Impurity mediated mechanism of photorefractive effect in BaTiO₃: A combination of Sangster and piezoelectric effects

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Abstract. An impurity mediated mechanism of photorefractive effect in $BaTiO_3$ is proposed. The photoinduced changes in the relative concentration of Fe^{3+} in $BaTiO_3$ results in an electro-optic coupling through a combination of the Sangster and piezoelectric effects. This is based on the examination of the extensive results on the EPR of Fe^{3+} in the $BaTiO_3$ lattice. This model explains the improved photorefractive behavior of $BaTiO_3$ on doping with Co^{2+}.

Keywords. Photorefractive effect; $BaTiO_3$; Electron paramagnetic resonance of Fe^{3+} in $BaTiO_3$.

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1. Introduction

The microscopic mechanism of the photorefractive effect and grating formation in $BaTiO_3$ is an important area of current interest particularly with regard to the role of impurities. As in $LiNbO_3$ [1], it is generally accepted that an Fe-impurity plays the role of an acceptor/donor in Kukhtarev's band conduction model [2] in nominally pure $BaTiO_3$. It has become apparent in recent times that the chemical nature of the impurity plays an important role in improving the strength of beam coupling such as Co^{2+} in $BaTiO_3$ [3, 4] and Rh in SBN [5]. In $BaTiO_3$, the Debye screening length is shorter than typical fringe width, and the photoinduced charge transfer, more often, results in charge redistribution in the bright region of the interference pattern caused by the writing beam. The net charge transport between bright and dark regions occurs to a significant extent only in the interfacial region between bright and dark regions. Cudney *et al* [6] have shown that the redistribution of charges, on laser illumination between different trapping levels at roughly the same spatial location does not produce any electro-optic coupling due to the absence of electric field, but it does produce an absorption grating. In this note we show that, if the light induced redistribution of charges in the illuminated regions brings changes in the relative concentration of $Fe^{2+}/Fe^{3+}/Fe^{4+}$, then an electro-optic coupling occurs through a combination of Sangster [7] and piezoelectric effects in $BaTiO_3$. In the present note, we propose an impurity mediated mechanism of the photorefractive effect (abbreviated as IMPRE) in $BaTiO_3$, and it is based on the large amount of information available from the electron

paramagnetic resonance (EPR) studies of Fe^{3+} in $BaTiO_3$ [8–15] and its analysis by Müller [12,14,15], Müller and Berlinger [13] and Siegel and Müller [11] using superposition model. This IMPRE model convincingly explains why doping with Co^{2+} enhances the photorefractive response in $BaTiO_3$. The description of this model is presented in three sections: (i) EPR information on the cubic crystal field constant and consequence of the Sangster effect, (ii) enunciation of IMPRE model and (iii) consequences of the IMPRE mechanism.

2. EPR information of Fe^{3+}: $BaTiO_3$

The EPR investigations of Fe^{3+} in $BaTiO_3$ were done first by Horning *et al* [8] and by Sakudo and coworkers [9, 10]. Greater insight in this area was obtained by Müller and coworkers [12–15] in their attempt to probe the nature of structural phase transitions in ABO_3 type perovskites and also to get a comprehensive understanding of the local behavior of a number of transition metal dopants at the Ti^{4+} site. It was identified quite early in these studies that Fe^{3+} impurity goes substitutionally at the Ti^{4+} site. Siegel and Müller [11] have shown, using a superposition model for ligand field effects, that Fe^{3+} remains centered in an octahedral environment in all structural modifications of $BaTiO_3$. The cubic field parameter a in the Hamiltonian,

$$H = a/6[S_x^4 + S_y^4 + S_z^4 - (1/5)S(S+1)(3S^2 + 3S - 1)], \quad S = 5/2 \text{ for } Fe^{3+}$$

remained constant ($97 \times 10^{-4} cm^{-1}$) within 10% in all the structural phases (cubic, tetragonal, orthorhombic and rhombohedral) of $BaTiO_3$. The systematics of a for Fe^{3+} in a number of cubic oxides has revealed that it follows an empirical relation $a = a_0/d^n$ (where $2d$ = lattice spacing), with $n = 7$ and $n = 6$ near $d = 2$ Å, with a significant exception in the case of $BaTiO_3$ and $KNbO_3$. In these two crystals a was found to be 2·5 times smaller than the one expected by the empirical relation $a = a_0/d^n$. This low value of a in $BaTiO_3$ and $KNbO_3$ was found to correlate with the existence of a strongly overdamped and anisotropic soft mode.

The centered position of Fe^{3+} in the octahedral cage of oxygens and the abnormally low value of a were explained by Müller and Berlinger [13] invoking the Sangster effect [7] and the role of electron occupancy of 3d orbitals of Fe^{3+}. Sangster effect [7] predicts that Fe^{3+} at Ti^{4+} site (with no local charge compensation) repels the negative O^{2-} ions. In addition to this repulsion, an extra repulsive force arises due to the electronic configuration of Fe^{3+} ($t_{2g}^3 e_g^2$). The e_g orbitals are antibonding and, therefore, add to the repulsive force between Fe^{3+} and O^{2-}. The t_{2g} orbitals are nonbonding; therefore for an ion-like Mn^{4+} (electron configuration t_{2g}^3) at the Ti^{4+} site, the Sangster effect is absent. (Müller has shown that Mn^{4+} is the most appropriate probe to give a true understanding of the Ti^{4+} site and its dynamics in the $BaTiO_3$ lattice [12]). Using the empirical relationship between a and d, Müller and Berlinger [13] have shown that the probing Fe^{3+} sees the oxygen atom in $BaTiO_3$ at 17% larger distance than what it should be for an inert oxide, i.e., for a situation where the Sangster effect is absent. This was estimated to enhance the anharmonicity of the local potential by 34%. Müller and Berlinger [13] have also shown that the explicit pressure dependence of a in $BaTiO_3$ was three times the average of $3·6 \times 10^{-4} K^{-1}$ found in other oxides. This has firmly established that the low value of a for Fe^{3+} in $BaTiO_3$ reflects locally expanded

octahedral cage which in turn causes local strains and also enhances the local compressibility. Therefore, careful analysis of the EPR results by Müller and coworkers, have shown beyond any doubt that Fe^{3+} at Ti^{4+} site acts as a source of considerable repulsive force on O^{2-} ligands. This, in our opinion, is extremely important in view of the piezoelectric nature of $BaTiO_3$, and also for other piezoelectric crystals like BSO, in understanding the microscopic nature of photorefraction. To our knowledge, this has not been considered by the 'photorefractive community' so far, and plays a key role in the model proposed in the next section.
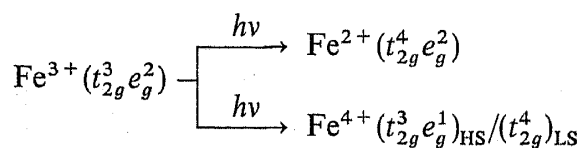
3. Enunciation of the model

The model for impurity mediated photorefractive effect (IMPRE) in $BaTiO_3$ may be enunciated as: When $BaTiO_3$ is doped with a transition metal impurity at the Ti^{4+} site whose valence can be changed by laser illumination, any interference pattern produced in the crystal results in a spatial modulation of strain field due to Sangster effect. This results in a modulation of the inter-atomic spacing with spatial period equal to that of the fringe width. As a consequence of the piezoelectric nature of $BaTiO_3$, modulation of internal electric field occurs and hence a phase grating is formed in the crystal. This is illustrated in figure 1.

In this model, the chemical nature of the defect plays an important role in the photorefractive effect. Table 1 gives a summary of the expected Sangster effect for different valence states of transition ions.

4. Consequences of IMPRE mechanism

EPR of Fe^{3+} in $BaTiO_3$ under laser illumination was investigated by Schwartz and coworkers [16] at 25 K and by Moghbel *et al* [17] at room temperature. In both cases it was observed that there is a net change in the concentration of Fe^{3+} even under uniform laser illumination. At room temperature, where most of the photorefractive experiments are conducted, the relative concentration of Fe^{3+} was found to go down on laser illumination. The photoinduced valence change, therefore, involves one or both of the following path ways.

$$Fe^{3+}(t_{2g}^3 e_g^2) \begin{array}{c} \xrightarrow{hv} Fe^{2+}(t_{2g}^4 e_g^2) \\ \xrightarrow{hv} Fe^{4+}(t_{2g}^3 e_g^1)_{HS}/(t_{2g}^4)_{LS} \end{array}$$

where HS and LS refer to high spin and low spin forms respectively. When the spin pairing energy is more than the crystal field splitting, the ion will exist in high spin (HS) form, and in the reverse situation the ion will exist in low spin (LS) form [18]. The valence change $Fe^{3+} - hv \rightarrow Fe^{2+}$ implies increased amount of Fe–O repulsion due to larger effective negative charge on Fe. On the other hand, $Fe^{3+} - hv \rightarrow Fe^{4+}$ results in considerably lowered Fe–O repulsion, much more so if Fe^{4+} is in low spin form. This obviously implies that, in bright and dark regions of the hologram, there is a strain modulation in view of the alternation of net Fe^{3+} concentration in bright and dark regions. Further, the piezoelectric nature of $BaTiO_3$ obviously helps in the creation of electric field modulation.
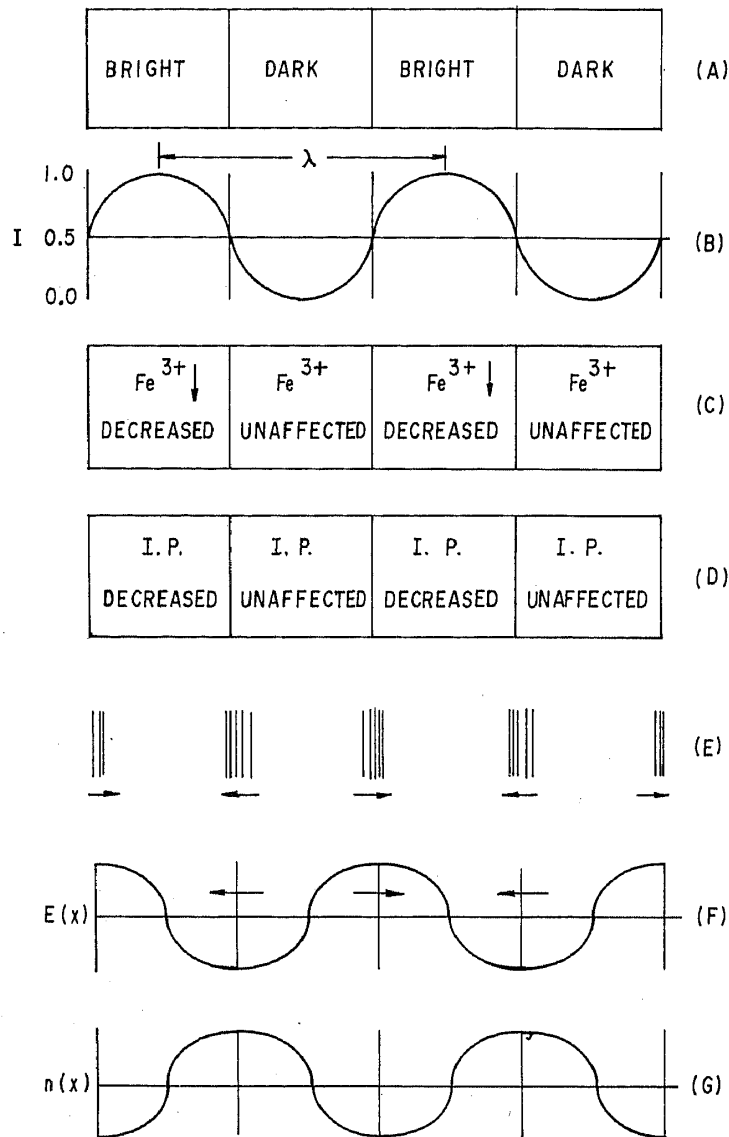
| BRIGHT | DARK | BRIGHT | DARK | (A) |

I 0.5 ... (B)

| $Fe^{3+}\downarrow$ | Fe^{3+} | $Fe^{3+}\downarrow$ | Fe^{3+} | (C) |
| DECREASED | UNAFFECTED | DECREASED | UNAFFECTED | |

| I. P. | I. P. | I. P. | I. P. | (D) |
| DECREASED | UNAFFECTED | DECREASED | UNAFFECTED | |

(E)

$E(x)$ ... (F)

$n(x)$ ... (G)

Figure 1. Schematic illustration of IMPRE model. **(A)** Typical illumination pattern. **(B)** Typical intensity profile. **(C)** Photoinduced valence change. (A typical example is $Fe^{3+} \rightarrow hv \rightarrow Fe^{4+}$ in Fe: $BaTiO_3$.) **(D)** Change in internal pressure via Sangster effect due to photo induced valence change. **(E)** Change in lattice spacings due to differential pressure in the bright and dark regions. The compression in the lattice spacings is expected to be maximum at the interfacial region. **(F)** The electric field modulation induced by piezoelectric effect due to the strain modulation caused by photo-induced valence change. **(G)** Modulation of refractive index caused by the modulation of electric field.

Schwartz *et al* [16] suggest that photoinduced valence change $[Co^{3+}]_{LS} - hv \rightarrow [Co^{2+} + h^{+}]_{HS}$ is involved in the $BaTiO_3$: Co crystal. It can be seen from table 1, that for high spin Co^{2+}, the Sangster effect is very significant whereas for low spin Co^{3+} it would be substantially smaller. This means that with photoionization of Co^{3+} along with the associated formation of high spin Co^{2+} the lattice is transformed into a more strained

Table 1. Summary of the presence of the Sangster effect for different valence states of transition ions in octahedral fields. The valence states lower than 4 + cause the Sangster effect at the Ti^{4+} site due to purely electrostatic reasons. In this table the contribution to repulsive forces only from the electronic configuration are given. The description of "strong" and "weak" refers to two and one antibonding electrons respectively.

| Ions | No. of electrons in d-shell | Electronic configuration in octahedral field | | Sangster effect due to antibonding electrons |
		High spin form	Low spin form	
Mn^{4+}, Cr^{3+}	d^3	t_{2g}^3	t_{2g}^3	Absent
Mn^{3+}, Fe^{4+}	d^4	$t_{2g}^3 e_g^1$	t_{2g}^4	Weakly present in HS form, absent in LS form
Mn^{2+}, Fe^{3+}	d^5	$t_{2g}^3 e_g^2$	t_{2g}^5	Strongly present in HS, absent in LS form
$Rh^{3+}, Co^{3+}, Fe^{2+}$	d^6	$t_{2g}^4 e_g^2$	t_{2g}^6	Strongly present in HS, absent in LS form
$Ni^{3+}, Rh^{2+}, Co^{2+}$	d^7	$t_{2g}^5 e_g^2$	$t_{2g}^6 e_g^1$	Strong in HS and weak in LS forms
Ni^{2+}, Co^{+}	d^8	$t_{2g}^6 e_g^2$	$t_{2g}^6 e_g^2$	Strongly present in both forms
Cu^{2+}	d^9	$t_{2g}^6 e_g^3$	$t_{2g}^6 e_g^3$	Present equally in both forms

state. Thus the Sangster effect may provide a physical reason why Co^{3+} prefers the low spin state, despite the closeness of $^5T_{2g}$ state of its high spin and $^1A_{1g}$ of low spin forms [19]. Compared to photoinduced valence change in $BaTiO_3$: Fe, i.e., $Fe^{3+} \leftrightarrow Fe^{2+}/Fe^{4+}$ (both high spin), the corresponding changes for cobalt doped $BaTiO_3$, $[Co^{3+}]_{LS} \leftrightarrow Co^{2+}]_{HS}$ would result in greater contrast in the grating element and hence higher grating efficiency. Similar behavior is expected for the Rh dopant, probably explaining the result reported by Vasquez et al [5] in Rh doped SBN. Similarly, the valence changes expected to give good contrast are: $Mn^{4+} \leftrightarrow Mn^{3+}$ and $Mn^{4+} \leftrightarrow Mn^{2+}$. In view of the half filled stability of Mn^{2+}, the latter process ($2e^-$ transfer) is quite probable, and is expected to give high grating efficiency. This is consistent with the reported enhancement of beam coupling in Mn doped $BaTiO_3$ by Wechsler et al [3].

The distortion in the lattice arising due to photoinduced strain is a result of the pressure differential generated by valence change and is expected to be maximum in the close vicinity of interfacial region of bright and dark fringes in an interference pattern. This suggests that the phase difference between the interference pattern and the phase grating is about 90° (figure 1). This is known to be responsible for the energy transfer in a two beam coupling experiment [20]. At room temperature, in the tetragonal phase of $BaTiO_3$, if the grating wave vector is parallel to c-axis, the crystallographic distortion

axis coincides with that of the spatially periodic distortion caused by the grating formation. Therefore, the tetragonal crystal structure allows their coexistence. However, if the grating formed is in (a, b) plane the superposed distortion destroys the crystallographic equivalence of a and b axes in the tetragonal phase itself. Therefore, the distortions associated with phase grating formation may not be sustained. Furthermore, such distortions may be averaged to zero due to motional averaging of off-centered $[Ti^{4+}]$ along four $\langle 111 \rangle$ directions in tetragonal phase with a time scale of 10^{-9}–10^{-10} s [13]. This probably explains why energy transfer does not take place when the grating wave vector is perpendicular to c-axes and the grating in (a, b) plane acts only as an absorption grating. However, if the phase conjugation studies are conducted in pulse mode with $\tau < 10^{-10}$ s, it may be possible to observe the energy transfer even when the grating vector is perpendicular to c-axis.

There exists a large body of transport data on photo-refractive materials, explaining the basic features of photorefractivity. We do not intend to suggest that photoconductivity is unimportant, but we want to highlight that there exists a possible mechanism which takes into account only the chemical nature of impurity and the photoinduced valence changes. The description of the phenomenon of photorefractive effect invoking only the chemical nature of defects would be incomplete without discussing some simple characteristics of photorefraction which are normally explained using charge transport model. We will attempt to find answers to the following in the framework of our model: (i) why grating formed in $BaTiO_3$ exhibits relatively slow relaxation? (ii) why the response time decreases with application of electric field? and (iii) can erasure with uniform light be explained without transport?

The lifetime of the grating depends upon the trap-depth of the electron/hole trap. Under charge transport model this should correspond to a trap in the darker regions of the interference pattern. The slow relaxation of grating implies that the thermal trap-depth should be more than kT at room temperature. This should be observable as a thermoluminescence (TL) peak above room temperature. In our model this trap can be filled even during uniform illumination and the (Fe) impurity site acts both as donor and acceptor (e/h trap). It is reported that $BaTiO_3$ shows a TL peak at 80°C, when the sample is uniformly irradiated with gamma rays [21]. This peak was found to decay in a few hours at room temperature. This phenomenon is independent of the route through which the traps were filled. They can be filled under conditions of uniform illumination which is analogous to uniform gamma irradiation.

It is known that external electric field decreases the response time. In our proposed mechanism, piezoelectric effect has an important role. In the presence of external field slight distortions produced by the interference pattern get strongly perturbed by the distortion induced by the electric field, resulting in the decrease of response time.

It is a common practice to erase the grating by exposing the $BaTiO_3$ crystals to intense uniform light. In our model, the lattice distortions occur most predominantly at the interfacial regions of the bright and dark fringes (i.e., in the regions of maximum intensity gradient). At the centre of the bright region, the pressure generated at one site gets balanced by that at another neighbouring site. At the interfacial regions the internal pressure differential would be the largest, resulting in the formation of grating 90° out-of-phase with the intensity pattern. Therefore, under the conditions of uniform illumination, the pressure differential goes to zero and the grating gets erased.

5. Conclusion

We have suggested a new mechanism for the photorefractive effect in $BaTiO_3$ doped with transition metal impurities. This is primarily centered around the valence dependent repulsive forces between the impurity ion and the ligand oxygens. This model explains the dependence of photorefraction on the chemical nature of the dopant.

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