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Photorefractive Properties of Co-Doped Potassium Sodium Strontium Barium Niobate Crystals

The transmissivity and the results of two-beam coupling and self-pumped phase conjugation (SPPC) experiments on Co-doped potassium sodium strontium barium niobate (KNSBN) single crystals are reported. The Co ions doped into KNSBN can form a deep energy level near 2.25 eV. The two-beam coupling gain coefficients of the Co-doped KNSBN are nearly 20 cm^{-1} at $2\theta \approx 37^0$ for the transmission photorefractive index grating and larger than 29.2 cm^{-1} for the reflecting photorefractive index grating. A striking single-beam asymmetric transmission was observed. The maximum SPPC reflectivity is larger than 70% at $\theta = 49.7^0$ for an intensity W = 77 mW, which is the largest value measured in the family of KNSBN crystals.

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Introduction

Photorefractive (PR) crystals have potential applications in many fields of nonlinear optics and have attracted much attention in recent years (EWBANK et al.). One of the most interecting PR crystals is $(K_xNa_{1-x})_z(Sr_yBa_{1-y})_{n-z}Nb_2O_6$ (KNSBN, $0 < x < 1$, $0.2 < y < 0.8$, $0.2 \leq z \leq 0.4$, $1.10 \leq n$ 1.20) with a unfilled or filled tungsten bronze (TB) type structure. They have the advantage of high Curie temperature, good mechanical stability, high optical quality, and large electro-optic coefficient (CHEN et al.). Their structure provides possibility for improving their properties by adjusting the composition and by doping with new ions. In this paper, we report the properties of the two-beam coupling and the self-pumped phase conjugation (SPPC) of the Co-doped KNSBN crystals, along with their crystal preparation and transmissivity.

Crystal preparation

The crystals were grown by the pulling method with a Crystalox MCGS-3 system. The starting materials are 99.99% K_2CO_3, Na_2CO_3, $SrCO_3$, $BaCO_3$, Nb_2O_5 and Co_2O_3. A typical composition of the crystals is $(K_{0.5}Na_{0.5})_{0.2}(Sr_{0.75}Ba_{0.25})_{0.9}Co_kNb_2O_6$ (KNSBN:Co, $0 \leq k \leq 0.005$). The main constituents were already well-mixed with stoichiometric proportion, an amount of 0.04 wt% Co_2O_3 was added. The processing of the mixture and the crystal growth parameters are the same as those described in our earlier paper (XIA et al.). The as-grown crystals with a volume of about 35 × 35 × 35 mm^3 were annealed at 1050 ^{0}C for 24 h to reduce residual stress formed during growth. The KNSBN is colorless and transparent, and the KNSBN:Co is brown. Powder x-ray data, obtained by a D/MaX-rA x-ray powder diffractometer and a R3m/E x-ray four-circle diffractometer at room temperature show, that there is no difference between their lattice parameters, and a = b = 1.2488 ± 0.0003 and c = 0.3955 ± 0.0002 nm. Atomic absorption analysis for the KNSBN:Co, using a 180-80 atomic spectrum absorptiometer shows, that the cobalt-content is about k = 0.0018. It implies that, on the average, about 110 unit cells can get one Co ion. The other main parameters are: space group P4bm, $T_c = 475 \pm 2$ K, $\varepsilon_{33}^{T}/\varepsilon_0 = 220$ and tgδ = 0.005 at a frequency of 1000 Hz at room temperature, $d_{33} = 70 \times 10^{-12}$ C/N, Moh's hardness 6.5, density 5.3 g/cm^3, specific heat C_p 0.33 Jg^{-1}K^{-1}, pyroelectric constant 2.7×10^{-4} Cm^{-2}K^{-1}, refractive indices $n_0 = 2.31$ and $n_e = 2.25$ at 632.8 nm, and effective electro-optic coefficient 59×10^{-12} m/V. The experimental results show that Co doping affect the crystal optical properties besides the P-E loops (XIA et al.), especially the PR properties. The KNSBN:Co crystal was cut into two samples with the sizes of 1.5 × 3 × 6 (sample 1) and 5 × 5.5 × 6 (sample 2) mm^3, respectively. The pure KNSBN crystal was cut into the same size as sample 1. All specimens were polished and oriented into single domain at 100 ^{0}C with a 6 kV/cm dc electric field along the crystal c-axis for about 1 h in silicone oil.

Results and discussion

The transmission spectra of both the samples 1 were measured on a Hitachi- 340 UV−VIS−NIR spectrophotometer with an auto-modified slit. The incident light with the electric field along the crystal c-axis was aligned along the crystal [100] direction. The experimental results as shown in Fig. 1 show that the Co ions effectively increase the absorption of the crystal in the visible range. An obvious absorption peak at a wavelength of about 550 nm, corresponds to a deep level of 2.25 eV, and implies that the Co-doped crystal can exhibit better PR properties at these wavelengths (VALLEY et al.). We choose a 514.5 nm wavelength beam from an argon-ion laser to perform the PR and SPPC experiments. Based on the ligand field theory for the transition metals, curve (a) in Fig. 1 implies the eigentransition of the d-electrons of Nb with an electron configuration [Kr]4d^{4}5s^1 and shows a band gap of about 3.18 eV (390 nm).

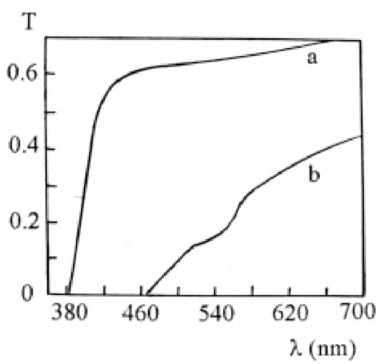

Fig.1: Transmissivities T versus incident light wavelength λ of undoped (a) and Co-doped (b) KNSBN.

The usual experimental setup (EWBANK et al.) for measuring the two-beam coupling gain coefficient Γ was used for the samples 1 for various external crossing angles 2θ of the optical beams. The extraordinarily polarized beam was split into two beams, signal (probe) beam I_S and reference (pump) beam I_R with an intensity ratio I_S/I_R of about 10^{-3}. They interfere with each other and from 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. Obviously, for our crystals and experimental configuration, the PR space-charge field produces a transmission index grating with the wave vector along the crystal c-axis. The experimental results for the two-beam coupling gain coefficients Γ at the various angles 2θ are shown in Fig. 2. The maximum gain coefficient measured in the KNSBN:Co is nearly 20 cm^{-1} at $2\theta \approx 37^0$. This is almost the same as measured in KNSBN:Cu (CHEN et al.), a little bit bigger than half of that of KNSBN:Mn (XIA et al.), and almost twice as large as that of undoped KNSBN. In the experiment, the gain is always positive. Therefore, the energy transfer direction is the negative c-direction, implying that (a) electrons play the dominant role in the charge transport mechanism, and that (b) the Co^{2+}/Co^{3+}, donor/acceptor pair is involved. The effective acceptor density (EWBANK et al.) of the KNSBN:Co was 13.7×10^{16} cm^{-3}.

The experimental arrangement for studying contradirectional two-beam coupling and single-beam asymmetric transmission along the c-axis was the same as that reported in our paper (XIA et al.). In this arrangement the index grating wave vector is perpendicular to the crystal c-axis, i.e., forming the reflecting index grate that is necessary to produce single-beam asymmetric transmission. In the experiments, the angle between the reference beam and the crystal [100] direction is the Brewster's angle ($\theta \approx 65^0$) and I_S/I_R is about 0.1. The gain coefficient Γ can be written in the form $\Gamma = d^{-1}\ln(T_S/T_R)$, where d is the thickness of the samples and $T_S = I_S'/I_S$ and $T_R = I_R'/I_R$ are the transmissivities of the signal and the reference beams with coupling, respectively. In our experiments, the ratio T_S/T_R of the two transmissivities was measured in the KNSBN:Co to be larger than 80 for $I_S \approx 0.1$ and $I_R \approx 1$ mW, which results in $\Gamma > 29.2$ cm^{-1}. The energy transfer between the two coherent beams was observed along the positive direction of the crystal c-axis, no energy transfer was observed in the undoped KNSBN crystal. The single-beam asymmetric transmission, i.e., the so called optical diode effect, was observed only in the Co-doped KNSBN crystal, which will therefor be a promising material for optical diodes. In the two-beam energy coupling process, the error of the transmission beam intensities, caused by the absorption at the wavelength of 514.5 nm, is difficult to estimate exactly.

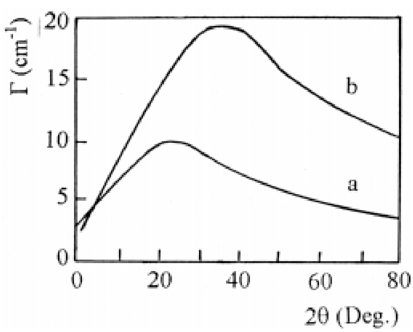

Fig.2: Two-beam coupling gain coefficients Γ at various angle 2θ of KNSBN (a) and KNSBN:Co (b).

The experimental arrangement for measuring the SPPC properties of the KNSBN:Co with the sample 2 was similar to that described in (SUN et al.). The reflectivity R versus angle of incident θ and versus the incident laser power W is shown in Fig. 3. From Fig. 3, we see that the maximum SPPC reflectivity R is higher than 70% at $\theta = 49.7^0$ as W = 77 mW, it decreases greatly when θ becomes very large, and it increases with the W and finally saturates. The R_{max} is the largest value measured in KNSBN crystals, e.g., R = 40% in KNSBN:Mn and R = 50% in KNSBN:Cu.

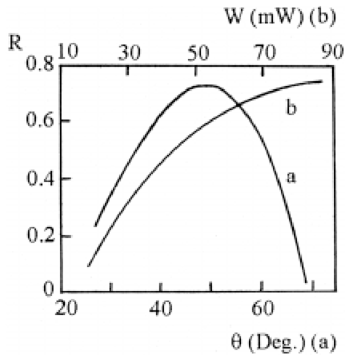

Fig.3: The SPPC reflectivity R versus incident angle θ (W = 77 mW) (a) and versus laser power W (θ = 49.7^0) (b) for KNSBN:Co

The relation between the response time assuming an exponential law and the input intensity for the SPPC was measured and is depicted in Fig. 4. An increase of the input intensity can greatly reduce the response time. We also observed that the reflected intensity on the sample 2 decreased by about 30% of its initial value while the SPPC beam increased. The phase conjugation formation time is 15 s for an incident intensity of 77 mW at an incident angle θ = 49.7^0. It needs another 15 s to reach its maximum value as shown in Fig. 5. The time response is a little faster than that measured in the KNSBN:Mn and much slower than that measured in KNSBN:Cu.

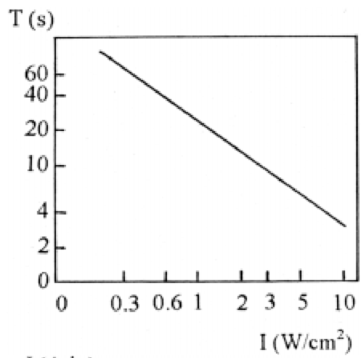

Fig.4: Response time T versus input intensity I

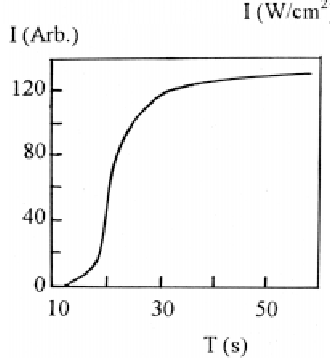

Fig.5: Time response T of the SPPC output intensity I

Because of the distortion of the Nb-O octahetra and the vacancies in TB type crystals (JAMIESON and ABRAHAMS et al.), the crystals exhibit useful nonlinear-optical properties, which can be changed by adjusting the composition and by doping. Now, the Mn-, Cu-, and Co-doped KNSBN are the promising PR materials.

Conclusion

The predominant feature of the Co-doped KNSBN crystal is that the SPPC reflectivity is much higher than that of the other cation-doped KNSBN crystals. The two-beam coupling gain coefficient of the contradirectional beams surpasses that of the symmetric beams. The SPPC reflectivity and the optical diode effect of the KNSBN:Co crystal are worth for further studies. Already now it was shown that the doped KNSBN crystals are promising PR materials.

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