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The influence of domains on tetrahedrally coordinated Cr^{5+} in ferroelectric BaTiO_3 : an electron paramagnetic resonance study

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Abstract

Electron paramagnetic resonance (EPR) spectra of quasi-tetrahedrally coordinated Cr^{5+} ions (named $\text{Cr}_{\text{II}}^{5+}$ in contrast to the octahedrally coordinated $\text{Cr}_{\text{I}}^{5+}$) in powdered ceramic samples of BaTiO_3 were investigated in the temperature range 50–220 K at 9.4 and 34.0 GHz (X and Q band). At 50 K, in the ferroelectric low-temperature phase with rhombohedral symmetry, two peaks in the powder spectrum of the 1/2-spin $\text{Cr}_{\text{II}}^{5+}$ centre show a frequency-dependent doublet splitting which is explained assuming the existence of two $\text{Cr}_{\text{II}}^{5+}$ centres with slightly different g tensors. The spontaneous polarization in the ferroelectric domains induces changes in the peak positions in the spectra and generates alignment effects of the off-centred Cr^{5+} ions. These effects are caused by the linear coupling of the electric dipole moment, associated with the off-centred Cr^{5+} ion within the octahedron of surrounding O^{2-} ions, and the polarization field. At 75 K a dynamic reorientation of the defect ions among the possible positions in the unit cell broadens the powder peaks. Above 150 K only an isotropic single-line spectrum is observed, the line width of which increases with rising temperature.

1. Introduction

Barium titanate (BaTiO_3) is the prototypical example of the very large perovskite oxide family. Due to the variety of phase transitions (cubic $\xrightarrow{398\text{K}}$ tetragonal $\xrightarrow{273\text{K}}$ orthorhombic $\xrightarrow{183\text{K}}$ rhombohedral) this material is a model system of the physical description of the ferroelectricity and has fundamental importance for a wide range of technical applications. Defects, particularly 3d- and 4d-ions, change the physical properties of this material and the technical application is supported by the possibility to tailor its physical properties by purposeful incorporation. During the past few years, extensive electron paramagnetic resonance (EPR), optical and electrical studies have provided a catalogue of the microscopic properties of

paramagnetic ions incorporated in BaTiO_3 . In the case of the Cr^{5+} ion with the $3d^1$ configuration, the single-crystal EPR spectra were observed for the first time in the low-temperature range by Posseriede [1–3]. Two different types of spectra ($\text{Cr}_{\text{I}}^{5+}$ and $\text{Cr}_{\text{II}}^{5+}$) with rhombic g tensors were detected. An interesting feature of these spectra is the exceptionally large number of magnetically non-equivalent centres and the unexpected directions of the principal axes of their g tensors. Recently, a microscopic model for the $\text{Cr}_{\text{I}}^{5+}$ defect explaining the somewhat surprising symmetry of the g tensor was given by the authors [4]. The $T_2 \otimes e$ Jahn–Teller effect stabilizes the vibronic ground state (d-orbital xy) of the $3d^1$ electron of the $\text{Cr}_{\text{I}}^{5+}$ ion incorporated on a Ti^{4+} site and leads to a tetragonally compressed defect- O_6 octahedron with the point symmetry D_{4h} . The spontaneous electrical polarization \vec{P}^s is a weak perturbation and induces charge displacements in the

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JT-distorted $\text{Cr}^{5+}\text{O}_6^{12-}$ complex, which change the electronic wavefunctions of the Cr_II^{5+} ion. Because the symmetry group of the JT-defect centre is D_{4h} only a quadratic polarization effect is expected. This polarization-induced interaction, reducing the tetragonal symmetry of the $\text{Cr}^{5+}\text{O}_6^{12-}$ complex, is taken into account by an additional Zeeman term in the spin-Hamiltonian. In the rhombohedral phase, the resulting g tensor has rhombic symmetry and one principal axis now points in the direction of one of the equivalent $\langle 110 \rangle$ axes.

The single-crystal spectra of the Cr_II^{5+} defect centre [3], measured in the X band (9.4 GHz), allowed the determination of the rhombic g tensor with the principal xyz axes along the crystallographic [001], $[1\bar{1}0]$ and [110] axes of the pseudocubic system. Furthermore, doublet splitting is observed for special orientations of the magnetic field with respect to the principal axes of the g tensor, for instance $\vec{B} \parallel z$ and $\vec{B} \parallel y$ (see figure 2.21 in [3]). As a possible reason of the peculiar principal values and the [110] symmetry of the Cr_II^{5+} g tensor the strong Jahn–Teller interaction was considered between the T_{2g} ground state of the Cr^{5+} ion and vibrations of local symmetry e_g . A theoretical explanation of the observed splitting of the lines in the rhombohedral phase was not given.

Also in SrTiO_3 two different Cr^{5+} defects exist which have been investigated intensively by EPR. One type causes a tetragonal [5, 6], the other type an orthorhombic EPR spectrum [7–9]. The latter was explained by Müller *et al* in the framework of an off-centre model [8]. By a displacement of the Cr^{5+} ion along one of the $\langle 110 \rangle$ directions, it becomes quasi-tetrahedrally coordinated by four O^{2-} ions in the perovskite unit cell (figure 1). In this position its electronic ground state is the $3z^2-r^2$ orbital directed along z , i.e. one of the equivalent $\langle 110 \rangle$ directions. Because the principal g values of the Cr_II^{5+} defect centres in the ferroelectric BaTiO_3 are quite close in magnitude and of the same symmetry to those in cubic SrTiO_3 , Müller also assigned the Cr_II^{5+} spectrum in BaTiO_3 to a tetrahedrally coordinated Cr^{5+} defect [8].

Kool *et al* investigated the EPR spectra of SrTiO_3 with this tetrahedrally coordinated Cr_II^{5+} defect under the influence of external electric fields [9]. By the linear coupling of the electrical dipole moment associated with the off-centred Cr^{5+} ion within the octahedron of surrounding O^{2-} ions and the external electric field an alignment of the dipoles takes place which induces changes in the intensities of the EPR line dependent on the strength of the external field. From intensity measurements the electrical dipole moment and the off-centred displacement were determined.

In this paper we investigated the peculiarities of the tetrahedrally coordinated Cr_II^{5+} defect centre in BaTiO_3 ceramic powder samples which were synthesized under different conditions (Cr concentration, excess of BaO, sintering temperature). X and Q band measurements reveal the existence of two types of Cr_II^{5+} defect centres with slightly different g tensors below 80 K. The difference in their principal values is explained by interaction of the electrical dipole moment of the tetrahedrally coordinated Cr_II^{5+} ion with the spontaneous polarization of the ferroelectric domains.

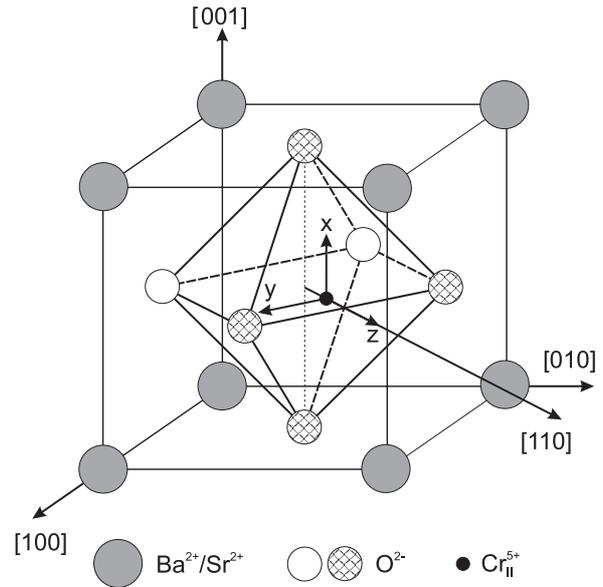


Figure 1. Perovskite unit cell with an off-centred Cr_II^{5+} ion at a quasi-tetrahedral site coordinated by the four oxygen ions marked by hatched circles. Two of the oxygen ions have a short and the other a longer $\text{Cr}^{5+}\text{O}^{2-}$ distance. The local symmetry of this defect centre is C_{2v} .

2. Experimental procedure

Ceramic powders with the nominal composition $\text{BaTiO}_3 + x\text{BaO} + y\text{Cr}_2\text{O}_3$ ($x = 0.02, 0.04, y = 0.0005, 0.0025, 0.005$) were prepared by the conventional mixed-oxide powder technique. After mixing (agate balls, water) and calcining (1373 K, 2 h) of BaCO_3 (Solvay, VL600, <0.1 mol% Sr) and TiO_2 (Merck, no. 808), the BaTiO_3 powder was fine-milled (agate balls, 2-propanol) and densified to disks with a diameter of 6 mm and a height of nearly 3 mm. The dopant Cr_2O_3 (Merck, p.a.) was added before fine-milling. The samples were sintered in air at temperatures T_s of 1573, 1623 and 1673 K for 1 h (heating rate 10 K min^{-1}). The overall phase composition was checked at room temperature by analysing the XRD powder pattern (STADI MP diffractometer, STOE, Germany). All samples were in the single phase state (3C modification).

EPR measurements of the finely pulverized ceramics were carried out in the X (9.4 GHz) and Q (34.0 GHz) band with Bruker devices. Temperatures between 5 and 240 K were achieved with an Oxford flowing He gas cryostat in connection with an Oxford ITC controller (temperature stability about 0.2 K). More details of the measuring procedure are given in [10]. The Cr^{5+} spectra of the chromium isotopes without nuclear magnetic moments ($^{50,52,54}\text{Cr}$) are described by a $S = 1/2$ spin-Hamiltonian consisting only of the anisotropic Zeeman term

$$\hat{H} = \beta \vec{B} \underline{\underline{g}} \hat{S} \quad (1)$$

with $\underline{\underline{g}}$ the electronic g tensor (symmetric) and β the Bohr magneton, respectively. For the determination of the spin-Hamiltonian parameters and the evaluation of the ceramic

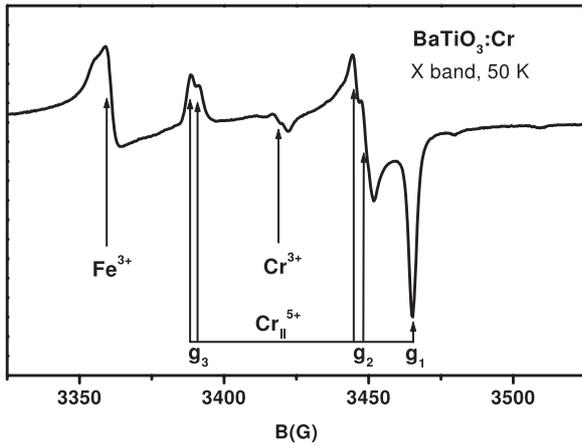


Figure 2. X band powder spectrum of the ceramic sample $\text{BaTiO}_3 + 0.02\text{BaO} + 0.005\text{Cr}_2\text{O}_3$ ($T_s = 1673$ K) in the rhombohedral phase. In addition to the peaks of the $\text{Cr}_{\text{II}}^{5+}$ spectra the central transitions of the Cr^{3+} and Fe^{3+} ions are visible.

powder EPR spectra the MATLAB toolbox⁵ for electron paramagnetic resonance ‘Easy Spin 2.0.3’ was used [11]. By simulating the Q band powder spectra by variation of the parameters of the standard spin-Hamiltonian (1) for the 1/2-spin system Cr^{5+} , a satisfactory accuracy in the determination of the spectral parameters was achieved.

3. Results

The room-temperature spectra of our chromium-doped samples show the powder pattern of the Cr^{3+} impurity (electron spin $S = 3/2$) substituted for Ti^{4+} at the centre of the octahedron of O^{2-} ions, where the charge compensating oxygen vacancy obviously has a sufficient distance from the impurity containing octahedron that no influence on the spectral properties of the powder pattern is observed. In samples with higher impurity concentration ($y = 0.0025, 0.005$) only the central transition ($M_S = +1/2 \leftrightarrow M_S = -1/2$) of the Cr^{3+} ion with satellite structure, caused by hyperfine structure of the ^{53}Cr isotope (natural abundance about 10%) with the nuclear spin $I = 3/2$, is observed. Due to the internal stress in the grains of these pulverized ceramics the other fine structure peaks ($M_S = \pm 3/2 \leftrightarrow M_S = \pm 1/2$) are so heavily broadened that they cannot be detected. In contrast to highly doped samples, all peaks of the Cr^{3+} spectrum are visible in samples with low Cr concentrations.

When the BaTiO_3 sample is cooled below 183 K, it undergoes a structural phase transition to a modification having rhombohedral symmetry (space group $R3m$) and a complicated EPR spectra in which the number of the peaks and their intensities are dependent on the preparation conditions (impurity concentration, stoichiometric ratio Ba/Ti, sintering temperature T_s). Figure 2 shows the EPR spectrum of the ceramic powder with the nominal composition $\text{BaTiO}_3 + 0.02\text{BaO} + 0.005\text{Cr}_2\text{O}_3$ ($T_s = 1673$ K) measured at 50 K.

⁵ MATLAB is a registered trademark of the MathWorks, Inc., Natick, MA, USA.

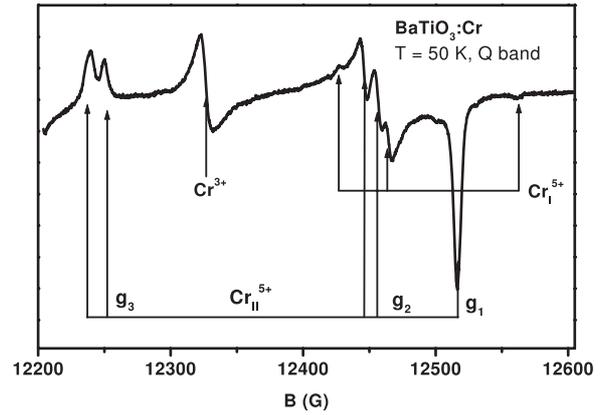


Figure 3. Q band powder spectrum of the ceramic sample $\text{BaTiO}_3 + 0.02\text{BaO} + 0.005\text{Cr}_2\text{O}_3$ ($T_s = 1673$ K) in the rhombohedral phase. The splitting of the g_2 and g_3 peaks of the $\text{Cr}_{\text{II}}^{5+}$ spectrum in a doublet is clearly visible. Further on, the weak g_2 peak of the $\text{Cr}_{\text{I}}^{5+}$ spectrum is observable near the g_y peak of the $\text{Cr}_{\text{II}}^{5+}$ defect.

Table 1. Principal values of the g tensors and line widths ΔB_{pp} of the $\text{Cr}_{\text{II}}^{5+}$ defects a and b in the rhombohedral and orthorhombic phase of BaTiO_3 .

Defect	T (K)	g_1	g_2	g_3	ΔB_{pp} (G)
$\text{Cr}_{\text{II}a}^{5+}$	50	1.9453(3)	1.9565(3)	1.9892(3)	4.5(2)
$\text{Cr}_{\text{II}b}^{5+}$	50	1.9453(3)	1.9543(3)	1.9876(3)	4.5(2)
$\text{Cr}_{\text{II}}^{5+}$	140		1.962(1) ^a		35(2)
$\text{Cr}_{\text{II}}^{5+}$	195		1.962(1) ^a		60(3)
$\text{Cr}_{\text{II}}^{5+ b}$	75	1.945(2)	1.955(2)	1.988(2)	—

^a Isotropic spectrum.

^b Principal values of g tensor determined by Possneriede [3] from X band single-crystal investigation.

The asymmetric peak with the g factor $g = 2.0054$ is assigned to the high-spin ion Fe^{3+} substituted on the octahedral Ti^{4+} site. The other peaks originate from chromium ions. In this powder spectrum the peak of the Cr^{3+} central transition has a very low intensity. By comparing of the principal g values of the three intensive peaks with the values, given by Possneriede [3], they are assigned to the $\text{Cr}_{\text{II}}^{5+}$ centre (see table 1). Also these peaks are surrounded by hyperfine lines of the ^{53}Cr isotope, which were not analysed in this study. The peculiarity of the $\text{Cr}_{\text{II}}^{5+}$ powder pattern is a badly resolved doublet splitting (about 3 G in X band) in the g_2 and g_3 peak which is independent of the preparation conditions. To find the reason for this splitting, all samples have been investigated at higher microwave frequencies at 50 K. In figure 3 the high-field part of the Q band (34.0 GHz) spectrum with the peaks of the Cr^{3+} and Cr^{5+} centres is depicted. The Fe^{3+} peak lies outside the field range of this spectrum. The doublet splitting (12 G in the Q band) is now well resolved in the g_2 and g_3 peaks, furthermore the g_1 peak reveals as a singlet. In the spectra of all samples in which the $\text{Cr}_{\text{II}}^{5+}$ defect centre is detectable the doublet splitting was observable, see figure 4. In this figure additionally to the Cr^{3+} and $\text{Cr}_{\text{II}}^{5+}$ peaks the powder pattern of the $\text{Cr}_{\text{I}}^{5+}$ centre is observed.

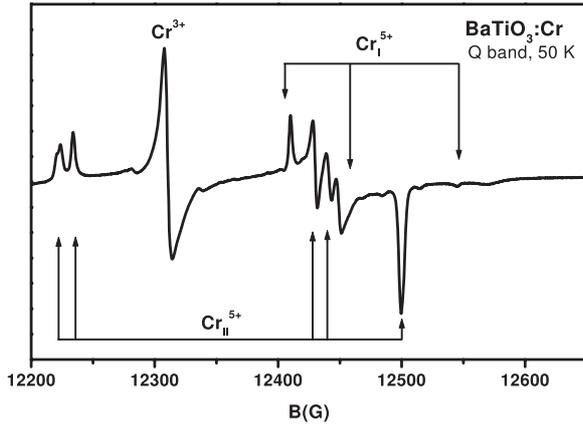


Figure 4. Q band powder spectrum of the ceramic sample $\text{BaTiO}_3 + 0.04\text{BaO} + 0.0005\text{Cr}_2\text{O}_3$ ($T_s = 1623$ K) in the rhombohedral phase. In this sample the Cr_I^{5+} and Cr_{II}^{5+} defect centres have about the same concentration.

Because the doublet splitting is frequency-dependent, a hyperfine interaction of the Cr^{5+} ion with a nuclear spin $I = 1/2$ must be excluded as a reason. It can be explained by assuming the existence of two Cr_{II}^{5+} centres (*a* and *b*) with slightly different *g* tensors. Under this assumption the principal values of the *g* tensors were estimated by simulation of the powder spectra and given in table 1. In figure 5 the results for the simulation of the experimental spectrum is represented.

The spectra of the Cr_{IIa}^{5+} and Cr_{IIb}^{5+} defect centres are strongly temperature-dependent (figure 6). The best spectral resolution was observed at the temperature of 50 K. Increasing the temperature above 75 K, the line widths of the $\text{Cr}_{IIa,b}^{5+}$ centres are broadened and the peaks are shifted, proving the frequencies of the reorientational motions of the centres are comparable to $f = \frac{(g_3 - g_1)\beta B}{h}$, *B* is the field in the centre of the spectrum. At 120 K the peaks collapse into a symmetrical single-line spectrum with an averaged *g*-value $g_{av} = \frac{g_1 + g_2 + g_3}{3}$, the width of which broadens with increasing temperature until it vanishes.

4. Discussion

To explain the splitting in the spectrum of the Cr_{II}^{5+} defects in BaTiO_3 , one must consider the special crystal structure of the low-temperature phase together with the existence of domains. The shape and symmetry of the unit cells and domains of ferroelectrics in thermal equilibrium are mainly determined by spontaneous deformations, which are the components S_{ik} of the symmetric deformation tensor [12]

$$S_{ik} = \sum_{m,n} Q_{mnik} P_m^s P_n^s. \quad (2)$$

Their occurrence is the direct consequence of the existence of the spontaneous electrical polarization \vec{P}^s with the components P_m^s . The quantities Q_{mnik} are the elements of the electrostriction tensor. The deformations are quadratic in the spontaneous polarization due to the centrosymmetric high-temperature phase (paraelectric) of barium titanate. At the phase transition temperatures the

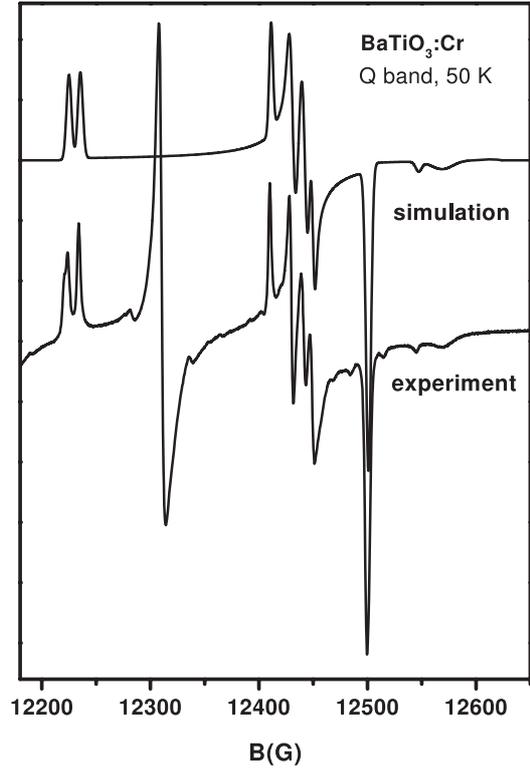


Figure 5. Experimental and simulated EPR powder spectrum of the ceramic sample $\text{BaTiO}_3 + 0.04\text{BaO} + 0.0005\text{Cr}_2\text{O}_3$ ($T_s = 1623$ K) in the rhombohedral phase. In the simulation only Cr_I^{5+} and Cr_{II}^{5+} defect centres without nuclear spins were considered.

vector \vec{P}^s changes its direction and absolute value and becomes successively oriented along the fourfold (tetragonal), twofold (orthorhombic) and threefold (rhombohedral) axes of the pseudo-cubic unit cell. In order that the macroscopic symmetry of a multi-domain crystal in the low-temperature phase agrees with the point group of the high-temperature one, the domains of the rhombohedral phase must be arranged according to the eight equivalent $\langle 111 \rangle$ directions of the spontaneous polarization [12].

The electrical polarization of the domains interacts with the electric moment associated with the off-centred Cr_{II}^{5+} ion. By a linear coupling of the dipoles with the polarization field, shifts of lines in the spectrum and alignment effects of dipoles in the \vec{P}^s orientation are induced. The polarization-induced interaction is taken into account by an additional spin-Hamiltonian changing the Zeeman energy of the defect centre [13]. Due to the linear coupling of the dipoles with \vec{P}^s the spin-Hamiltonian may be described by

$$\hat{H}^s = \sum_{ijk} \beta D_{ijk} B_i \hat{S}_j P_k^s = \sum_{ij} \beta g_{ij} B_i \hat{S}_j \quad (3)$$

where

$$g_{ij}^s = \sum_k D_{ijk} P_k^s \quad (4)$$

are the components of the symmetric, polarization-dependent g^s tensor. For the point symmetry C_{2v} (local symmetry group of the Cr_{II}^{5+} defect centre, C_2 axis and dipole moment are parallel to $[110]$ which is the *z* axis, see figure 1) and related

to the xyz system, the relevant third-rank tensor D_{ijk} has the form [14]

$$D_{ijk} = \begin{pmatrix} 0 & 0 & d_{13} \\ 0 & 0 & d_{23} \\ 0 & 0 & d_{33} \\ 0 & d_{42} & 0 \\ d_{51} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (5)$$

The first index of the elements d_{ij} refers to the Voigt notation ($1 = xx, 2 = yy, \dots, 6 = xy = yx$). Using the eight vectors of the electrical polarization from the differently orientated domains of the rhombohedral phase, transformed into the xyz system, one gets eight additional g^s tensors:

$$\begin{aligned} g_{1,2}^s &= \sqrt{\frac{2}{3}} P^s \begin{pmatrix} d_{13} & 0 & \pm \frac{d_{51}}{\sqrt{2}} \\ 0 & d_{23} & 0 \\ \pm \frac{d_{51}}{\sqrt{2}} & 0 & d_{33} \end{pmatrix}, \\ g_{3,4}^s &= \sqrt{\frac{2}{3}} P^s \begin{pmatrix} -d_{13} & 0 & \mp \frac{d_{51}}{\sqrt{2}} \\ 0 & -d_{23} & 0 \\ \mp \frac{d_{51}}{\sqrt{2}} & 0 & -d_{33} \end{pmatrix}, \\ g_{5,6}^s &= \sqrt{\frac{2}{3}} P^s \begin{pmatrix} 0 & 0 & \pm \frac{d_{51}}{\sqrt{2}} \\ 0 & 0 & d_{42} \\ \pm \frac{d_{51}}{\sqrt{2}} & d_{42} & 0 \end{pmatrix}, \\ g_{7,8}^s &= \sqrt{\frac{2}{3}} P^s \begin{pmatrix} 0 & 0 & \pm \frac{d_{51}}{\sqrt{2}} \\ 0 & 0 & -d_{42} \\ \pm \frac{d_{51}}{\sqrt{2}} & -d_{42} & 0 \end{pmatrix}. \end{aligned} \quad (6)$$

By addition of the diagonal tensor with the elements g_x, g_y, g_z of the undisturbed defect centre one gets the total g tensors where the principal values of the tensors 1–4 are:

$$\begin{aligned} g_1 &\approx g_x \pm \sqrt{\frac{2}{3}} d_{13} P^s - \frac{d_{51}^2 (P^s)^2}{3(g_z - g_x)} \approx g_x \pm \sqrt{\frac{2}{3}} d_{13} P^s \\ g_2 &= g_y \pm \sqrt{\frac{2}{3}} d_{23} P^s \end{aligned} \quad (7)$$

$$g_3 \approx g_z \pm \sqrt{\frac{2}{3}} d_{33} P^s + \frac{d_{51}^2 (P^s)^2}{3(g_z - g_x)} \approx g_z \pm \sqrt{\frac{2}{3}} d_{33} P^s$$

and

$$g_1 \approx g_x \quad g_2 \approx g_y \quad g_3 \approx g_z \quad (8)$$

for the other ones (linear approximations in P^s). The off-centred $\text{Cr}_{\text{II}}^{5+}$ ions with dipole moments oriented perpendicular to the spontaneous polarization of the domains have polarization-independent principal g -values to a first-order approximation.

Assuming the electrical dipole moments of the defect centres are distributed with the same probability over the equivalent $\langle 110 \rangle$ directions one expects that each of the g_x, g_y and g_z peaks splits into a triplet ($g_i - \sqrt{\frac{2}{3}} d_{i3} P^s, g_i, g_i + \sqrt{\frac{2}{3}} d_{i3} P^s, i = x, y, z$) with the relative intensity ratio 1:2:1 at 50 K. However, a doublet splitting with the relative intensity ratio of about 1:1 is observed in two peaks. Therefore, one can conclude that in the low-temperature phase the $\text{Cr}_{\text{II}}^{5+}$ ions

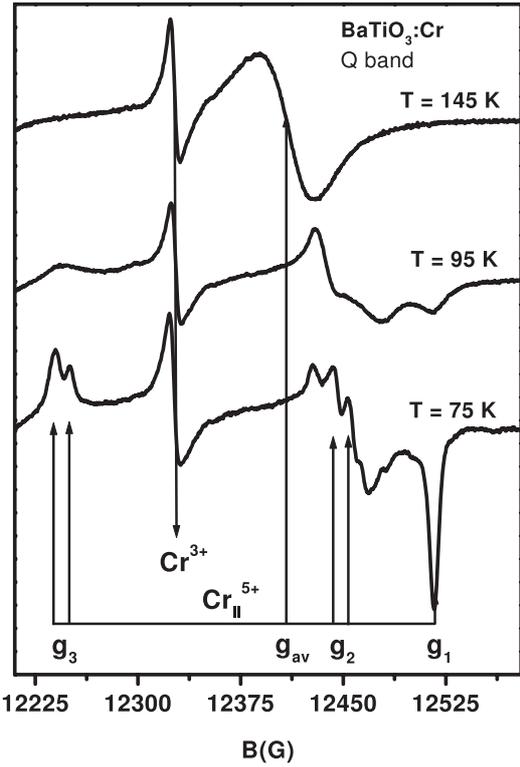


Figure 6. Temperature dependence of the EPR powder spectrum of the ceramic sample $\text{BaTiO}_3 + 0.02\text{BaO} + 0.005\text{Cr}_2\text{O}_3$ ($T_s = 1673$ K) measured at 34.0 GHz.

capture only specific positions in the domains in which the dipole moments have a component parallel to the spontaneous polarization. Owing to their mobility at higher temperatures the capture of the $\text{Cr}_{\text{II}}^{5+}$ ions in positions with special dipole orientations is only feasible by cooling below 70 K. These defect centres have principal g values which are linear-dependent on the magnitude of the spontaneous polarization. Because the high-field g_1 peak shows no splitting, the d_{13} coefficient of the D_{ijk} tensor (5) is about zero. The values of $g_{2a,b}$ and $g_{3a,b}$ result in the estimated relation $d_{23} \approx 1.4d_{33}$. Using the value of the macroscopic electrical polarization ($P^s = 0.08 \text{ C m}^{-2}$) [15] in the rhombohedral phase one gets $d_{23} = 1.7 \times 10^{-2} \text{ C}^{-1} \text{ m}^2$.

Müller *et al* have also observed, in tetragonal SrTiO_3 , a line splitting in the angular dependence of the spectra of tetrahedrally coordinated Cr^{5+} defect centres [8]. In contrast to BaTiO_3 , this doublet splitting is only caused by rotations of the g tensor around the $[001]$ axis (x axis, figure 1) with the rotation angles $\pm\alpha$. The splitting clearly vanishes towards to the tetragonal–cubic phase transition near 105 K. The rotation angle has been measured as a function of the temperature and is dependent on the intrinsic order parameter of this cubic–tetragonal phase transition, which is the rotation angle of the corner-sharing octahedra.

5. Conclusions

Two possibilities of the incorporation of paramagnetic Cr^{5+} ions with the electron configuration $3d^1$ exist in the barium titanate lattice: octahedrally and quasi-tetrahedrally

coordinated Cr^{5+} . In the case of the octahedrally coordinated Cr^{5+} the tetragonal Jahn–Teller distortion of the $\text{Cr}^{5+}\text{O}_6^{12-}$ complex is weakly disturbed by a *quadratic* field effect and the D_{4h} symmetry of the complex is reduced. EPR spectra with rhombic symmetry are detected in the rhombohedral phase. The abnormal position of the principal axes of the g tensor can be accounted for in a polarization model. The quasi-tetrahedral coordination of the Cr^{5+} ion arises from a displacement of the ion along the $\langle 110 \rangle$ direction. A *linear* coupling of the electrical spontaneous polarization and the electric dipole moments, associated with the off-centred Cr^{5+} ion within the octahedron of surrounding O^{2-} ions, induces the alignment of the dipoles and the polarization-dependent g tensors. This coupling causes a doublet splitting of the peaks in the EPR powder spectrum of the quasi-tetrahedrally coordinated Cr^{5+} defect. At 75 K a dynamic reorientation of the defects among the possible positions in the unit cell broadens the powder peaks. Above 150 K only an isotropic single-line spectrum is observed, with a line width which increases with rising temperature. The experimental results confirm the assumption of the off-centre displacement of the $\text{Cr}_{\text{II}}^{5+}$ defect in ferroelectric barium titanate.

Acknowledgments

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References

- [1] Posseriede E, Schirmer O F, Albers J and Godefroy C 1990 *Ferroelectrics* **107** 313
- [2] Posseriede E, Jacobs P and Schirmer O F 1992 *J. Phys.: Condens. Matter* **4** 4719
- [3] Posseriede E 1992 *PhD Thesis* University of Osnabrück
- [4] Böttcher R, Langhammer H T and Müller T 2009 *J. Phys.: Condens. Matter* **21** 075904
- [5] de Jong H J and Glasbeek M 1976 *Solid State Commun.* **19** 1197
- [6] Glasbeek M, de Jong H J and Koopmans W E 1979 *Chem. Phys. Lett.* **66** 203
- [7] de Jong H J and Glasbeek M 1978 *Solid State Commun.* **28** 683
- [8] Müller K A, Blazey K W and Kool Th W 1993 *Solid State Commun.* **85** 381
- [9] Kool Th W, de Jong H J and Glasbeek M 1994 *J. Phys.: Condens. Matter* **6** 1571
- [10] Böttcher R, Erdem E, Langhammer H T, Müller T and Abicht H-P 2005 *J. Phys.: Condens. Matter* **17** 2763
- [11] Stoll St 2003 Spectral simulation in solid-state EPR *PhD Thesis* ETH Zürich
- [12] Strukov B A and Levanyuk A P 1998 *Ferroelectric Phenomena in Crystals: Physical Foundations* (Berlin: Springer)
- [13] Pake G E and Estle T E 1973 *The Physical Principles of Electron Paramagnetic Resonance* (Reading, MA: Benjamin)
- [14] Haussühl S 2007 *Physical Properties of Crystals: An Introduction* (Weinheim: Wiley-VCH)
- [15] Merz W J 1949 *Phys. Rev.* **76** 1221