Copper-ion point defects in the photorefractive material $(K_xNa_{1-x})_{0.4}(Sr_yBa_{1-y})_{0.8}Nb_2O_6$

Jiang Quanzhong, Lu Xinliang, Song Yongyuan, Sun Daliang, and Chen Huanchu
Institute of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China

(Received 9 November 1993; revised manuscript received 28 February 1994)

We show that Cu ions doped in $(K_xNa_{1-x})_{0.4}(Sr_yBa_{1-y})_{0.8}Nb_2O_6$ (KNSBN) form two energy levels in the band gap, which increase the effective charge-combination-center concentration N_{eff}. The two-wave coupling gain and the response speed of KNSBN crystals are increased while the photoconductivity and the effects of a dc field on the photorefractive properties are reduced. Self-pumped phase conjugation (SPPC) experiments have revealed that the effects of Cu ions on the photorefractive properties have a wavelength dependence. The SPPC response time at the e^{-1} level can be shortened to 200 ms.

During recent years, many related papers[1] have suggested that photorefractive (PR) materials can be applied in many aspects of optical image processing and optical computing. However, some of their properties have given rise to many problems in practical applications. For example, $LiNbO_3$ has strong light scattering that will decrease the strength of the propagating beam considerably. Although $BaTiO_3$ has excellent PR properties, it is difficult to grow perfect single crystals. Besides, at room temperature, there exists a phase transition $4mm\text{-}mm2$ which causes spontaneous polarization in the [011] direction. $Sr_xBa_{1-x}Nb_2O_6$ (SBN) crystals have large electro-optic coefficients, but the Curie temperatures T_C are quite low ($Sr_{0.75}Ba_{0.25}Nb_2O_6$, $T_C = 39\,^\circ C$), so, in crystal processing or at room temperature, they will depolarize. In 1981, Chen and Xu developed a ferroelectric crystal $(K_xNa_{1-x})_{0.4}(Sr_yBa_{1-y})_{0.8}Nb_2O_6$ (KNSBN),[2] which has the advantages of high Curie temperature, high electro-optic figure of merit (n^3r_{ij}/e; for KNSBN it is 6.00 and for $BaTiO_3$ it is 4.01),[3] and good mechanical properties. It has no phase transition at room temperature. It is expected that this crystal will become one of the most promising PR materials through modification.

As we know, the PR process includes free-electron (and/or hole) stimulation, transformation, and recombination to form an internal electric field. Thus, it is well accepted that doping new centers for charge stimulation and combination into a material is an effective way of improving the PR properties of a material. This idea has been proved in the cases of $LiNbO_3$:Fe,[4] SBN:Ce,[5] InP:Fe,[6] GaAs:Cr.[7] The KNSBN crystal has three kinds of lattice sites, *A*, *B*, and *C*, so it is suitable for introducing a large amount of transition-metal ions or rare-earth ions as dopants. This paper focuses on the effects of Cu ions on the PR properties of KNSBN crystals and the related mechanism.

All the KNSBN:Cu crystals were grown by the pulling method using the MCGS-3 system. The starting materials we used are 99.99% $BaCO_3$, $SrCO_3$, K_2CO_3, Na_2CO_3, Nb_2O_5, and CuO. They were mixed according to the compositions reported in Ref. 8. A very small amount of CuO was added to the mixture. The crystal growth procedures and conditions are the same as those reported in Ref. 8. The as-grown KNSBN:Cu crystals were annealed at 1050 °C for 24 h and then cut into samples with sizes of $5\times6\times6$ mm^3 along the *a*, *b*, and *c* axes. The samples were polished and polarized at 100 °C under a 6 kV/cm electrical field.

The transmission properties of the doped crystal are a reliable criterion for determining whether the ions will affect the PR properties of a material.[6] In addition, the wavelength at which the PR material exhibits better PR properties can be determined from the spectrum of the doped crystal. Figure 1 shows the transmission properties of the Cu-doped and undoped KNSBN crystals. From this figure we can see that the Cu ions have caused two absorption peaks at 475 and 495 nm. Because the positions of the peaks are not affected by the doping amount of CuO, we think these two peaks correspond to the intrinsic energy levels of Cu ions in KNSBN (i.e., 2.61 and 2.50 eV, respectively). These two deep energy levels formed by Cu ions can decrease the lifetime of free electrons[9] as well as the electron mobility and optical conductivity of KNSBN.

A ferroelectric material usually shows abnormal photovoltaic (APV) effects,[10] i.e., a high electrical voltage, which is hundreds of times that corresponding to the energy band gap, can be built up along the spontaneous polarization direction under a light beam of several milliwatts. In a closed circuit containing a photoferroelec-

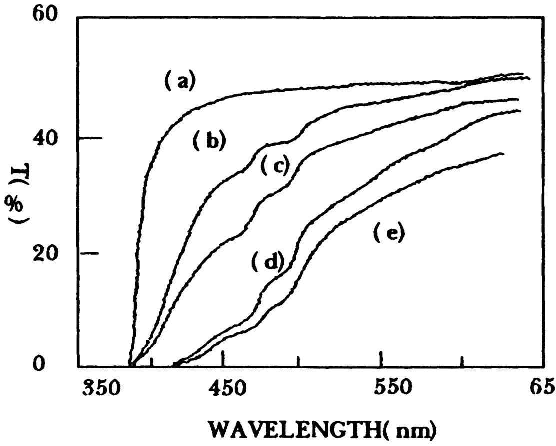

FIG. 1. Transmission spectra of doped and undoped KNSBN. (a) KNSBN; (b) KNSBN:Cu, 0.03 wt % CuO; (c) KNSBN:Cu, 0.04 wt % CuO; (d) KNSBN:Cu, 0.07 wt % CuO; (e) KNSBN:Cu, 0.1 wt % CuO.

0163-1829/94/50(6)/4185(4)/$06.00

tric crystal, the electrical current density can be represented by

$$j=j_{\mathrm{ph}}+(\sigma_d+\sigma_{\mathrm{ph}})V/L \ , \tag{1}$$

where j_{ph} is the APV current density, σ_d and σ_{ph} are the dark conductivity and photoconductivity, respectively, V represents the applied voltage, and L is the thickness of the sample. If $j=0$, the value of the APV electrical field can be represented by[11]

$$E_{\mathrm{ph}}=j_{\mathrm{ph}}/\sigma_d+\sigma_{\mathrm{ph}} \ . \tag{2}$$

The emission from a halogen-tungsten lamp is focused on a sample which is connected to a dc source and a 10^{-14} A galvanometer. Figure 2 shows the relations between the applied voltage and the photocurrent of (a) KNSBN and (b) KNSBN:Cu. From this figure, we can see the following. (a) The value of E_{ph} corresponding to the intersection point between the E axis and the straight line of photocurrent density vs the applied electrical field is not obviously affected by the light intensity for each sample. (b) The value of E_{ph} of KNSBN:Cu is larger than that of KNSBN. Up to now, this phenomenon still cannot be explained. (c) Compared to KNSBN, KNSBN:Cu has smaller photo- and dark conductivity. This is consistent with the above theoretical prediction.

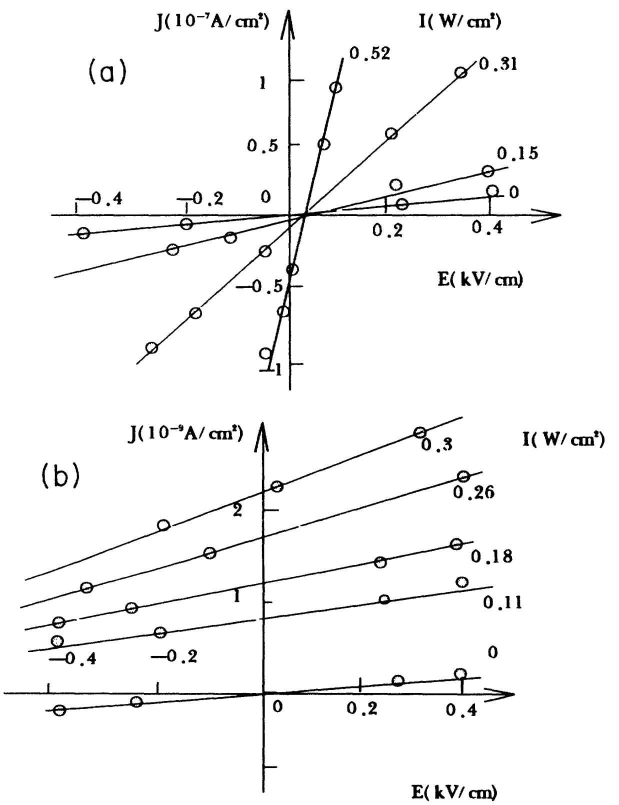

FIG. 2. Relation between the optical intensity I, the applied dc field E, and the current density j of (a) KNSBN and (b) KNSBN:Cu.

It is well accepted that the variation of the two-wave coupling properties can quantitatively reflect the influence of the doping ions on PR properties.[12] Two extraordinary polarized beams interfere with each other along the [001] direction in a sample and the energy distribution can be represented by

$$I(x)=I_0[1+m\cos(kx)] \ , \tag{3}$$

where $I_0=I_sI_R/(I_s+I_R)$,

$$m=2(I_RI_s)^{1/2}/(I_R+I_s)\cos 2\theta' \ ,$$

where I_R, I_s are the intensity of input pump beam and signal beam, respectively, and θ' is the angle formed by the beams in the sample, and $k=4\pi\sin\theta'/\lambda$ is the space frequency of the interference pattern or the modulus of the grating vector K. In the case of no external electrical field and $m \ll 1$, the amplitude of the PR electrical field is[13]

$$E=-\mathrm{Im}(k_BT/q)k/[1+(k/k_0)^2]^{1/2}\alpha(k) \ , \tag{4}$$

were $k_0=q(N_{\mathrm{eff}}/\epsilon\epsilon_0k_BT)^{1/2}$ is the Debye screening constant, ϵ is the permittivity in the direction of the PR electric field, N_{eff} represents the effective PR charge concentration, and $\alpha(k)$ is the electron-hole competition coefficient. For KNSBN:Cu crystals, $\alpha(k)$ is approximately equal to unity (this will be demonstrated by the following experimental results shown in Fig. 3 below). The gain coefficient can be represented by

$$\Gamma=i(2\pi/n_e)r_{\mathrm{eff}}E/\cos\theta' \ , \tag{5}$$

where r_{eff} is the effective electro-optic coefficient. When the grating vector is parallel to the c axis, it can be represented by

$$r_{\mathrm{eff}}=-n_0^4r_{13}(\sin\theta')^2+n_e^4r_{33}(\cos\theta')^2 \ . \tag{6}$$

We assume $K_u=k/[1+(k/k_0)^2]^{1/2}$, and K_u is a function of k (or θ'), K_u has its maximum value under the condition $k=k_0$. From this condition the effective charge concentration can be calculated. When the dependence of Γ on θ' (or k) is determined from experiment, then that of K_u on k (or θ') can be calculated by using formulas (4)–(6) with $n_e=2.28$, $n_0=2.30$, $\epsilon_{11}=588$, $\epsilon_{33}=500$, $r_{13}=50$ pm/V, $r_{42}=400$ pm/V, and $r_{33}=270$ pm/V.

We used the usual experimental setup for two-wave coupling in our experiments[14] and selected $I_s/I_R \ll 1$, so the gain is

$$\Gamma=d^{-1}\ln[I_s(I_R=0)/I_s(I_R=0)] \ , \tag{7}$$

where d is approximately equal to the thickness of the sample. Figure 3 shows the relation between the gain Γ and the angle 2θ formed by the two beams outside the sample and that between K_u and 2θ of KNSBN:Cu and KNSBN.

(a) For KNSBN:Cu, K_u get its maximum value at $2\theta=35°$ and the calculated effective charge density is 5.10×10^{16} cm^{-3}. For KNSBN, K_u get its maximum value at $2\theta=23°$ and the calculated effective charge density is 2.83×10^{16} cm^{-3}. As the value of N_{eff} is improved due to the doping of Cu ions, the constant k_0 increases and k/k_0 decreases. Because, in formula (4), the decrease of k/k_0 results in the increase of K_u for $k/k_0 \gg 1$, the PR electrical field is increased and the gain becomes larger for the doping of Cu ions in KNSBN.

(b) Since the gain is always positive, the electrons play

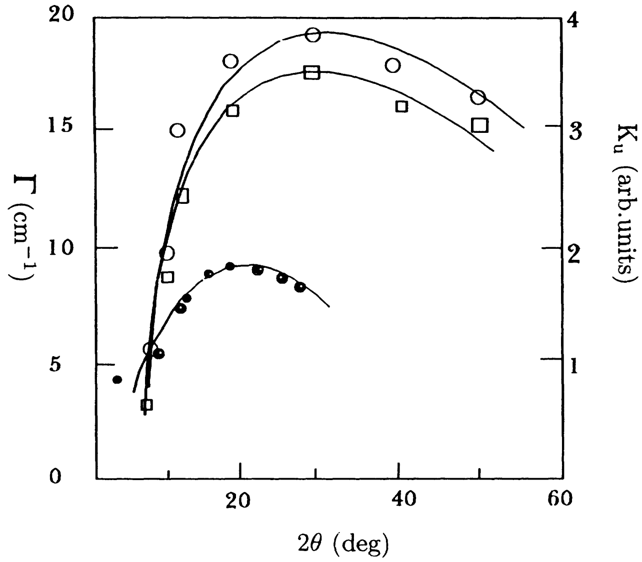

FIG. 3. Two-wave coupling gain coefficient (● for KNSBN and ○ for KNSBN:Cu) and K_u (□) of KNSBN:Cu as a function of 2θ, $\lambda=488$ nm.

the dominant role in the electron-hole competition. That is to say, $\alpha(k)$ is approximately equal to unity.

(c) Although they have decreased the electron mobility, Cu ions have improved the response speed (Fig. 4). We think that this phenomenon is attributable to a larger number of optical free electrons induced by the Cu ions, which have shortened the response time required for electron simulation, combination, and transition to reach an equilibrium state.

Figure 5 shows the experimental results of degenerate four-wave mixing (DFWM) of KNSBN:Cu and KNSBN in a dc electrical field, under experimental conditions $I_s=46$ mW/cm^2, $I_1/I_2=2$, $2\theta=40^\circ$. From Fig. 6, we can see that (a) with increase of the external electrical field, the DFWM reflectivities of KNSBN:Cu and KNSBN are both increased; (b) compared to KNSBN, KNSBN:Cu shows less increase in DFWM reflectivity. These two phenomena can be well explained by the following theory.

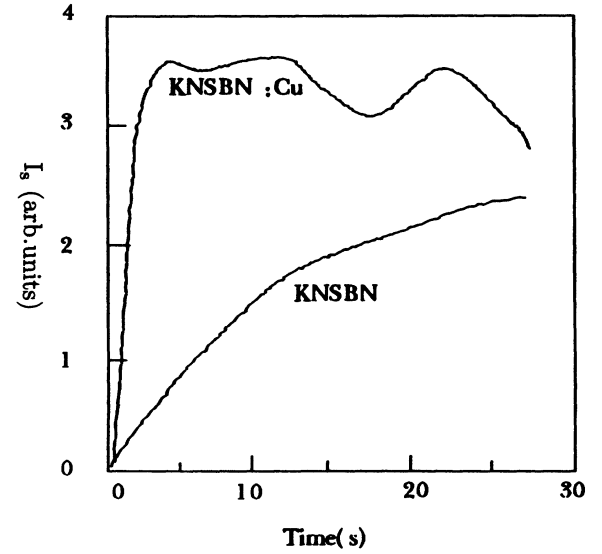

FIG. 4. Time response in two-wave coupling of KNSBN and KNSBN:Cu.

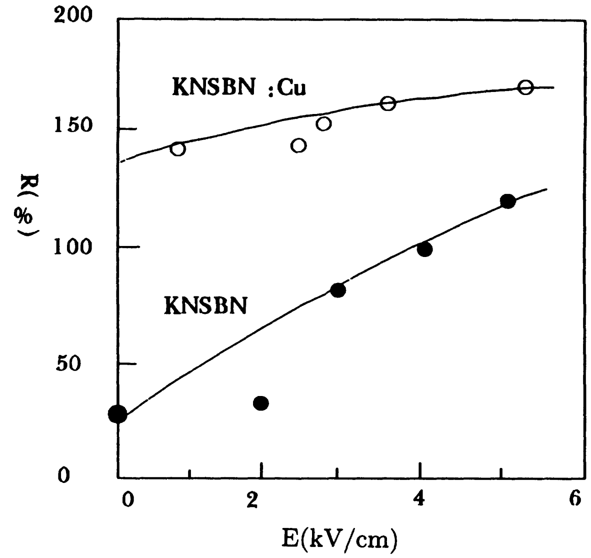

FIG. 5. Dependence of the DFWM reflectivity on dc electrical field. $\lambda=488$ nm.

As we know, the DFWM reflectivity essentially depends on the $\pi/2$-phase-shifted PR field represented by[15]

$$E(90^\circ)=mE_q[(E_q+E_D)E_D+E_0^2]/[(E_q+E_D)^2+E_0^2]\,, \tag{8}$$

where $E_D=kk_BT/e$ is the diffusion field, $E_q=2\pi N_{\text{eff}}/k\epsilon\epsilon_0$ is the PR electrical field limit, k_BT represents the thermal energy, and E_0 represent the applied electrical field. If $y=E_0^2$, we have

$$d[E(90^\circ)]/dy=mE_q^2(E_q+E_D)/[(E_q+E_D)^2+E_0^2]^2\,. \tag{9}$$

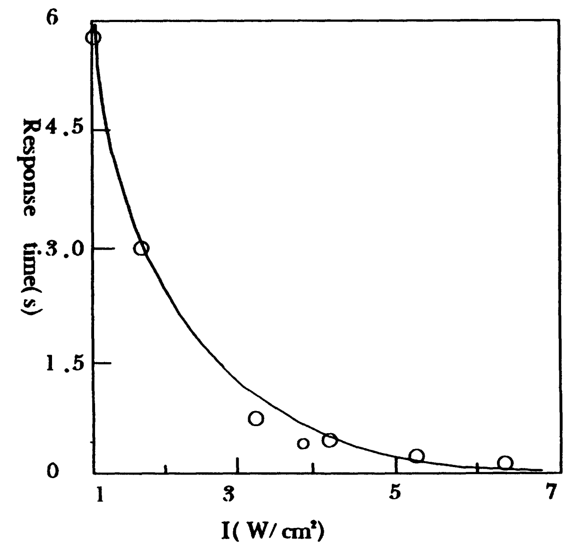

FIG. 6. Response time (at the e^{-1} level) vs input energy at $\lambda=514.5$ nm.

This formula shows that $d[E(90°)]/dy > 0$. That is to say, $E(90°)$, along with the DFWM reflectivity, increases with the applied electrical field for both KNSBN and KNSBN:Cu. For KNSBN:Cu under the experimental conditions, $E_D = 2.28 \times 10^5$ V/m and $E_q = 2.56 \times 10^6$ V/m. For KNSBN, $E_D = 2.28 \times 10^5$ V/cm and $E_q = 1.15 \times 10^6$ V/m. In our experiment, the applied electrical field is much smaller than E_q, so E_0 in (9) can be neglected. The formula is converted into

$$d[E(90°)]/dy = ME_q^2/(E_q + E_D)^3 \ . \tag{10}$$

Thus,

$$d^2E(90°)/dy\, dE_q = ME_q(2E_D - E_q)/(E_q + E_D)^4 \ .$$

For both KNSBN and KNSBN:Cu crystals, $E_q > 2E_D$ and $d^2[E(90°)]/dy\, dE_q < 0$, that is to say, with increasing E_q (or N_{eff}), the effect of the applied field on the PR effect is decreased.

Since the PR properties have been modified by doping with Cu ions, there is a possibility of realizing self-pumped phase conjugation (SPPC) by using KNSBN:Cu. Now we have demonstrated cat SPPC using KNSBN:Cu at different wavelengths. The mechanism is studied in detail in Ref. 16 and is different from that reported in Ref. 17. The basic SPPC properties of KNSBN:Cu are given in Table I. This table shows that the SPPC output at a certain wavelength depends greatly on the doping concentration. At $\lambda = 514.5$ nm, increase of the doping concentration will greatly reduce the SPPC output. This is due to enhanced absorption at this wavelength from the increased amount of doping ions. However, at $\lambda = 632.8$ nm, as the doping ions increase, the SPPC output is improved. This phenomenon is because, at this wavelength that is far from the intrinsic wavelength of Cu ions in KNSBN, the Cu ions only act as electron recombination centers and other ions such as Nb^{4+} ions or ions from the starting materials provide the free electrons in the PR process. The increase of the amount of Cu ions will improve the effective recombination-center concentration as well as the PR electrical field and the SPPC reflectivity. Thus, at this wavelength, the PR properties show a dependence on the doping concentration.

TABLE I. The dependence of SPPC reflectivity R (%) on the dopant concentration (wt % CuO) and wavelength λ (nm).

		CuO		
λ	0.03	0.04	0.07	0.1
632.8		40	55	63
514.5	62	68	40	29
488.0	42	38		

The relation between the response time at the e^{-1} level and the input energy when a cylindrical lens was used is shown in Fig. 6. The increase of the input energy can greatly reduce the response time, to 200 ms.

In conclusion, we present a comprehensive study on the effects of Cu ions on the PR properties of KNSBN. The Cu ions can form two energy levels in the band gap and act as centers for free-electron stimulation and recombination to increase the coupling gain coefficient, shorten the response time, and improve the SPPC reflectivity, which properties enable KNSBN:Cu to be a promising PR material for applications in optical information processing.

---

[1] P. Günter and J.-P. Huignard, in *Photorefractive Materials and Their Applications (I) and (II)*, edited by P. Günter and J.-P. Huignard, Topics in Applied Physics Vols. 61 and 62 (Springer-Verlag, Berlin, 1989).

[2] H. C. Chen and Y. H. Xu, Physics (China) **10**, 729 (1981).

[3] R. R. Neurgaokar, W. K. Cory, J. R. Oliver, M. D. Ewbank, and W. F. Hall, Opt. Eng. **25**, 392 (1987).

[4] H. Kurz, E. Knatzig, W. Keune, and H. Engelman, Appl. Phys. **2**, 355 (1977).

[5] G. Rakuljic, A. Aariv, R. R. Neurgaonkar, and W. K. Cory, Opt. Eng. **25**, 1212 (1986).

[6] G. C. Valley, A. S. Smirl, M. B. Klein, K. M. Bohnort, and T. F. Boggess, Opt. Lett. **11**, 647 (1986).

[7] H. Mao, F. Li, and X. Deng, Opt. Lett. **15**, 888 (1990).

[8] Q. Z. Jiang, Y. Y. Song, D. L. Sun, and H. C. Chen, Chin. Phys. Lett. **36**, 637 (1991).

[9] *Semi-insulating III-V Materials,* edited by P. C. Look and J. S. Blakemore (Shiva, Mantwich, England, 1984), Sec IV.

[10] A. M. Glass, D. Von der Linde, and T. J. Negran, J. Appl. Phys. **25**, 233 (1977).

[11] D. Von der Linde and A. M. Glass, Appl. Phys. **8**, 85 (1975).

[12] P. Günter, Phys. Rep. **93**, 199 (1982).

[13] F. P. Slrohkendll, J. M. C. Jonath, and R. W. Hellwarth, Opt. Lett. **11**, 312 (1986).

[14] Q. Z. Jiang, Y. Y. Song, D. L. Sun, and H. C. Chen, Chin. Sci. Bull. **36**, 637 (1991).

[15] K. Walsh, A. K. Powell, and T. L. Hall, J. Opt. Soc. Am. **7**, 288 (1990).

[16] Q. Z. Jiang, Y. Y. Song, L. X. Liang, D. L. Sun, and H. C. Chen, Nonlinear Opt. **1**, 307 (1991).

[17] J. Feinberg, Opt. Lett. **7**, 486 (1982).