

**PHOTOSENSITIVE CENTERS AND CHARGE TRANSFER
PROCESSES IN BARIUM CALCIUM TITANATE**

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Abstract The results of the study of charge transfer processes in barium calcium titanate crystals, $\text{Ba}_{0.77}\text{Ca}_{0.23}\text{TiO}_3$, in the temperature range between 4.2 K and 300 K are reported. The nominally pure and Rh doped BCT crystals were investigated with the help of electron paramagnetic resonance, optical absorption spectroscopy and light induced absorption change measurements.

Keywords: EPR; optical absorption; defects; charge transfer.

Large electro-optic coefficients and high holographic sensitivity of crystals from barium titanate (BT) family make them promising candidates for various applications. For instance, $\text{BaTiO}_3:\text{Rh}$ is infrared sensitive material showing fast photorefractive response and large self-pumped phase-conjugate reflectivity. However, the use of it in photorefractive devices operating at room temperature meets a difficulty, since BT has a tetragonal-orthorhombic phase transition at about 280 K. Barium calcium titanate, $\text{Ba}_{0.77}\text{Ca}_{0.23}\text{TiO}_3$ (BCT), gives a chance along with the overcoming this drawback to get even better characteristics than BT by the optimization of defect related properties.

Photosensitive centers and charge transfer processes in BT were rather well investigated [^{1, 2, 3, 4, 5, 6, 7, 8, 9, 10}]. Some impurity centers were

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studied in the more complex BCT crystals also [11, 12, 13, 14, 15, 16]. In the good quality BT crystals the lines of electron paramagnetic resonance (EPR) are usually very narrow, that allows easily to follow their angular dependencies and to get reliable information about extrinsic and intrinsic defects. This previously acquired knowledge gave us a good background for our present research. Due to the random distribution of Ca ions in BCT this crystal has rather high disorder and strong fluctuations of crystal fields, which result in EPR line broadening and complicate the spectra treatment and interpretation. The nominally pure and Rh doped BCT crystals were investigated with the help of the EPR, optical absorption spectroscopy, light induced EPR and absorption change measurements and in the temperature range between 4.2 K and 300 K. BT and BCT samples (both “as-grown” and poled to single domain state) were used in our study for comparison.

Broad overlapped EPR lines were registered in all studied crystals before illumination. Analyzing angular dependencies of the EPR lines and comparing them with ones for BT we could identify four different centers of iron as a trace impurity. The first two of them, $\text{Fe}_{1,2}^{3+}$ has nearly cubic surrounding. The third center is low-symmetry Fe_3^{3+} ($S=5/2$, $g\approx 2.00$, dominated parameter of axial crystal field $b_2^0\approx 0.18 \text{ cm}^{-1}$; the spin-Hamiltonian definition and fitting procedure for parameter determination are described in details in Refs. [17, 18]). And the fourth Fe_4^{3+} center has very strong axial crystal field parameter ($b_2^0\approx 6 \text{ cm}^{-1}$, the center axis is parallel to $\langle 100 \rangle$ crystal axis). The BT lattice has a tetragonal symmetry at room temperatures and some rhombohedral distortion at temperatures below 180 K. Most of elementary cells of BCT crystals are additionally distorted by random substitution of Ca for Ba: Ca_{Ba} . Therefore, we can suppose that the $\text{Fe}_{1,2}^{3+}$ centers has only regular Ba, Ti and O ions in the surrounding (nearly cubic center with the similar parameters was observed in BT). The Fe_3^{3+} center, which is registered in BCT only, has one Ca ions in the nearest neighborhood (Fig. 1b). Dominated contribution to the crystal field of the Fe_4^{3+} center gives strong intrinsic defects in nearest neighborhood at $\langle 100 \rangle$ axis - oxygen vacancy (Fig. 1a). Similar $\text{Fe}^{3+} - \text{V}_\text{O}$ center was also observed in BT [1], what supports suggested interpretation of Fe_4^{3+} center (Table 1). The presence of the $\text{Fe}-\text{V}_\text{O}$ centers is evidence of the oxygen non-stoichiometry of BCT crystals.

The lines of four other paramagnetic defects (Table 2) were found after illumination at low temperatures by the light of xenon lamp with different filters (i.e. with different light energies). Two of them were

identified with the two families of intrinsic defects: localized electron or Ti^{3+} ($S=1/2$, g -factors in the range of 1.91-1.93), localized hole or O^- -like defects ($g \sim 2.013$ -2.03). Both localized electron and hole are probably stabilized by Ca_{Ba} (Fig. 1c and 1d). Two other centers are dopant impurity Rh^{2+} ($g_{||}=2.03$, $g_{\perp}=2.30$, $A_{||}\leq 0.0015$ cm^{-1}), and non-controlled impurity Pt^{3+} ($S=1/2$, $g_{||}=1.96$, $g_{\perp}=2.45$, $A_{||}=0.0015$, $A_{\perp}=0.02$ cm^{-1} for isotope ^{195}Pt). These four defects are stable at temperatures 4.2-50K, but they disappear after heating to 240-300 K.

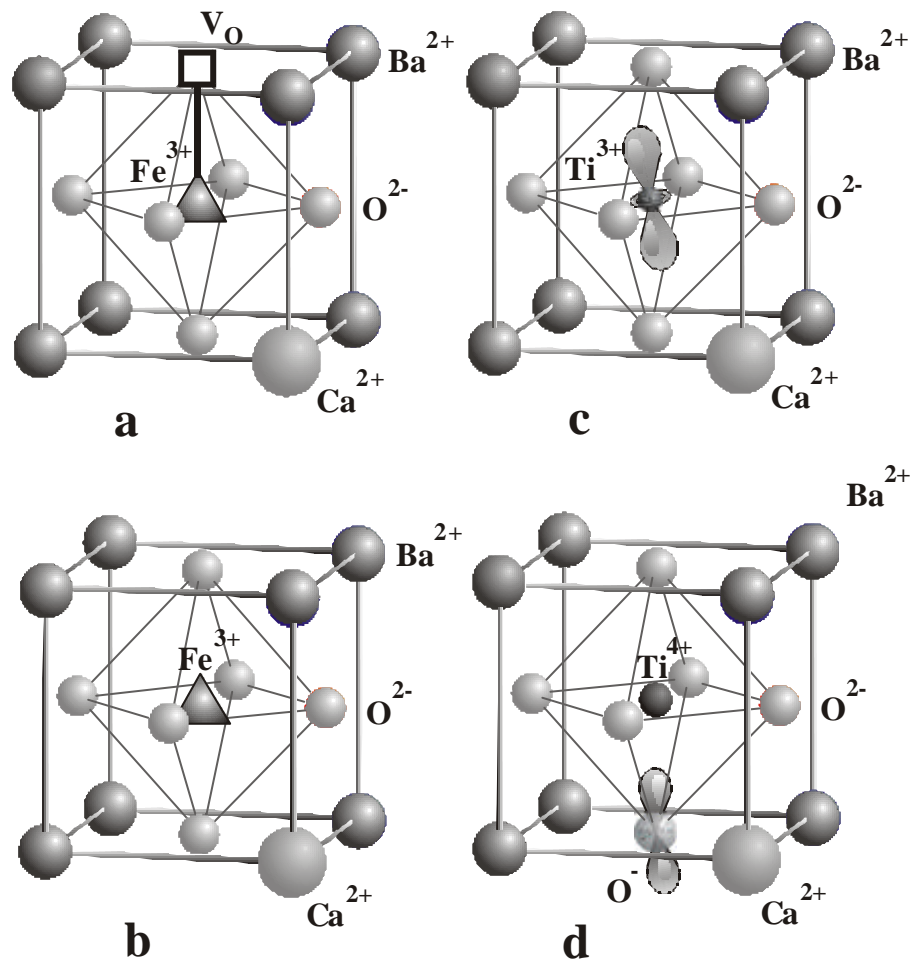


FIGURE 1. Models of paramagnetic defect centers derived from EPR data: a – Fe_4^{3+} with oxygen vacancy, V_O ; b – Fe_3^{3+} with Ca_{Ba} ; c – localized electron or Ti^{3+} ; d – localized hole or O^- center.

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All found intrinsic and extrinsic defects are participants of charge transfer processes and have correlated light induced EPR and absorption changes. At the light energy $h\nu$ about 1.3 eV the holes abandon Ti^{4+} creating the paramagnetic electronic Ti^{3+} . At $h\nu > 2.3$ eV hole O^- centers appear. This leads to the simultaneous increase of Ti^{3+} concentration. It means that O^- ions capture the holes and create hole O^- centers. Non-controlled or intentionally introduced impurities (Sr, K, Na etc.) or Ca ions, located in the nearest neighborhood, may serve as pins for the fixation of the electrons and holes.

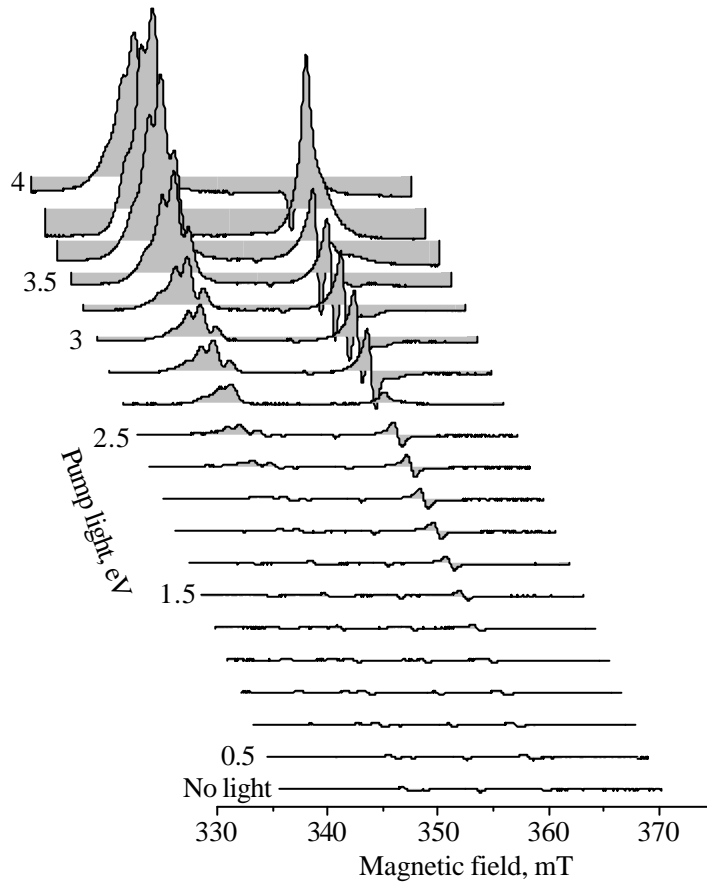


FIGURE 2. Fragments of EPR spectra of BCT for different pump energies. Magnetic field $\mathbf{B} \parallel \langle 100 \rangle$, microwave frequency 9.85 GHz, $T=20$ K.

Additional correlated changes were found at the light energy $h\nu > 3.2$ eV (band-band transition), when EPR lines of Rh^{2+} , Pt^{3+} appear and intensities of Ti^{3+} , O and Fe^{3+} groups further essentially increase. The dominated charge transfer from Ti^{4+} to O^{2-} is accompanied with the parallel processes, involving both intrinsic ions and impurities.

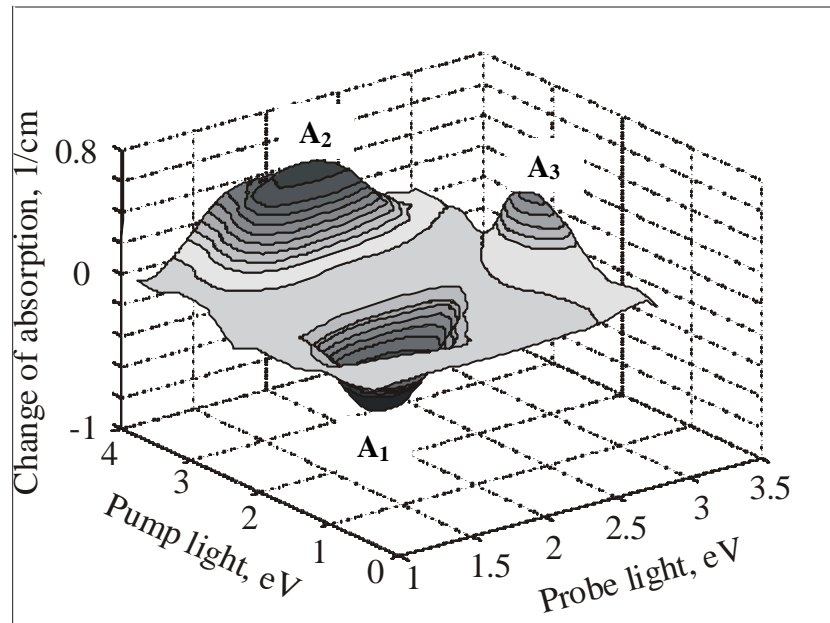


FIGURE 3. Light induced changes of absorption coefficient for BCT:Rh crystal at 150 K.

Measurements of light induced absorption change (Fig. 3) allow to obtain an additional information about photosensitive centers, since they reflect absorption changes of both paramagnetic and non-paramagnetic defects. Due to overlapping of broad optical bands the interpretation of optical data is not a simple task, especially in the case of BCT. The comparison of optical and EPR data helped us to understand the recharge processes. However, the conditions of the observation of charge transfer processes by the EPR and absorption changes do not coincide often (for instance, the optimal temperature of the EPR and optics measurements, the rates of relaxation processes), what hampers to ascertain definite correlations.

The deep valley on Fig. 3 corresponds to the decrease of the concentration of defects, which have optical absorption band A_1 at 1.8-

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2.2 eV, whereas two hills A_2 and A_3 corresponds to accompanied increase of the concentration of other defects. Since no one EPR line decrease at the illumination, we have to attribute the A_1 band to defects, which give only very weak or even zero EPR signal. In BT:Rh the A_1 and A_2 bands were associated with Rh^{4+} (1.9 eV) and Rh^{5+} (1.6 eV) [2, 3]. The A_3 band can be related to EPR-silent defects (for instance, to Rh^{3+}) as well as to one of paramagnetic centers, which appears after illumination with $h\nu > 2.3$ eV. The sharp increase of the EPR lines of Fe^{3+} centers for $h\nu > 2.8$ eV reflects the recharge of Fe^{4+} to Fe^{3+} .

The obtained results show that many quantitative and qualitative differences of EPR and optical spectra, and charge transfer processes were found for BT and BCT despite of similarity of their crystal structures.

TABLE 1. Iron centers in BT (1-4) and BCT (5-8) crystals

No	Center	g-tensor	Crystal field, cm^{-1}		T, Ref.	Comment	
			b_2^0	b_4^q	K		
1	Fe^{3+}	2.005	-0.0019	$a = -0.0113$	20	1, 19	
2	Fe^{3+} -V _O	$g_{[001]+\tau} = 2.00,$ $g_{[110]} = 5.71,$ $g_{[1-10]+\tau} = 6.26$			20	20	$\tau = 0.8^\circ,$ $b_2^0 = 1.04,$ $b_2^2 = 0.048$
3	Fe^{4+} -V _O	$g_{\parallel[001]} = 2.010,$ $g_{\perp[100]} = 0.0$		$a = 0.279$	20	1	
4	Fe^{5+}	$g_{\parallel[111]} = 2.010,$ $g_{\perp[110]} = 2.013$	1.15		20	17, 21, 22	
5	Fe^{3+}	$g_{xx} = 2.0107,$ $g_{yy} = 2.0092,$ $g_{zz} = 1.9531$	0.0020	$b_4^0 = 0.0035,$ $b_4^4 = 0.0212$	20	23	
5	Fe^{3+}	2.008	0.0020	$b_4^0 = 0.0032,$ $b_4^4 = 0.0230$	20	This work	
6	Fe^{3+}	2.002	0.0092	$b_4^0 = 0.0018,$ $b_4^4 = -0.0116$	20	This work	
7	Fe^{3+}	2.00	0.1856		20	This work	Low-symmetry
8	Fe^{3+}	2.00	6.0, $b_2^2 =$ -0.07	$b_4^0 = -0.06,$ $b_4^4 = 5.0$	20	This work	

TABLE 2. Other paramagnetic centers in BT and BCT crystals

No	Center	g -tensor	Hyperfine interaction, cm^{-1}	T, K	Ref.	Comment
1	Ti^{3+}	$g_{[100]} = 1.913,$ $g_{[010]+\tau} = 1.926,$ $g_{[001]+\tau} = 1.938$		20	1	BT $\tau = 26^\circ$
2	Ti^{3+} $-\text{V}_\text{O}$	$g_{[001]+\tau} = 1.937,$ $g_{[110]} = 1.931,$ $g_{[1-10]+\tau} = 1.898$		20	1, 5	BT $\tau = 12.5^\circ$
3	Ti^{3+}	$g_{[001]+\tau} = 1.937,$ $g_{[110]} = 1.933,$ $g_{[1-10]+\tau} = 1.899$		20	1	BT $\tau = 13.1^\circ$
4	Ti^{3+}	$g_{\parallel[111]} = 1.93,$ $g_{\perp[110]} = 1.91$		20	11, this work	BCT
5	Rh^{2+}	$g_{\parallel[100]} = 2.030,$ $g_{\perp[110]} = 2.298;$ $g_{\parallel[100]} = 2.03,$ $g_{\perp} = 2.3$	$A_{\parallel} = 0.0005,$ $A_{\perp} = 0.0015;$ $A \leq 0.0015$	25	1, this work	BT BCT
	Rh^{4+}	$g_{\parallel[111]} = -1.386,$ $g_{\perp[110]} = -1.461$	-0.0026	25	1	
6	Pt^{3+}	$g_{\parallel[100]} = 1.95,$ $g_{\perp[010]} = 2.459$	$^{195}\text{Pt}: A_{\parallel[100]} = 0.0,$ $A_{\perp[010]} = 0.0135$	5	24	BT
7	Pt^{3+}	$g_{[001]} = 1.958,$ $g_{[110]} = 2.452,$ $g_{[1-10]} = 2.458;$ $g_{\parallel} = 1.96,$ $g_{\perp} = 2.45$	$^{195}\text{Pt}: A_{[001]} = 0.0015,$ $A_{[110]} = 0.0111,$ $A_{[1-10]} = 0.0112;$ $A_{\parallel} = 0.0015,$ $A_{\perp} = 0.02$	9	1, this work	BT BCT
8	Pt^{5+}	$g_{[100]} = -1.35,$ $g_{[010]+\tau} = -1.31,$ $g_{[001]+\tau} = -2.05$	$^{195}\text{Pt}: A = -0.0229$	20	1	BT, $\tau = 33^\circ$
9	O^-	$g \sim 2.013-2.03$ $g \sim 2.013-2.03$		20	4, this work	BT, BCT

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