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Abstract

The results of theoretical and experimental studies of the photorefractive effect in two different classes of materials--perovskite $BaTiO_3$ and tungsten bronze SBN--have been examined. The interesting features of these measurements indicate that two-beam coupling coefficients, response times, and absorption coefficients enhanced significantly in doped crystals which appear to be suitable for future device concepts. A comparison of these materials showed that Ce-doped SBN:60 single crystals are superior to $BaTiO_3$ for use in photorefractive applications due to higher two-beam coupling, sensitivity, and overall flexibility of tungsten bronze crystals.

Introduction

A given photorefractive material is considered useful for optical processing applications such as phase conjugate optics if it possesses three important features: low response time, large coupling coefficient and high optical quality. Speed is necessary if the crystal is to be used in real-time applications, while large photorefractive coupling is required for the construction of efficient devices. However, a crystal of poor optical quality is of little practical importance, regardless of its speed and gain. Although a material is yet to be found which completely satisfies all three requirements, here we show how well $BaTiO_3$, SBN:60, and SBN:Ce approximate these properties.

Material Properties

Strontium barium niobate (SBN) belongs to a class of tungsten bronze ferroelectrics which is pulled from a solid solution of alkaline earth niobates. The crystal is transparent and can be grown with a variety of ferroelectric and electrooptic properties depending on the specific cation ratios introduced into the structure. In SBN the unit cell contains ten NbO_6 octahedra with only five alkaline earth cations to fill ten interstitial sites.[1,2,3] The structure is thus incompletely filled which permits the addition of a wide range of dopants into the host crystal. The general formula for SBN is $Sr_xBa_{1-x}Nb_2O_6$ so that SBN:60 represents $Sr_{.6}Ba_{.4}Nb_2O_6$.

The point group symmetry of SBN at room temperature is 4mm which implies that its electrooptic tensor is non-zero. The dominant electrooptic coefficient is r_{33} which ranges from 100 pm/V in SBN:25 to 1400 pm/V in SBN:75. SBN:75 would, therefore, appear to be the best photorefractive SBN crystal were it not for the fact that optical quality diminishes with increasing Sr concentration. Hence, SBN:60 was selected as the candidate SBN photorefractive material on the basis of its high optical quality and moderately large electrooptic coefficient.

Barium titanate has the prototype cubic perovskite structure above 120^0C. It transforms successively to three ferroelectric phases below 120^0C: first to 4mm tetragonal, then to mm orthorhombic at 5^0C, and to a 3m trigonal phase, finally, below -90^0C. Although $BaTiO_3$ has the same point group symmetry at room temperature as SBN:60, its largest electrooptic coefficient is r_{42}, whose value is approximately 1600 pm/V, rather than r_{33}. This means that in $BaTiO_3$ any intensity variations whose grating vectors are parallel to a crystal axis will not result in refractive index modulation. In order to obtain the large values of electrooptic coefficients in these crystals, they must, in practice be poled by first heating them above their Curie points and then allowing them to cool to room temperature with applied DC electric fields on the order of 1-10 kV/cm. It has been observed that SBN:60 is significantly easier to pole than $BaTiO_3$ since the latter crystal will often be permanently damaged as its temperature approaches its Curie point or too high an electric field is applied. SBN:60 crystals, on the other hand, can sustain fields up to 10 kV/cm while its temperature can be varied to practically any value, regardless of the rate, without fear of damaging the crystal.

Photorefractive Properties

   Single crystals of SBN:60 and SBN:Ce, grown at Rockwell International Corporation, and BaTiO$_3$, obtained from Sanders Associates, Inc. were studied using the two-wave mixing experiment shown in Figure 1 to determine their effectiveness as photorefractive media. In Figure 1 beams 1 and 2 are plane waves which intersect in the crystal and thus form an intensity interference pattern. Charge is excited by this periodic intensity distribution into the conduction band, where it migrates under the influence of diffusion and drift in the internal electric field, and then preferentially recombines with traps in regions of low irradiance. A periodic space charge is thus created which modulates the refractive index via the electrooptic effect. This index grating, being out of phase with the intensity distribution, introduces an asymmetry that allows one beam to be amplified by constructive interference with light scattered by the grating, while the other beam is attenuated by destructive interference with diffracted light. This process is shown graphically in Figure 2.
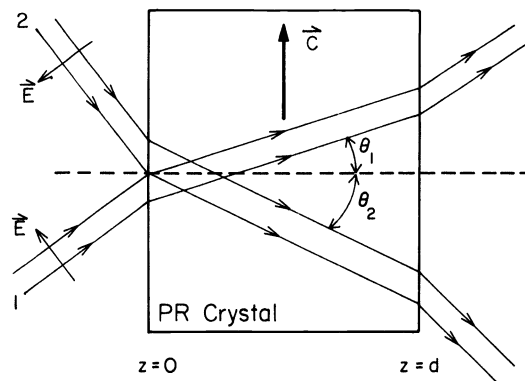
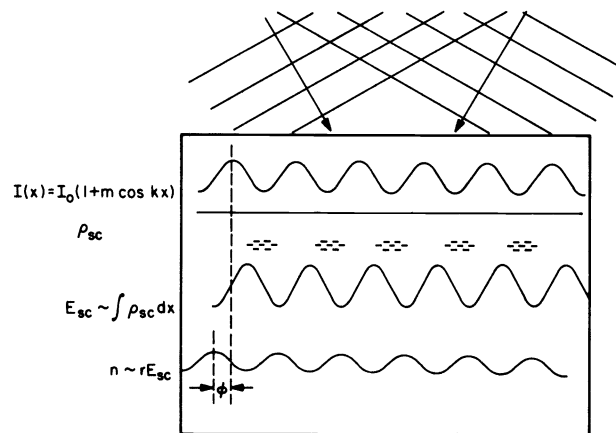Figure 1. Experimental set-up for two-beam coupling experiments

Figure 2. The photorefractive mechanism. Two laser beams intersect, forming an interference pattern. Charge is excited where the intensity is large and migrates to regions of low intensity. The electric field associated with the resultant space charge operates through the electrooptic coefficients to produce a refractive index grating.

Mathematically, this two-beam coupling may be described in the steady-state as follows:

$$\cos\theta_1 \frac{dI_1}{dz} = \Gamma \frac{I_1 I_2}{I_1 + I_2} - \alpha I_1$$

$$\cos\theta_2 \frac{dI_2}{dz} = -\Gamma \frac{I_1 I_2}{I_1 + I_2} - \alpha I_2$$

where I_1, I_2 are the intensities of beam 1 and 2 inside the crystal, respectively, Γ is the two beam coupling coefficient and α is the absorption coefficient. The transient behavior is modeled by the following:

$$I_i(z,t) = (1 - e^{-t/\tau})I_i(z,t \to \infty) + e^{-t/\tau}I_i(z,t = 0), \quad i = 1,2$$

where τ is a characteristic time constant and

$$I_i(z,t \to \infty) \equiv I_i(z).$$

By measuring the four intensities $I_1(0)$, $I_2(0)$, $I_1(d)$, and $I_2(d)$, both in the steady-state and as a function of time, the two-beam coupling coefficient Γ and the response time τ can, therefore, be obtained from the above equations.

Figures 3, 4, and 5 show the absorption spectra of SBN:60, SBN:Ce, and $BaTiO_3$, respectively. Several interesting observations can be made. For one, the band edge shifts from 400 nm in SBN:60 to 430 nm in SBN:Ce, while in $BaTiO_3$, a distinct band edge is not identifiable due to, presumably, the presence of a large Urbach tail.[4] Secondly, although the SBN:60 sample was not intentionally doped, there are signs of deep level impurities evidenced by perturbations in the spectrum near 550 nm. In the spectrum of $BaTiO_3$ at 550 nm and, to a lesser extent, near 620 nm similar observations can also be made. Finally, from Figure 4 is seen that the addition of cerium into SBN results in a crystal with a spectrum that is rather featureless with a broad deep level centered at 480 nm.
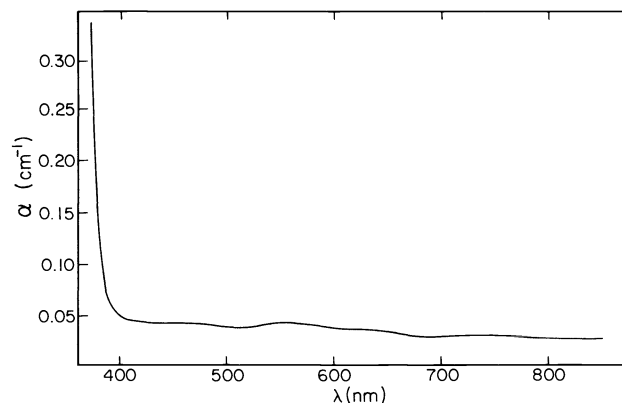

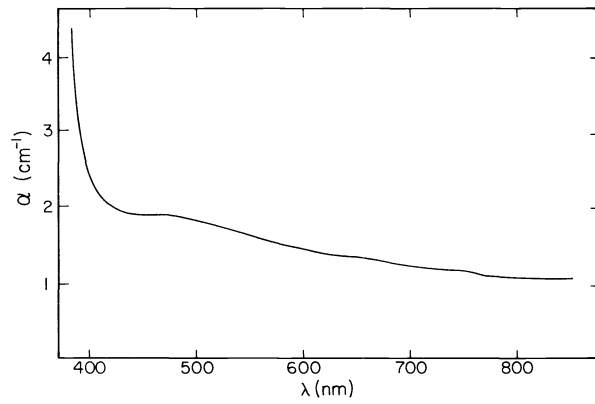Figure 3. Absorption spectra of SBN:60
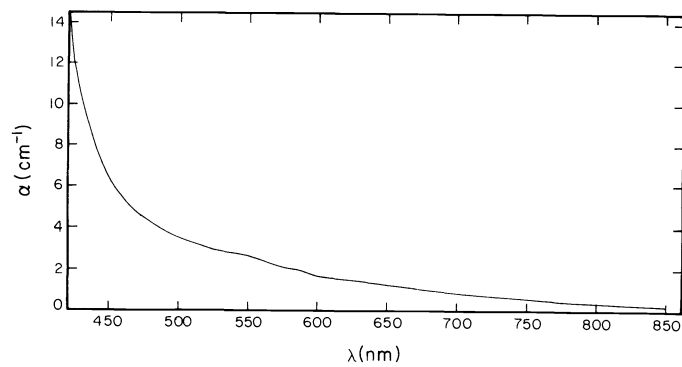
Figure 4.   Absorption spectra of SBN:Ce

Figure 5.   Absorption spectra of BaTiO$_3$

First principle calculations using the band transport model[5] can be used to derive expressions for Γ and τ. Solutions to the photorefractive equations developed most fully by Kukhtarev[6,7,8] show that Γ and τ can be represented functionally as follows:

$$\Gamma = \Gamma(k_g, E_o, \lambda, T; r, N_D, N_A, \varepsilon, n)$$

$$\tau = \tau(k_g, E_o, \lambda, T, I_o; s, \gamma_R, \mu, N_o, N_A, \varepsilon)$$

where the experimentally controlled variables are

k_g = grating wave number

E_o = applied field (normal to grating planes)

λ = wavelength of incident light

T = temperature

I_o = total irradiance

while the material parameters are

r = effective electrooptic coefficient

s = photoionization cross-section

γ_R = two-body recombination rate

μ = mobility

N_D = number of donors under dark conditions

N_A = number of traps under dark conditions

ε = static dielectric constant

n = background refractive index

These equations were applied to cerium doped SBN(10^{18}cm^{-3} Ce atoms) and the theoretical results obtained are displayed in Figures 6-9.
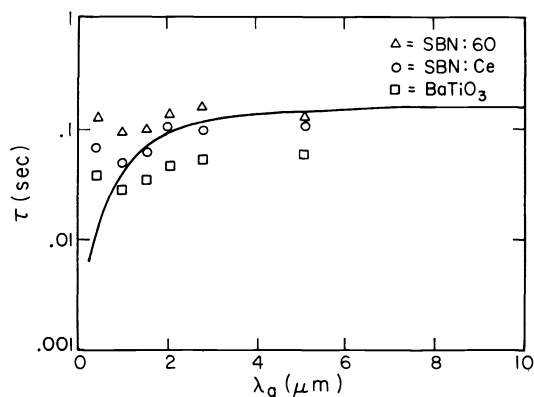

Figure 6: Response time vs. grating wavelength at I_o = 1W/cm^2 and λ = 0.5145 μm

Figure 6 gives the actual response times as a function of grating wavelength for the three crystals along with the theoretical curve for SBN:Ce while Figure 7 displays the corresponding two-beam coupling coefficients. Although BaTiO$_3$ is currently the fastest material of the three, it is significantly less photorefractive than SBN:Ce. Therefore, a method was sought for SBN:Ce in which coupling strength could be traded for speed in order to

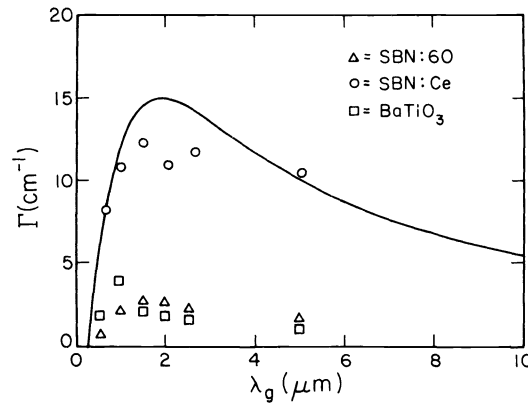produce a crystal with a 1 msec response time at $1W/cm^2$ irradiance while still keeping Γ greater than $1\ cm^{-1}$.

Figure 7. Coupling coefficient vs. grating wavelength for $E_O = 0V/cm$ and $\lambda = 0.514\ \mu m$

Such a scheme was proposed in Reference 9 which suggested that Γ and τ could be modified as indicated in Figures 8 and 9 by varying the trap density N_A through reduction and oxidation treatments. In principle, if in SBN:CE N_A could be reduced from its current value of $10^{16}\ cm^{-3}$ to $5 \times 10^{14}\ cm^{-3}$, the crystal would then possess a coupling coefficient of $2\ cm^{-1}$ with a response time of only 0.001 sec. Therefore, an effort was undertaken in which the SBN:Ce sample was heated to temperatures ranging from $300°C$ to $800°C$ for various lengths of time in atmospheres of differing oxygen partial pressures and then quickly cooled to room temperature at which point the crystal would be repoled, its absorption spectrum taken, and finally, its photorefractive properties measured.
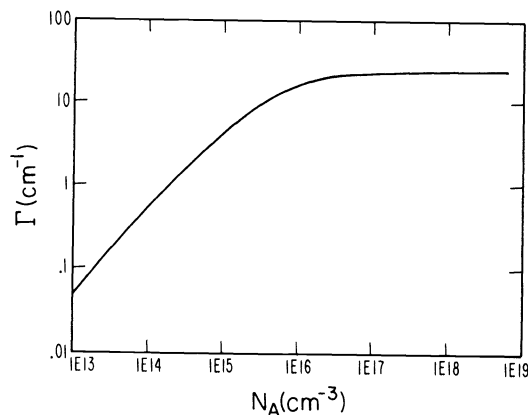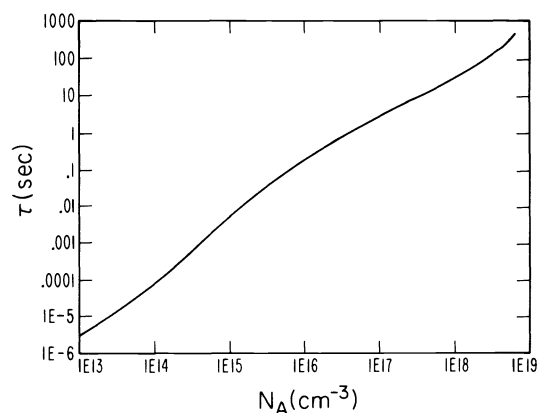

Figure 8. Coupling coefficient vs. trap density

Figure 10. Response time vs. trap density at I_o = 1W/cm^2

After performing this exercise many times we first observed that the SBN:Ce crystal was never irreversibly damaged by this treatment which is a significant result since BaTiO$_3$ would often crack when subjected to the same process. Secondly, we were able to show that the two-beam coupling coefficient can be controlled with the heat treatment technique. In fact, values of Γ ranging from less than 0.1 cm^{-1} to 15 cm^{-1} were measured in treated SBN:Ce. However, unfortunately, the desired decrease in response time was never witnessed regardless of the specifics of the oxidation and reduction technique. Rather, τ remained unchanged at its typical value of 100 msec at 1W/cm^2 irradiance. As of yet, we have no satisfactory explanation for this behavior, but we do believe this result may bring some further insight into the photorefractive mechanism in SBN:Ce.

BaTiO$_3$ crystals were also subjected to this treatment in the hope of increasing its speed. As was the case for SBN:Ce, only the two beam coupling coefficient was affected by the oxidation and reduction process. The response time remained virtually unchanged.

Although cerium is apparently an important photorefractive species for SBN:Ce, the active impurity or impurities in SBN:60 and BaTiO$_3$ remain unknown. As an attempt to discover these elements, an analysis was performed by nuclear activation of SBN:60, SBN:Ce, and BaTiO$_3$. Table 1 shows the results. Since undoped SBN:60 is photorefractive, while containing only trace quantities of cerium, we much conclude that Ce is not the only photorefractive species for SBN:60. In fact, Table 1 indicates that there are significant amounts of Fe, Ni, Mo, and Ta impurities present in the undoped SBN:60 crystal, and Fe and Ni, for example are known to be effective photorefractive centers in LiNbO$_3$.[10] In BaTiO$_3$ we similarly see large quantities of iron along with considerable Sr content. Since strontium has not yet been directly associated with the photorefractive effect, we attribute the activity in BaTiO$_3$ to iron. Further studies in the response of BaTiO$_3$ versus iron concentration, however, are needed to verify this claim.

Comparison of Photorefractive SBN:60, SBN:Ce, and BaTiO$_3$

In order to decide if a given crystal is a useful photorefractive material, several criteria must first be defined on which to base the evaluation. The optical quality of the material is usually the property given most attention to initially. A crystal with striations, defects, or other imperfections, for example, will not find much practical use in an optical system. The optical quality of each of the three crystals we considered was excellent. Both of the SBN crystals were striation-free and their optical quality was independent of whether the crystal was poled or not. However, high optical quality in BaTiO$_3$ was only observed when the crystal was fully poled--partial depoling by a laser beam, for example, would dramatically decrease its optical clarity. Therefore, on the basis of optical quality all three crystals were similar with the only exception that the SBN crystals are better suited for high-power laser applications.

Since the two-beam coupling coefficient Γ directly describes the magnitude of the photorefractive effect in a crystal, Γ can be used directly as a quantity with which to compare photorefractive materials. A crystal with a coupling coefficient less than 1 cm^{-1} is considered weakly photorefractive, while one with 1 cm^{-1} < Γ < 10 cm^{-1} is rated moderately

photorefractive. Crystals whose coupling coefficients are greater than 10 cm^{-1} are labeled very photorefractive.

Table 1. Elemental Analysis by Weight of BaTiO$_3$, SBN:60 and SBN:Ce

Elements & Units	BaTiO$_3$	SBN:60	SBN:Ce
U PPM	< 0.1	< 0.1	< 0.1
TH PPM	< 0.2	< 0.3	< 0.2
NA PPM	< 30.0	30.0	< 30.0
SC PPM	1.2	0.04	0.03
CR PPM	< 5.0	< 5.0	< 5.0
FE %	0.040	0.029	0.014
CO PPM	0.2	0.3	0.3
NI PPM	< 50.0	50.0	50.0
ZN PPM	5.0	7.0	5.0
AS PPM	< 1.0	< 1.0	< 1.0
SE PPM	< 10.0	< 5.0	< 5.0
BR PPM	< 0.5	< 0.5	< 0.5
MO PPM	< 2.0	11.0	4.0
SB PPM	0.7	0.5	0.5
CS PPM	< 1.0	< 0.2	< 0.2
BA PPM	540000.0	160000.0	150000.0
LA PPM	0.4	0.2	1.0
HF PPM	< 1.0	< 0.2	< 0.2
TA PPM	< 0.5	12.0	13.0
W PPM	< 3.0	< 3.0	1.0
AU PPB	< 5.0	< 5.0	5.0
CE PPM	2.0	< 1.0	47.0
ND PPM	INTERFER	INTERFER	INTERFER
SM PPM	0.05	0.01	0.32
EU PPM	< 0.05	0.07	0.10
TB PPM	< 0.1	< 0.1	< 0.1
YB PPM	< 0.50	< 0.05	0.05
LU PPM	< 0.06	< 0.01	< 0.01
SR PPM	900.0	148000.0	135000.0
RB PPM	< 5.0	< 5.0	< 5.0

Using these definitions as a criterion for evaluation, we see that while both SBN:60 and BaTiO$_3$ are moderately photorefractive, the SBN:Ce sample, whose coupling coefficient approaches 15 cm^{-1}, is considered very photorefractive. On the basis of this criterion, therefore, SBN:Ce is the best photorefractive material of the three.

In order to use a given crystal in a high-speed optical system, its response time needs to be sufficiently short. Therefore, using τ, the photorefractive response time, we see that BaTiO$_3$ is better suited for high-speed applications than are SBN:Ce and SBN:60, although SBN:Ce is only a factor of 2 to 3 slower.

A difficulty arises when, as in our case, crystals with different coupling coefficients and response times need to be compared. In systems using the transient response of a photorefractive material it is possible that a slow crystal with a large Γ may, in fact, exhibit higher coupling in a given unit of time than a crystal with a fast response but small Γ. Therefore, the two-beam coupling sensitivity S_2 was defined. It is given by

$$S_2 = \frac{e^{(\Gamma - \alpha)\cdot(1cm)}}{I_o \tau}$$

Physically, it describes how much coupling a given crystal of unit length will provide when irradiated with a finite amount of energy.

On the basis of this criterion we obtain the following values of two-beam coupling sensitivity for the three crystals considered:

$$S_2 \simeq 9.0 \times 10^1 \ cm^2/J \qquad (BaTiO_3)$$

$$S_2 \simeq 2.0 \times 10^2 \ cm^2/J \qquad (SBN:60)$$

$$S_2 \simeq 1.0 \times 10^5 \ cm^2/J \qquad (SBN:Ce)$$

We, therefore, can see that both of the SBN crystals are more sensitive than $BaTiO_3$. In fact, S_2 for SBN:Ce is 3 orders of magnitude larger than the corresponding value for $BaTiO_3$. Thus, in systems which rely on the transient response of a photorefractive crystal, the best candidate of the three we considered is SBN:Ce.

Conclusion

A major goal of our work has been the growth of high optical quality SBN crystals which would be more photorefractive than $BaTiO_3$. This was accomplished by growing striation-free SBN:60 and SBN:Ce. In fact, optically excellent crystals of SBN:60 and SBN:Ce can now be had as cubes approaching 1 cm a side. When their photorefractive properties were measured they were found to be, in most cases, better photorefractive crystals that $BaTiO_3$. In fact SBN:Ce was shown to have a significantly larger two-beam coupling coefficient and two-beam coupling sensitivity than that of $BaTiO_3$. However, the photorefractive process would reach steady-state sooner in $BaTiO_3$ than it would in either SBN:60 or SBN:Ce due to the shorter response time in $BaTiO_3$.

Acknowledgements

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