Influence of Ba-Sr Substitution on the Optical Properties of BaB_2O_4 Single Crystals

Adamiv V., Krupych O., Dyachok Ya., Teslyuk I., Romanyuk G., Malynych S., Burak Ya.

Institute of Physical Optics, 23 Dragomanov Str., 79005, Lviv, Ukraine

Received 30.12.2003

Abstract

The results of studies for the optical transmission spectra, radiation hardness and the refractive indices of $Ba_{1-x}Sr_xB_2O_4$ (x=0.1) single crystals grown with the Czochralsky technique are presented. The investigations have shown that the substitutive Sr impurity improves the technological process of single-crystal growth, though leads simultaneously to worsening the transmittance and the radiation hardness. The assumption about the additional influence of incontrollable Na impurity on the mentioned properties of $Ba_{0.9}Sr_{0.1}B_2O_4$ single crystals is made.

Key words: α-BaB_2O_4 single crystals, impurities, transmission spectra, radiation hardness, refractive index

PACS: 42.70.Hj

Single crystals of both modifications of BaB_2O_4 have been considered to be promising for the optical instrument engineering. The low-temperature modification, β-BaB_2O_4 (abbreviated as BBO), belongs to the space group R3 and represents a promising material for the generation of higher harmonics of laser radiation [1], whereas the high-temperature one, α-BaB_2O_4 (or ABO; the space group R $\bar{3}$c) is used for construction of optical elements, in particular, the acoustooptic ones [2]. Nevertheless, both mentioned crystals have remained to be rather "complicated" materials from the technological viewpoint, i.e. with regards to the growth of high-quality single crystals. Among the reasons of the latter, we could mention the presence of a phase transition between the α and β phases at 925^{o}C, which causes the appearance of strains and defects in these crystals and so worsens their optical parameters, in particular the radiation hardness. That is why the purpose of this work is to investigate the possibility for increasing the workability of the ABO single crystals and improving their optical quality by means of particular cationic substitutions, for example, Ba with Sr. We have chosen to check the optical quality of crystals using the studies of optical transmittance, the radiation hardness and the refractive indices.

Single crystals of $Ba_{1-x}Sr_xB_2O_4$ compound at small x values ($x < 0.13$) were grown from the corresponding stoichiometric melt with the direct Czochralsky technique. In order to synthesize the $Ba_{1-x}Sr_xB_2O_4$ growth mixture, we used the multi-graded synthesis technique developed previously for borates [3], with the application of extra-pure materials – the $BaCO_3$ carbonates, the boric acid H_3BO_3, and $SrCO_3$. Issuing from technological considerations, we added a small (0.4 weight %) quantity of Na_2O into the melt. We found it possible to grow successfully $Ba_{1-x}Sr_xB_2O_4$ single crystals of a high-grade optical quality only up to the value of x = 0.1. All the grown single crystals had the α-phase crystal structure. It was observed that the workability of the ABO single crystals was improved after injection of Sr impurity. In other words, a tendency to cracking the samples then lowered and the percentage of crystals having a high optical quality grew.

The studies of the transmission spectra, the optical damage threshold and the refractive indices were performed on the $Ba_{0.9}Sr_{0.1}B_2O_4$ (x = 0.1) single crystals grown by us. For the measurements of the transmittance spectra in the range of 140 – 900 nm we used the samples with the dimensions 10×10×0.2 mm^3. The transmittance measurements in the range of 140 – 220 nm were performed with the spectrophotometer “McPherson VUV 2000” in the pure nitrogen atmosphere and at the room temperature, while the range of 200 – 900 nm was studied with the aid of “Specord M40” spectrophotometer. We used the technique described in the work [4] for determining the damage threshold, with the application of pulsed Nd^{3+} laser (τ = 6 ns; the output radiation energy 60 mJ) and the sample of 15×8×5 mm^3 dimensions. The refractive indices were determined with the Obreimov’s index-matching technique (see, e.g., [5]) in the range of 420 – 680 nm, using the 7.8×5.1×4.1 mm^3-sized sample, whose faces were oriented along the principal crystallographic axes.

The transmittance spectra in the range of 140 – 220 nm for both the pure α-BaB_2O_4 and $Ba_{0.9}Sr_{0.1}B_2O_4$ single crystals are shown in Figure 1 (for a comparison, the transmittance for β-BaB_2O_4 single crystal of the same thickness is given as well). As seen from the figure, the substitutive Sr impurity lowers somewhat (almost by 20%) the transmission coefficient in the range above 200 nm, i.e., above the absorption edge equal to 190 nm. However, in this just stage we cannot state for sure that the decrease in the transmittance is associated with the Sr impurity. Some incontrollable impurities entering into the lattice of single crystal during its growth might also cause such the phenomenon. This conclusion may be arrived at after comparing the transmittance spectra of $Ba_{0.9}Sr_{0.1}B_2O_4$ (Figure 1, curve 3) and the pure α-BaB_2O_4 (curve 1) with the spectrum for β-BaB_2O_4 (curve 2). Notice that the growth technique for β-BaB_2O_4 single crystals also makes a presence of Na_2O in the melt quite possible. As a result, the presence of

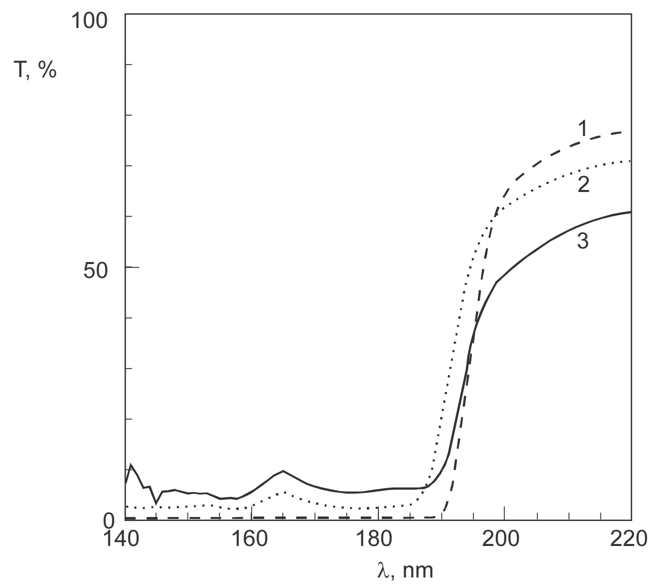

Fig. 1. The transmittance spectra of α-BaB_2O_4 (1), β- BaB_2O_4 (2) and $Ba_{0.9}Sr_{0.1}B_2O_4$ (3) single crystals in the range of 140 – 220 nm.

incontrollable impurity of Na^+ ions might be possible in this single crystal. It is worthwhile that we do not observe any additional absorption bands in the transmittance of all the mentioned crystals in the range of 220 – 900 nm. Here the spectral curves are parallel and practically do not differ one from another.

The results on the radiation hardness investigation for the $Ba_{0.9}Sr_{0.1}B_2O_4$ single crystal are represented in Figure 2 as the damage dimensions dependence on the focused laser beam power. When we compare the obtained results with those of the studies for $CsLiB_6O_{10}$ (CLBO), the pure ABO, BBO and the $Li_2B_4O_7$ (LTB) single crystals [4], it becomes clear that the radiation hardness of $Ba_{0.9}Sr_{0.1}B_2O_4$ has the value located between the corresponding values for the CLBO and the pure ABO crystals.

The results for the refractive indices n_o and n_e in the range of 420 – 680 nm are presented in Figure 3. As seen from the figure, $Ba_{0.9}Sr_{0.1}B_2O_4$ single crystals have sufficiently high values of optical birefringence in all the range under test. For example, we have $\Delta n \approx 0.125$ ($n_o = 1.6590$, $n_e = 1.5343$) at 533 nm. It is necessary to note that the n_o and n_e values at 533 nm somewhat differ from the refractive indices characteristic of the pure ABO ($n_o = 1.6776$, $n_e = 1.5359$ [6]). As a consequence, the birefringence has a larger value ($\Delta n = 0.142$).

Hence, one can conclude from the obtained results that the substitutive impurity of Sr, together with a possible incontrollable impurity of Na, do affect the optical properties of the ABO single crystals. They decrease the transmittance of the latter, weaken the radiation hardness and lead to changes in the refractive indices.

The authors are thankful to the Ministry of Education and Science of Ukraine (the Project N0103U000703) for financial support .

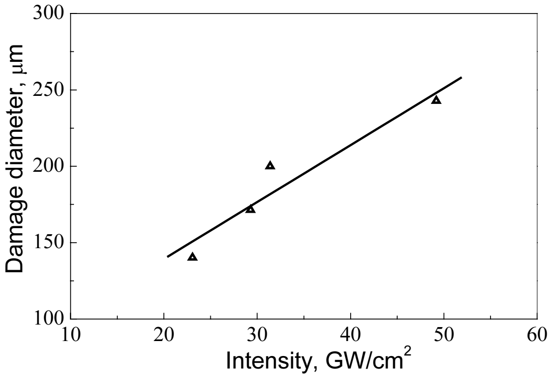

Fig. 2. Dependence of the damage diameter on the laser light intensity.

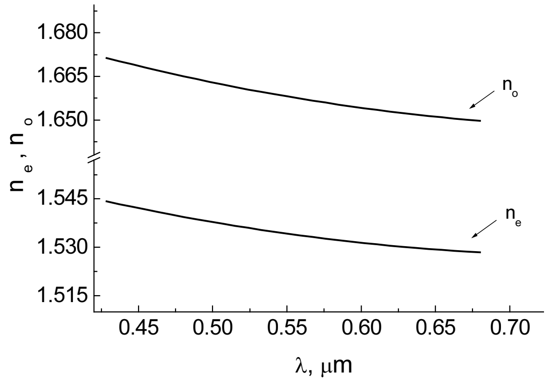

Fig. 3. Dispersion of the refractive indices of $Ba_{0.9}Sr_{0.1}B_2O_4$ single crystals at T=20°C.

References

1. Kato K. IEEE J. Quant. Electronics **22** (1986) 1013.
2. Martynyuk-Lototska I., Mys O., Krupych O, Adamiv V., Burak Ya., Vlokh R. and Schranz W. Ferroelectrics (2004) to be published.
3. Patent 1415663 USSR MKI S 30 B 15 00. Process of obtaining of anhydrous lithium tetraborate. Burak Ya.V., Lyseiko I.T., Prostopchuk V.V., Kvasnytsia O.A., Tesliuk M.I. 1988.
4. Vlokh R., Dyachok Ya., Krupych O., Burak Ya., Martynyuk-Lototska I., Andrushchak A., Adamiv V. Ukr. J. Phys. Opt. **4** (2003) 101.
5. Romanyuk M.O. Crystal Optics, Kyjv, IZMN, 1997 (in Ukrainian).
6. S.Wu, G.Wu, J.Xie, X.Wu, Y.Zhang, X.Lin. J. Cryst. Growth **245** (2002) 84.