron.

THEORY

The ground state of atomic Ti^{3+} ($3d^1$ configuration) has fivefold orbital degeneracy and is 2D . An octahedral crystal field splits this degeneracy into a lower orbital triplet $^2T_{2g}$ and an upper orbital doublet 2E_g with an energy separation of $10Dq$. In a low symmetry, tetragonal (C_{4v}) field the $^2T_{2g}$ and 2E_g levels are split into 2B_2 , 2E and 2B_1 and 2A_1 levels (Ballhausen & Gray, 1962) as shown in Fig. 1.

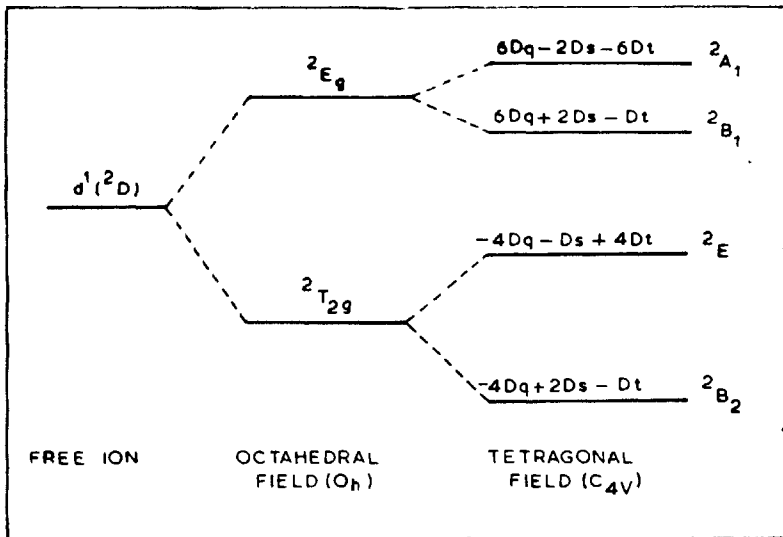


FIG. 1. Splitting of energy levels Ti^{3+} in octahedral (O_h) and tetragonal (C_{4v}) fields.

The EPR spectrum of a given Ti^{3+} centre ($S = 1/2$) consists of a main intense central line ($I = 0$) for ^{46}Ti , ^{48}Ti and ^{50}Ti (abundance 87 per cent). The nuclear spins of ^{47}Ti , and ^{49}Ti (abundance 7.7 per cent and 5.5 per cent respectively) are $5/2$ and $7/2$ respectively and their interactions might give six and eight ($Am = 0$) (hyperfine lines appearing as satellites (Premovic & West, 1975).

RESULTS AND ANALYSIS

EPR Measurements

The EPR spectrum of titanite (powder) at 300°K (9.2GHz and 1mW) is shown in Fig. 2. A broad line at the centre is primarily due to the zero nuclear spin isotopes. The measured g -factors (at 3359G and 3414G) are $g_{\parallel} = 1.957$ and $g_{\perp} = 1.926$ indicating the ground state as 2B_2 . The central eight line transition superposed on Ti spectrum and the components (four lines) on either side may be attributed to VO^{2+} present in the sample (Sastry & Venkateswarlu, 1967). No significant changes were observed at 80°K . Though such a broad line was observed for Ti^{2+} in SrCl_2 (Herrington *et al.*, 1972), the existence of Ti^{2+} in the present sample has no evidence in the optical absorption spectrum of titanite.

Optical Absorption Studies

The optical absorption spectrum of titanite (recorded on DMR-21 spectrophotometer, Fig. 3) consists of a broad ligand field peak at 13700 cm^{-1} , typical of Ti^{3+} with a shoulder at 16130 cm^{-1} and a weaker band at 7140 cm^{-1} . Such asymmetric

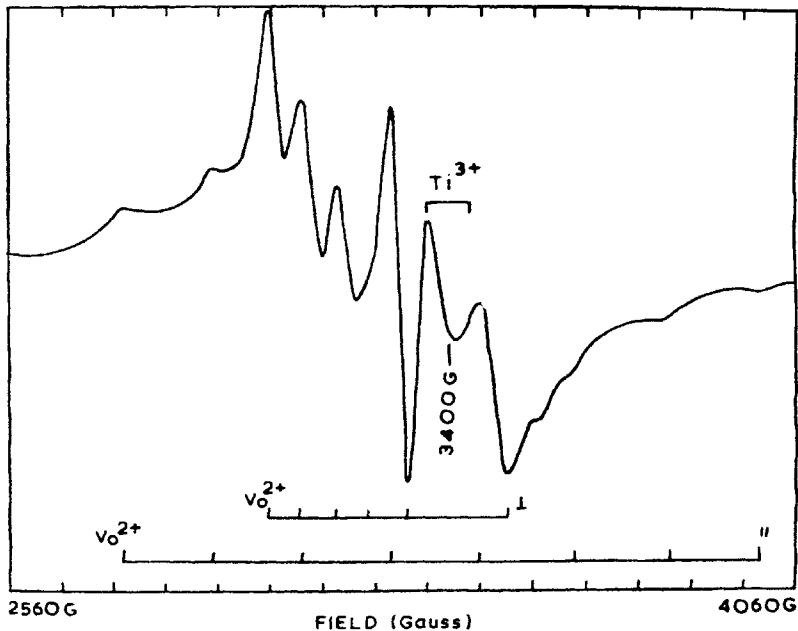


FIG. 2. EPR spectrum of titanite at 300°K .

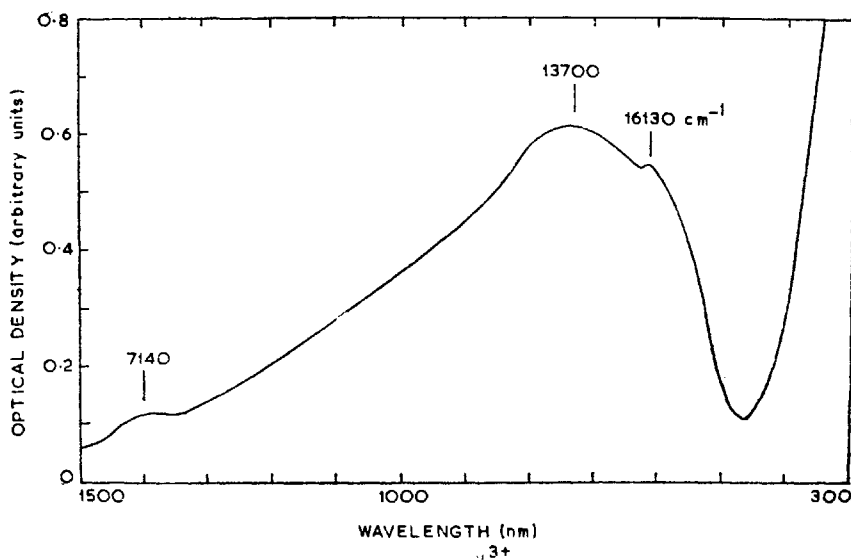


FIG. 3. Optical absorption spectrum of Ti^{3+} in titanite at 300 °K.

absorption peaks were observed by many previous investigators (McClure, 1962; and Manning & Harris, 1970). The three peaks at 7140, 13700 and 16130cm^{-1} are accordingly assigned to the transitions ${}^2B_2 \rightarrow {}^2E$, ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2A_1$ respectively, of Ti^{3+} in a tetragonally distorted crystal field. The value of $10Dq$ ($= 13700\text{cm}^{-1}$) is in good agreement with the data for Ti^{3+} complexes given by Burns and Huggins (1973). Using the following formulae for the various transitions (Fig. 1)

$${}^2B_2 \rightarrow {}^2E; \quad -3Ds + 5Dt$$

$${}^2B_2 \rightarrow {}^2B_1; \quad 10Dq$$

$${}^2B_2 \rightarrow {}^2A_1; \quad 10Dq - 4Ds - 5Dt$$

the octahedral (Dq) and tetragonal (Ds , Dt) field parameters are evaluated from the observed band positions. They are $Dq = 1370\text{cm}^{-1}$, $Ds = -1367\text{cm}^{-1}$ and $Dt = 608\text{cm}^{-1}$.

DISCUSSION

Rawal and MacCrone (1978) studied the optical absorption spectra of individual Ti^{3+} and Ti^{4+} ions and of their combination in borosilicate glasses. The observed optical spectrum of titanite does not possess the features of Ti^{4+} or $Ti^{3+} + Ti^{4+}$ ions in glasses and has close resemblance of the spectrum of Ti^{3+} only and therefore attributed to Ti^{3+} in a low-symmetry site. For the Ti^{3+} ion in titanite, it is evident that a further distortion of octahedron has destroyed the trigonal symmetry which normally exists at trivalent sites since Ti^{3+} ion would occupy the site of B of the structure $ABXSiO_4$ given by Higgins and Ribbe (1976). Further, just as in alums

(Dionne, 1968) the purple colour of the sample indicates the presence of Ti^{3+} in titanite. Also, Burns' (1970) suggestion that titaniferous augites have their purple colour arising from Ti^{3+} ions, might apply to the present sample. The value of D_t will have the same sign as D_q in tetragonal field if there is an axial elongation (Ferguson *et al.*, 1975). Conclusion derived in the present study is in conformity with the above statement.

Premovic and West (1975) observed similar values of g for trans $[Ti(H_2O)_4F_2]^+$. Using their expressions for tetragonal distortion for Ti^{3+} site,

$$\text{Covalency factor} = K \frac{\lambda(\text{covalency})}{\lambda(\text{ionic})} = \frac{\Delta g \cdot \Delta E}{n\lambda(\text{ionic})}$$

where $n = 8$ for C_{4v} , $\Delta g = 2.003 - g_{\parallel}$, $\Delta E =$ energy of appropriate transition, K is orbital reduction factor and $\lambda = 154\text{cm}^{-1}$, we get the above factor to be 0.51. So, both in plane σ -bonding and π -bonding of metal ion with ligands appear to be relatively covalent.

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