Photorefractive properties of manganese-modified potassium sodium strontium barium niobate crystals

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The crystal preparation, the transmissivity, and the properties of the two-beam coupling and the self-pumped phase conjugation (SPPC) of manganese-modified potassium sodium strontium barium niobate (KNSBN) single crystals are reported. The Mn ions doped in the KNSBN can form a deep energy level of 2.53 eV. The two-beam coupling gain coefficients of Mn-doped KNSBN crystal are larger than 37 and 35.3 cm^{-1} for the transmission and the reflecting photorefractive index gratings, respectively. The very striking optical diode effect is observed in our experiment. The maximum SPPC reflectivity is higher than 40%. [S0163-1829(97)03204-9]

The potential of photorefractive (PR) crystals has exhibited a wide range of nonlinear optical applications, including phase conjugation, image amplification, information processing, optical computing, optical resonators, inertial navigation devices, associative memories, etc.[1] Most of these experiments have been performed using $BaTiO_3$ because of its excellent PR properties. However, it is difficult to grow perfect $BaTiO_3$ single crystals, and its tetragonal-orthorhombic phase transition occurs at 5–6 °C, which causes a rotation of the spontaneous polarization from the [001] direction to the [011] direction. $LiNbO_3$ has relatively low PR sensitivity, and strong light scattering decreases the strength of the propagating beam considerably. $KNbO_3$ is easy to crack at the phase transition $4mm$-$mm2$ when it is cooled down to room temperature after growth. $Sr_xBa_{1-x}Nb_2O_6$ crystals have quite low Curie temperatures, so they will depolarize in crystal processing or at room temperature. Now, one of the leading PR crystals is potassium sodium strontium barium niobate (KNSBN) single crystal with nonfilled tungsten bronze (TB) type structure, which has the advantages of high Curie temperatures, large electro-optic coefficient, good mechanical properties, and no phase transition at room temperature.[2] This crystal structure provides a possibility of improving crystal properties by adjusting the compositions of the material and doping a new ion in it. The purpose of this work is to study the PR properties of Mn-modified KNSBN crystals, including the crystal growth, the transmissivity, and the properties of two-beam coupling and self-pumped phase conjugation (SPPC).

The typical designed compositions of the crystals are $(K_{0.5}Na_{0.5})_{0.2}(Sr_{0.75}Ba_{0.25})_{0.9}Mn_kNb_2O_6$ (KNSBN:Mn, $0 \leqslant k \leqslant 0.005$). The starting materials are 99.99% K_2CO_3, Na_2CO_3, $SrCO_3$, $BaCO_3$, Nb_2O_5, and MnO_2. The main constituents in stoichiometric proportions were already mixed. A very small amount of 0.06 wt % MnO_2 was added to the mixture. The processing of the mixture and the crystal growth conditions are the same as those described in Ref. 2. From the experimental results of the crystal growth that the Mn can be easily doped, we think that its distribution coefficient is greater than unity. The as-grown crystals were annealed at 1050 °C for 24 h to reduce residual stress formed during growth. The crystals obtained in this way have good optical quality. The KNSBN is colorless and transparent, and the KNSBN:Mn is pale brown. Their crystal structure and lattice parameters were measured by a D/MaX-rA x-ray powder diffractometer. The experiment results show that they have the same diffraction peak position belonging to class $4mm$ at room temperature and there is no difference between their lattice parameters: $a=b=1.2488\pm0.0001$ nm and $c=0.3955\pm0.0001$ nm. Atomic absorption analysis using a 180-80 atomic spectrum absorptiometer shows that the manganese content is about $k=0.0026$, which implies, on the average, about one Mn ion in 77 unit cells. The KNSBN:Mn crystal was cut, along the a, b, and c axes, into two samples with the sizes of $1.5\times3\times6$ (sample 1) and $4\times5\times6$ (sample 2) mm^3, respectively, and the KNSBN crystal was cut into the same size as sample 1. Then they were optically polished and oriented into single domain at 100 °C with a 6 kV/cm dc electric field for about 1 h in silicone oil.

The transmission property of a doped crystal is a reliable criterion for determining if the ions will affect the PR properties of the crystal.[3] Furthermore, the wavelength at which the PR crystal exhibits better PR properties can be determined from the transmission spectrum of the doped crystal. Curves (a) and (b) in Fig. 1 show the transmission spectra of KNSBN and KNSBN:Mn crystals, respectively, which were measured with samples 1 on a Hitachi-340 UV-VIS-NIR spectrophotometer with a slit width of 2 nm. The incident light with the electric field along the crystal c axis was aligned along the crystal a axis. Obviously, the Mn dopant effectively increases the absorption of the crystal in the wavelength range of 390–560 nm. So we close a 514.5 nm wavelength beam from an argon-ion laser to perform our PR and SPPC experiments. Based on the ligand field theory for the transition metals, curve (a) implies the eigentransition of the d electrons of Nb with an electron configuration (Kr)

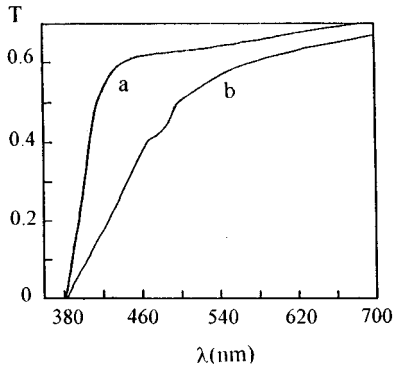

FIG. 1. Transmissivities vs incident light wavelength of undoped (a) and Mn-doped (b) KNSBN.

$4d^4 5s^1$ and shows a band gap of about 3.18 eV (390 nm), and curve (b) shows an obvious absorption peak at a wavelength of about 490 nm, which corresponds to a deep energy level of 2.53 eV. The deep level which was formed by the Mn ions implies that the Mn ions are able to act as centers for free-charge carrier stimulation and recombination, and the PR properties will be modified.

The predominant feature of the PR effect is that there exists a phase shift between an interference pattern and the PR index grating, which results in the energy transference, causing one beam to gain intensity at the expense of the other beam, i.e., two-beam coupling. The variation of the two-beam coupling properties can quantitatively reflect the influence of the doping ions on the PR properties of crystals.[4] The usual experimental setup[1] was used in our experiments. The two-beam coupling gain coefficients Γ,[1] as a function of various external crossing angles 2θ of the optical beams, were measured with samples 1 in which the PR space-charge field produces a transmission PR index grating with the wave vector along the crystal c axis. An extraordinarily polarized beam emitted from an argon-ion laser at 514.5 nm was split into two beams, signal beam I_S and reference beam I_R with an intensity ratio I_S/I_R of about 10^{-3}, to interfere with each other and to form an interference pattern along the [001] direction in the single-domain crystal. The photoelectric detector D connected to an X-Y recorder was used to record the variation of the signal beam. The experimental results for Γ at various angles 2θ are shown in Fig. 2. The maximum gain coefficient measured in KNSBN:Mn crystal is larger

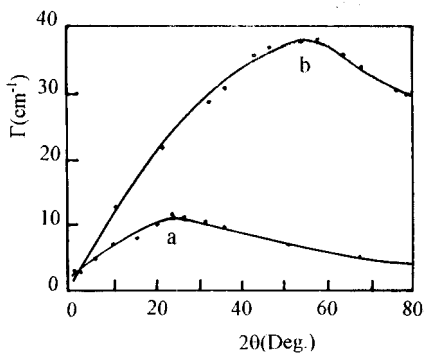

FIG. 2. Two-beam coupling gain coefficients Γ at various angle 2θ of undoped (a) and Mn-doped (b) KNSBN.

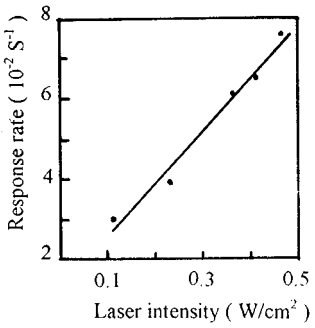

FIG. 3. Two-beam coupling response rate vs input laser intensity of KNSBN:Mn crystal.

than 37 cm^{-1} at $2\theta \approx 57°$, which is the largest value measured in KNSBN family crystals.[2] The inverse of the response time for the two-beam coupling in sample 1 of KNSBN:Mn crystal was also measured as shown in Fig. 3. The effective acceptor density[1] of KNSBN:Mn crystal was calculated to be 14.2×10^{16} cm^{-3}.

The gain is always found to be positive in our experiment. Therefore, the energy transfer directions is in the negative c direction, implying that electrons play the dominant role in the charge transport mechanism. Probably, there are three donor/acceptor pairs (Mn^{2+}/Mn^{3+}, Mn^{3+}/Mn^{4+}, and Mn^{6+}/Mn^{7+}) for the exact ionic valence of Mn in the crystal to be determined. In the TB-type structure, the C site is ninefold coordinated, and has smaller space size compared with the $A1$ and $A2$ sites.[5] The Mn ions, having small effective ionic radius in the oxygen coordination, prefer to occupy the C sites. Indeed, we have also demonstrated that the Mn ions doped in the KNSBN crystals occupy only the C site.[6] We can see that the Mn-O ninefold coordination polyhedron has the site symmetry D_{3h}, and that the relative splitting of the $3d$ orbit of the Mn ions in the C site can be shown in Fig. 4 based on the ligand field theory and the group theory. Take Mn^{3+}/Mn^{4+}, for example, and simply postulate it as the only donor/acceptor pair; a possible distribution in the split orbits of the d electrons of the Mn^{3+} ions with the electron configuration $(Ar)3d^4$ and of the Mn^{4+} ions with the electron configuration $(Ar)3d^3$ can also be shown in Figs. 4(b)

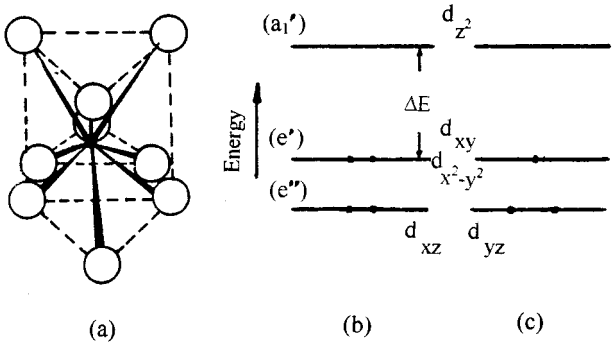

FIG. 4. (a) Nearest-neighbor oxygen atoms around Mn doped in C site. (b) The relative splitting of the $3d$ orbit of the Mn ion, the symmetry of the split orbits, and a possible distribution in the split orbits of the d electrons of the Mn^{3+} ions. (c) Same illustration as (b) for Mn^{4+} ions.

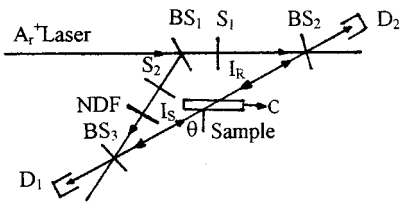

FIG. 5. Experimental arrangement of studying the contradirectional two-beam coupling.

and 4(c), respectively, based on the Pauli exclusion principle and the law of lowest energy. Compared with Fig. 1, ΔE is 2.53 eV.

An experimental arrangement with the above-mentioned setup, as shown in Fig. 5, was used to study the contradirectional two-beam coupling with samples 1 in which the PR space-charge field produces a reflecting PR index grating, which is necessary to cause the energy transference between the contradirectional two beams, with the wave vector perpendicular to the crystal c axis. The gain coefficient Γ can be written in the form $\Gamma = L^{-1}\ln(T_S/T_R)$, where $T_S = I_S'/I_S$ and $T_R = I_R'/I_R$ are the transmissivities of the signal and the reference beams with coupling, respectively. In our experiments, the Brewster angle was $\theta \approx 65°$ and the intensity ratio I_S/I_R was about 0.1. When $I_S \approx 0.1$ and $I_R \approx 1$ mW, the ratio T_S/T_R was measured in KNSBN:Mn to be larger than 200, so $\Gamma > 35.3\ \mathrm{cm}^{-1}$. The energy transference between the two coherent beams was observed along the positive direction of the c axis of the KNSBN:Mn crystal. No energy transference was observed in undoped KNSBN crystal. We also observed that the single-beam asymmetric transmission in the KNSBN:Mn along the crystal c axis, i.e., the so-called optical diode effect, was very striking.

In the two-beam energy coupling process, the energy transference is considered as an exponential gain per unit length with the gain coefficient Γ.[1] For our KNSBN:Mn crystal, the absorption occurs in a wavelength range shown in Fig. 1, and should have little effect on the measurements reported in Figs. 2 and 5. However, the error in measuring the transmission beam intensity, caused by the absorption at

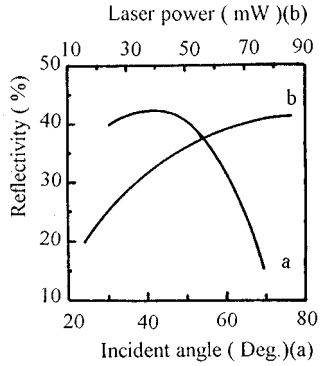

FIG. 6. The SPPC reflectivity R vs incident angle θ ($W = 74$ mW) (a) and vs laser power W ($\theta = 45°$) (b) of KNSBN:Mn crystal.

the wavelength of 514.5 nm, is difficult to exactly estimate now.

The experimental arrangement of studying the SPPC properties of KNSBN:Mn crystal with sample 2 was the same as that shown and described in Ref. 7. The relations of reflectivity R versus incident angle θ and versus incident laser power W were measured as shown in Fig. 6. From Fig. 6, we see that the maximum SPPC reflectivity R is higher than 40%; R decreases greatly when the θ becomes very large, and it increases with W and then saturates.

The time response is relatively slow if compared with Cu-doped KNSBN crystal. When $W = 60$ mW, it needs about 20 s before the conjugation wave appears, and needs another 20 s to reach its maximum value. The response time is quicker at 488.0 nm and slower at 632.8 nm than that at 514.5 nm.

In conclusion, the predominant feature of KNSBN:Mn crystal is of large two-beam coupling gain coefficients compared with other cation-doped KNSBN crystal, especially for the contradirectional two-beam coupling. The practices of the above-mentioned optical diode effect of KNSBN:Mn crystal are significant and worth further study.

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