Electron paramagnetic resonance studies of photorefractive crystals II: Fe^{3+} doped $Bi_{12}SiO_{20}$ with copper vapour laser illumination in 10–100 K range

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Abstract. Photo-induced charge transfer and its kinetics were investigated in $Bi_{12}SiO_{20}$ in 10–300 K temperature range, using EPR of Fe^{3+} centre, under *in situ* illumination with copper vapour laser (CVL). The decay kinetics was found to follow double exponential behaviour. Relaxation of the photo-induced electron transfer to the preillumination condition occurred even at 10 K. Shallow traps were, therefore, associated with the electron trapping, leading to a better understanding of the fast photorefractive response of BSO.

1. Introduction

Over the last decade the photorefractive behaviour, a change in the refractive index of crystals due to the spatial variation in the intensity of the incident light, has been a subject of intense research. Prominent crystals exhibiting this phenomenon are $LiNbO_3$, $BaTiO_3$, $Bi_{12}GeO_{20}$, $Bi_{12}SiO_{20}$, $Bi_{12}TiO_{20}$, etc. Among these, $LiNbO_3$ and $BaTiO_3$ are the most thoroughly investigated photorefractive materials primarily because of very large values of the electro-optic tensor component, yielding correspondingly large values of grating efficiency, beam coupling strength, and four-wave mixing reflectivity when interference pattern is produced in the body of the crystal [1]. The grating formation is primarily due to net charge transfer from the bright regions of the interference pattern to the dark regions. In spite of the many advantages in beam coupling and phase conjugation characteristics, $BaTiO_3$ and more significantly $LiNbO_3$ suffer from sluggish growth and decay of the gratings in the body of the crystals. A crystal which exhibits much faster and contrasting photorefractive response is bismuth silicon oxide ($Bi_{12}SiO_{20}$). Photo-induced charge transfer processes in photorefractive materials are of immense current interest because of their potential applications in optical data processing [2].

Bismuth silicon oxide (BSO), having the formula $Bi_{12}SiO_{20}$ and belonging to the sillenite family of crystals, has interesting photorefractive properties [1]. It has some

distinct characteristics, which are in sharp contrast with the better known photorefractive crystals, $BaTiO_3$ and $LiNbO_3$. Whereas $BaTiO_3$ and $LiNbO_3$ are ferroelectric, BSO is a paraelectric cubic crystal at room temperature. Unlike the other two crystals, BSO has fast response times and lower beam coupling strengths. In BSO, the photoinduced electron transport is known to be longer than Debye screening length, so that the electron/hole trapping is not in the immediate vicinity of the donor sites. In the case of $BaTiO_3$ and $LiNbO_3$, the Fe^{3+} impurity is believed to play an important role in the photorefractive mechanism. We have investigated $LiNbO_3$ with a less common impurity ion U^{5+}, for photoinduced electron transfer and its kinetics [3]. The present paper is the second in the series of our papers on photorefractive materials; and deals with $Bi_{12}SiO_{20}$.

Jani and Halliburton [4] have investigated the effect of photoillumination on the EPR of Fe^{3+} in BSO. They found that excitation with 350 nm light indeed changed the valence of Fe^{3+} at 77 K and it recovered to its original state only on warming the crystal to room temperature. They did not, however, find any photoinduced valence change of Fe^{3+} at room temperature. BSO crystal has a band gap of 3·25 eV ($\approx$ 380 nm). Excitation at energies more than the band gap would result in interband electron transfer and subsequent trapping of electron at defect sites. Therefore, it is not surprising that the system relaxes back only on thermal stimulation which releases the trapped electrons. In view of the role of Fe^{3+} as a trapping site for electrons in the sub-room temperature region, they suggested that Fe^{3+} ions may play an important role in the photorefractive effect at room temperature. Baquedano *et al* [5] have also investigated the EPR of BSO, by illuminating with He/Cd (442 nm) laser, and xenon arc lamp. They identified an intrinsic trapped hole center which was bleached by photoexcitation. In the present work we have investigated the effect of *in situ* laser illumination with 10 W copper vapor laser on the EPR of Fe^{3+} in BSO in 300–10 K range.

2. Experimental

The BSO crystal used in the present study was grown using Czochralski technique. A CVL, having 10 W average power and emission wavelengths at 510 nm and 578 nm was used for *in situ* illumination of BSO crystal inside the optical transmission cavity of EPR spectrometer. The EPR spectra were recorded using a Bruker ESP-300 spectrometer equipped with an optical transmission cavity and operating in the x band. An APD cryogenics closed cycle helium refrigerator together with a lakeshore model 330 autotuning temperature controller was used for temperature variation in the range of 10–300 K.

3. Results

The EPR spectrum of Fe^{3+} in BSO single crystal at room temperature, consisted of a broad line around $g \approx 2·00$. The line position was found to be isotropic. The line width, however, was found to be anisotropic with maximum width for $H^{\parallel}\langle 100\rangle$. This suggests that this line contains unresolved structure whose anisotropy is such that it is best resolved for $H^{\parallel}\langle 100\rangle$. The intensity of the line increased with lowering of
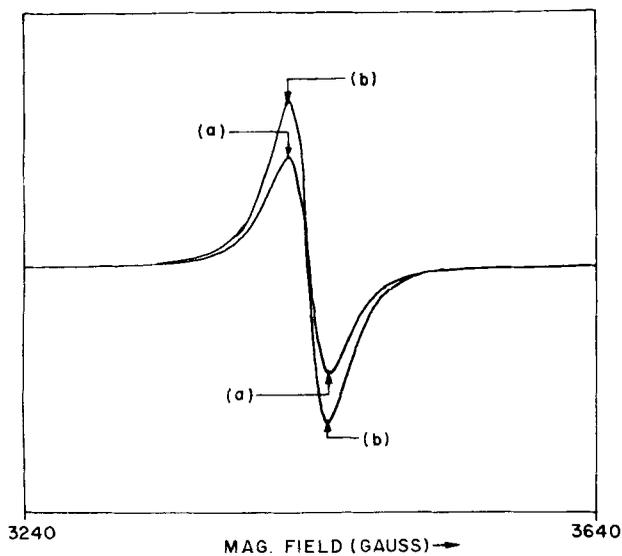
Figure 1. EPR spectrum of Fe^{3+} in BSO at 10 K: **(a)** with and **(b)** without laser illumination. A clear reduction in intensity with laser illumination can be seen.
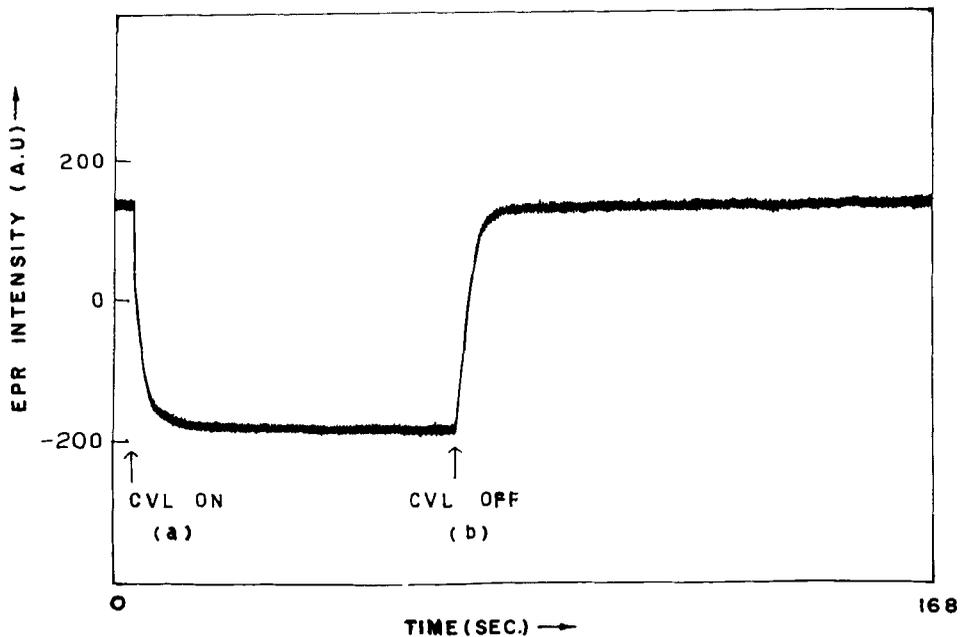

Figure 2. Decay **(a)** and recovery **(b)** of Fe^{3+} signal with laser illumination on and off respectively (temp. 10 K).
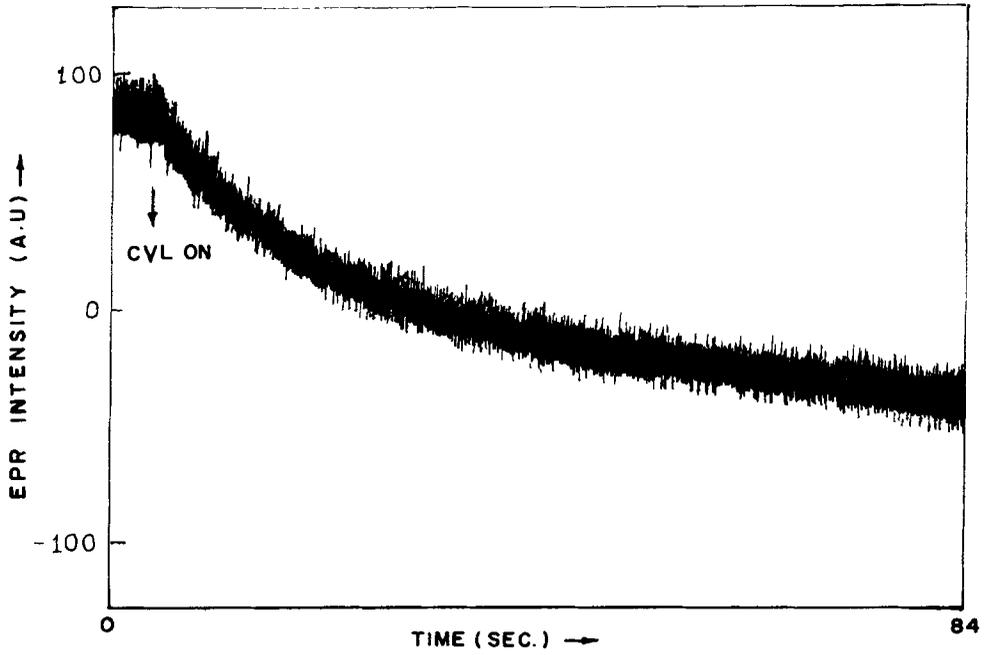
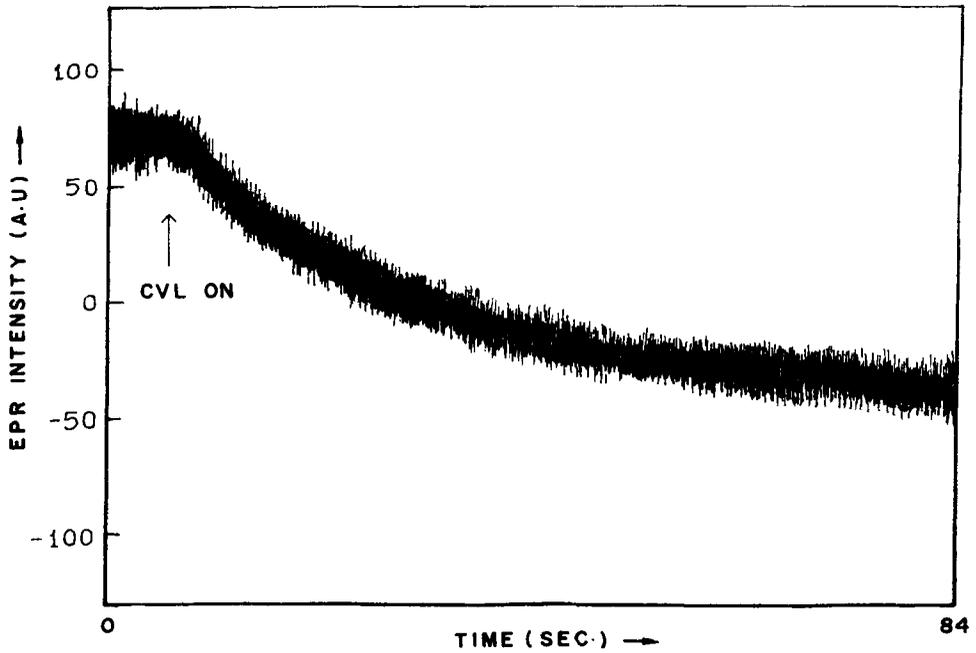**Figure 3a.** Decay of Fe^{3+} signal at 70 K with expanded time axis.

Figure 3b. Decay of Fe^{3+} signal at 100 K with expanded time axis.

Table 1. Time constants for the double exponential decay of Fe^{3+} EPR signal intensity on CVL illumination.

Temperature (K)	τ_1 (s)	τ_2 (s)
10	7	210
40	7	40
70	7	33
100	7	30

temperature from 300 K to 10 K and the line became sharper. In order to investigate the photoinduced charge transfer, the intensity of the line was monitored with and without illumination by copper vapour laser (10 W average power). The intensity reduced significantly on laser illumination at 10 K (figure 1). The kinetics of the changes were monitored by locking the magnetic field to the peak position of the line in the derivative presentation (not the resonance field) and following the change in intensity as a function of time with and without CVL illumination. Typical growth and decay patterns obtained at different temperatures are shown in figures 2, 3(a) and (b). Intensity of the spectrum went down on laser illumination and its intensity recovered completely when the laser illumation was stopped. The decay curves were fitted to a double exponential expression. The time constants obtained at different temperatures are given in table 1. These results are in contrast with those of Jani and Halliburton [4] and also Baquedano *et al* [5]. BSO crystal was illuminated at 77 K with CVL and its TL was monitored by warming the sample to room temperature. The sample did not show any TL between 100 and 300 K region.

4. Discussion

EPR spectrum of Fe^{3+} at cubic sites would consist of five $(\Delta M_S = \pm 1)$ fine structure transitions, which are often unresolved or partially resolved due to small value of fourth order cubic crystal field constant.

The crystal structure of BSO has been studied by Abrahams *et al* [6]. The possible sites for Fe^+ occupancy in BSO lattice are:

(a) Si^{4+} *site*: $Bi_{12}SiO_{20}$ has a body centred cubic cell with SiO_4 tetrahedra occupying the corners and centre of the cube. The four oxygen atoms around each Si atom form a geometrically perfect terrahedron. The $\langle 111 \rangle$ axes of the cube pass through the respective three-fold axes of all the SiO_4 tetrahedra.

(b) Bi^{3+} *site*: Bi^{3+} is coordinated to seven oxygen atoms with a coordination which is somewhat a mixture of an octahedron and a tetrahedron. Five of the seven oxygens take the places of nearly regular octahedral positions, and the sixth position of the ligand is taken by two oxygens, with O–Bi–O angle of $107 \cdot 3°$, which is nearly equal to the tetrahedral angle.

The larger line width for $H^\parallel \langle 100 \rangle$ is consistent with the unresolved cubic fine structure in that direction. The fine structure would be most resolved only along this direction. Fe^{4+} at Si^{4+} site makes the site negatively charged and hence will be a good hole trap.
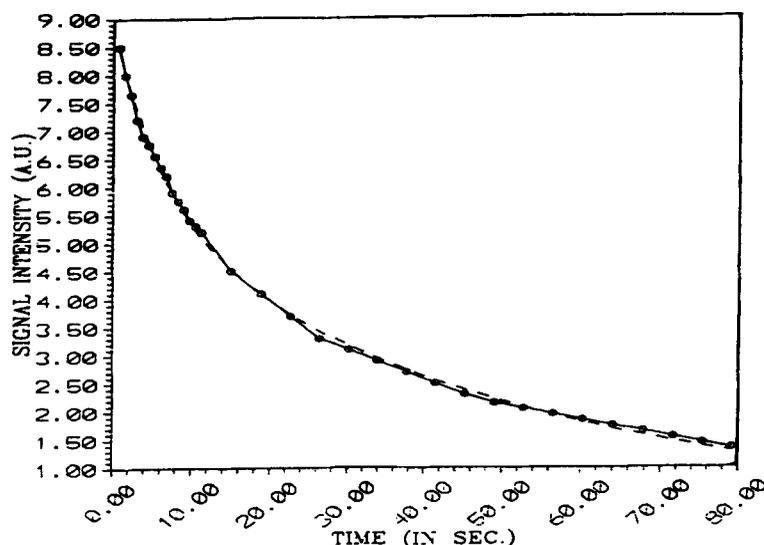
Figure 4. The fitting of the decay of EPR signal of Fe^{3+} to a double exponential (at 40 K). The dashed curve is the theoretical fit.

Therefore on photoillumination any hole generated in the lattice could be trapped making it Fe^{4+}. Due to the half filled nature, Fe^{3+} is more stable compared to Fe^{4+} and hence the system relaxes back to its original state after the laser illumination was put off.

The decay (with light on) of Fe^{3+} signal was monitored at different temperatures and satisfactory fit was obtained with a double exponential. The theoretical fit with exponential points at 40 K is shown in figure 4. In the computing process one time constant ($\tau_1 = 7$ s) was found to be nearly temperature independent whereas the other one (τ_2) has shown strong temperature dependence (see table 1).

Absence of TL between 100 and 300 K together with the observation of the recovery of the signal after putting off the illumination even at 10 K, shows that the electron/hole centres we are dealing with are not those reported by Jani and Halliburton [4] and Baquedano et al [5]. The double exponential form of the decay suggests that there are two modes of charge transfer from/to Fe^{3+} impurity. The temperature independent one probably involves a charge transfer between two Fe^{3+} and another close by defect.

The temperature dependent τ_2 has shown an activation energy of 0.36×10^{-3} eV. This is expected to be associated with the mobility of the charge carriers, as such a low energy cannot be associated with any e/h trap. Therefore the photoinduced electron transfer at 510 nm appears to be associated with

$$Fe^{3+} \underset{\text{light off}}{\overset{\text{light on}}{\rightleftharpoons}} Fe^{4+} \text{ process.}$$
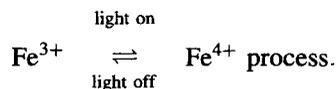
The life time of decay constants extrapolated to room temperature was found to be ≈ 20 s. It may be pointed out that Attard and Brown [7] using a two wave mixing experiment have postulated the existence of trapping centres with 100 ms, 120 s and 400 s

decay time constants. The process in the present experiment can be identified with the faster in Attard and Brown [7]. The apparent differences of 100 ms and 20 s arise due to the infinite fringe width approximation valid for uniform illumination in EPR, in contrast to the much smaller fringe width in two-wave mixing experiments.

In summary, by EPR experiments we have shown that $Fe^{3+} \leftrightarrow Fe^{4+}$ processes are involved, without any associated deep trap, in photoinduced charge transfer.

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