Paramagnetic Defects in Benitoite

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In clear, blue, transparent bipyramidal crystals of the rare mineral benitoite, $BaTiSi_3O_9$, paramagnetic defects have been investigated by electron paramagnetic resonance at room temperature and 9.43 GHz. They are attributed to Sn^{3+} and Fe^{3+}. A pair of satellites recorded for a wide angular rage around $\boldsymbol{B}_0 \parallel \boldsymbol{c}$ ($\sim 40°$) and a relative intensity of $\sim 13\%$ to the central signal is most likely due to hyperfine interaction with ^{117}Sn and ^{119}Sn isotopes. Attempts to bleach the colour of the crystal were unsuccessful.

Key words: Electron paramagnetic resonance, Radiation defects, Minerals, Sn^{3+}, Fe^{3+}.

Introduction

The study of substitutional paramagnetic impurities in naturally occurring minerals is important as a source of possible new maser materials. Benitoite ($BaTiSi_3O_9$), named after the only locality where it has ever been found (San Benito County) [1], has great interest by its own structure.

It is a cyclosilicate mineral belonging to the space group D_{3h}^2-P6c2 with two formula units per unit cell. Its ditrigonal bipyramidal structure is based upon three SiO_4 tetrahedra, each sharing two of their oxygen atoms to form rings [2]. The Ba and Ti atoms lie on trigonal axes parallel to the *c*-axis in two-fold positions on either side of a mirror plane, respectively. Both cations are six-fold coordinated with the Ba-octahedron. The mean distance Ti–O is 1.94 Å, and for Ba–O it is 2.77 Å. Six other oxygen atoms are located about 3.43 Å from the Ba site, but evidently they cannot be considered as belonging to the first coordination sphere of Ba (Figure 1).

A benitoite specimen, containing a small amount of tin has been recovered from a drill core of recrystallized limestone taken at Rush Creek in Eastern Fresno County, California, with an SnO_2 content ranging from zero to 4.1 weight%. This corresponds to 11.4% substitution of pabstite (the tin analogoue of benitoite) for benitoite [3]. Indeed, substitution of Sn for Ti seems not unlikely due to the small difference in the ionic radii of Sn^{4+} (0.71 Å) and Ti^{4+} (0.68 Å).

The paramagnetic resonance spectrum of Fe^{3+} in benitoite has been studied by Burley and Troup (1965) [4]. They reported results for Fe^{3+} substituting Ba and Ti in axial site symmetries with the first one preferentially occupied. No local charge compensation seems to occur in both cases, and therefore the substitution should lower the site symmetry. Both, Fe^{3+} and Cr^{3+} were found to substitute for Ti in ferroelectric $BaTiO_3$ [5, 6] and $SrTiO_3$ [7].

Experimental

Our samples were small, transparent, clear blue crystals of benitoite with the shape of bipyramidal pinacoids of ~ 1 mm height and well developed shining natural faces. The measurements were carried out with an ER-200 D X-band spectrometer of Bruker Analytische Meßtechnik GmbH, Karlsruhe, at room temperature. Rotations around three mutually perpendicular axes, $\boldsymbol{c}$, $\boldsymbol{a}$, and $\boldsymbol{b}$ ($= \boldsymbol{c} \times \mathbf{a}$) were performed in order to follow the angular variation of the *g*-factors. Piceine [8] was used as a standard for the measurement of the microwave frequency, and the exact field positions were determined by using an NMR gaussmeter. Powder spectra, before and after heating at 350 °C for 1 h, were also recorded.

Results and Discussion

The recorded EPR spectra and the resulting rotational diagrams revealed the existence of two different paramagnetic defects. Figure 2 shows an example with the magnetic field $\boldsymbol{B}_0$ along the $\boldsymbol{c}$ axis.

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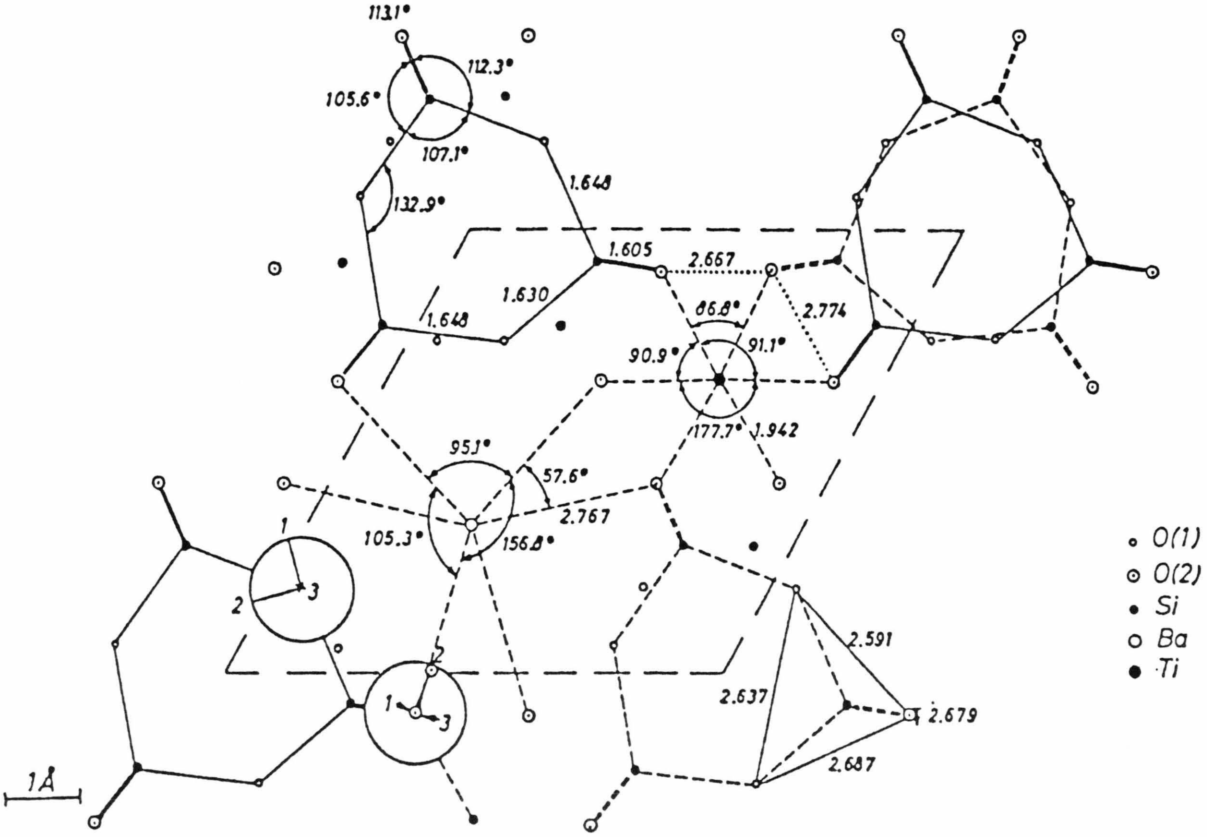

Fig. 1. Projection of the benitoite structure on the (001) plane [2]. The distances are given in Å, the angles in degrees.

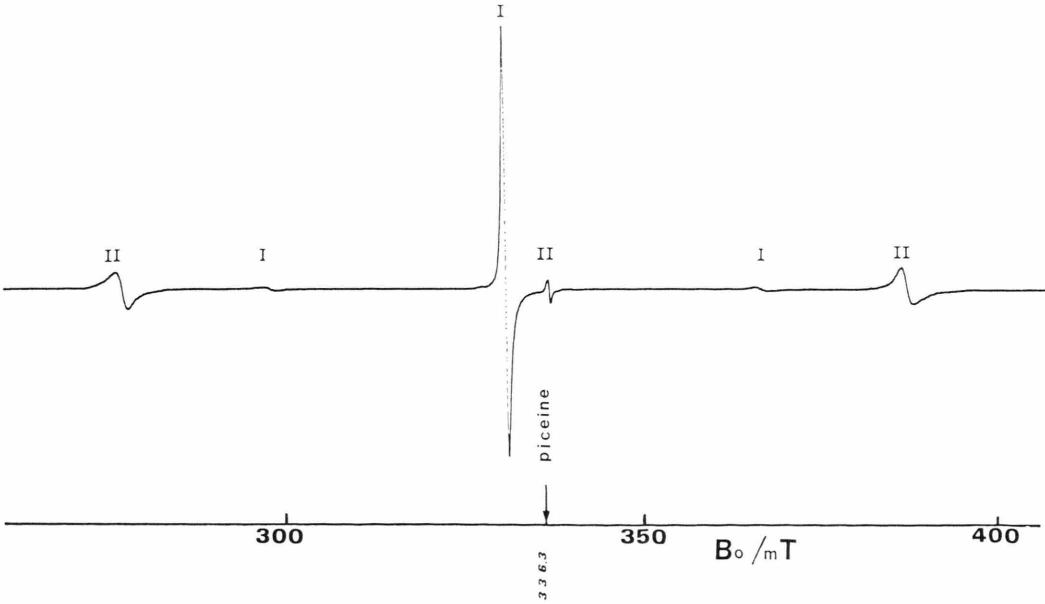

Fig. 2. EPR spectrum of benitoite at RT, X-band for $B_0 \parallel c$ axis. The signals from the two different centers are shown (I, II). The position of the microwave standard (piceine) is shown by an arrow.

1) A singlet with a doublet of satellites marked as signals I in Figure 2. The linewidths varied from 0.7 mT for the singlet to 1.5 mT for the satellites. The splitting is well resolved for about 40 degrees around the ***c*** axis. The true intensity ratio ($I \propto A \times H_{\mathrm{pp}}^2$, A: amplitude, H_{pp}: linewidth) between satellites (I_s) and central signals (I_c) is equal to $I_s/I_c = 13\%$. For rotation around the ***a*** and ***c*** axes, splitting of the singlet into three magnetically non-equivalent centers (related by symmetry operations of the space group) occurred, suggesting occupation of a monoclinic site.

The spin-Hamiltonian parameters along the three crystallographic axes were derived by the application of the equation

$$\mathscr{H} = \beta B g S + SAI$$

and were found:

$$g_x = 1.968, \quad g_y = 1.892, \quad g_z = 2.094,$$

$$A_z = 617.5 \times 10^{-4}\ \mathrm{cm}^{-1}.$$

Sn^{3+} electron centers were created in an Sn-doped $AlPO_4$ synthetic crystal since this tetravalent cation can act as electron trap upon X-ray irradiation [9]. It is likely that the same defect gives rise to the spectrum I detected in our benitoite. The doublet satellites have an intensity relative to the singlet one not far from that expected for the sum of the natural abundances (n. abund.) of ^{117}Sn ($I = 3/2$, n. abund. = 7.61%) and ^{119}Sn ($I = 3/2$, n. abund. = 8.58%). The closeness of the nuclear magnetic moments, μ_N, of the above isotopes (−1.000 and −1.046 nuclear magnetons, respectively) is expected to result in slightly different hyperfine splitting constants. This may produce some broadening of the satellites leading to the observed deviation of the relative intensities I_c/I_s from the calculated ones.

2) The second spectrum, signals marked II in Fig. 2, must result from fine structure transitions of a transition metal ion with $S > 1/2$; possible candidates are Fe^{3+} or Cr^{3+}. However, for several reasons the presence of Fe^{3+} is more likely. Some of them are listed below:

The value of b_2^0 of 0.0232 cm^{-1} obtained for $\boldsymbol{c} \parallel \boldsymbol{B}_0$ fits with the value of 0.0245 cm^{-1} reported for the axial Fe^{3+} center at a Ti site [4]. The zero field splitting is rather small, much smaller than the X-band microwave frequency; thus high field spectra are expected. Due to the long bond distance (1.94 Å for Ti–O(2)) large relaxation times are possible that tend to decrease the distortions due to the R_i^{-7} dependence [10]. In the powder spectrum, a weak broad signal near 228 mT is about in the right position for the outer fine structure component of Fe^{3+}. The corresponding high field signal may well be too broad to be observable at RT. Some forbidden transitions are also present at lower fields (Figure 3).

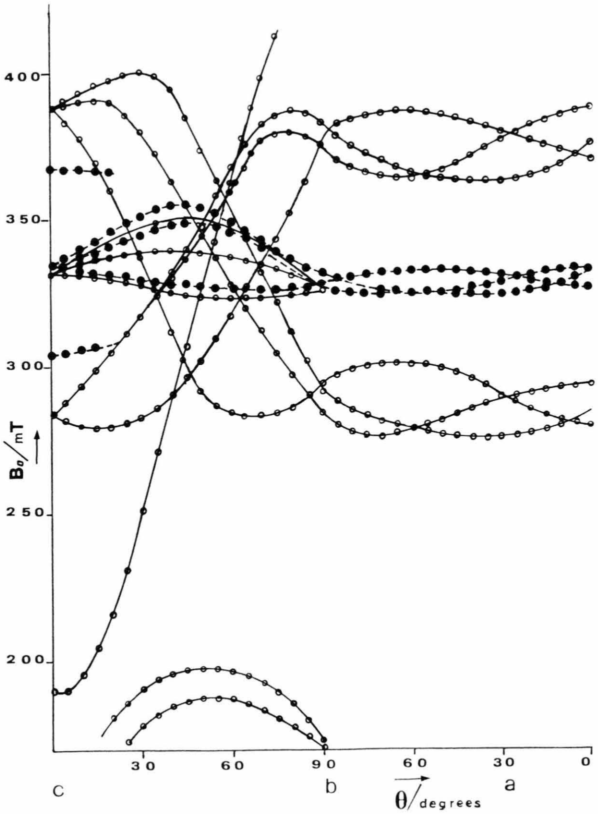

Fig. 3. Angular variation of the EPR signals for rotation of the crystal along the *a* and *c* axes. (– – – Sn^{3+} center, —— Fe^{3+} center). Due to the low splitting, the curve of the Fe^{3+} center is not depicted for rotation around *c*.

Attempts to bleach the colour by heat treatment were unsuccessful; thus its origin may rather be due to a paramagnetic impurity than to an electron trapped at an anion vacancy. Blue colours are sometimes observed with simultaneous presence of both Fe^{3+} and Fe^{2+} and an intervalence transition between them. For Cr^{3+} a green colour would be expected at least for higher concentrations near 0.5% per mol.

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