Dispersion of quadratic optical susceptibility of lithium niobate and barium sodium niobate crystals

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We measured, for the first time, the dispersion of the components χ_{31} and χ_{33} of single-crystal lithium niobate and barium sodium niobate in the visible and near-ultraviolet regions of the spectrum. It is shown that the dispersion is determined by the dependence of the dispersion of the quadratic polarizability of the Nb–O bonds on their length.

1. The quadratic optical susceptibility of ferroelectrics was investigated in many studies, but data on its frequency dispersion near the electron absorption bands have not been published. We have therefore investigated the dispersion of several components of the quadratic susceptibility tensors χ of the well known crystals lithium niobate $LiNbO_3$ (LN) and barium sodium niobate $Ba_2NaNb_5O_{15}$ (BSN) in the visible and near-ultraviolet regions of the spectrum. The results are interpreted from the point of view of the dispersion of the effective nonlinear polarizability of the Nb—O bonds.

2. In the experiments we used the emission of an LTIPCh-7 neodymium-doped aluminum-yttrium-garnet laser and its second harmonic, and also the emission of a ruby laser and of the first two SRS Stokes components excited by it in liquid nitrogen. We determined the components χ_{31} and χ_{33} of the LN and SBN crystals for the frequency doubling ($\lambda_{sh} = 347$, 415, 532 nm) and frequency addition ($\lambda_{sum} = 355$, 378, 458 nm) processes. The measurements of χ_{ij} were carried out by a wedge procedure[1] relative to crystalline quartz, which has $\chi_{11} = 0.8 \times 10^{-9}$ cgs esu in the wavelength interval considered by us.[2] The intensity I of the converted radiation was registered with the aid of an FEU-39 photomultiplier and an oscilloscope.

The dispersion of the quadratic susceptibility was measured at room temperature with single-domain samples of congruent composition, for which we determined beforehand the absorption coefficients α and the refractive indices N for the ordinary and extraordinary rays (the SBN crystals are practically uniaxial[3]). For the wavelengths of the fundamental and transformed radiations, the refractive indices were determined by interpolation and extrapolation of their values, measured by us by a prism method at wavelengths 355, 405, 408, 436, 492, 546, 577, 589, 633 nm. The values of χ_{ij} were determined from I, α, and N in analogy with[4,2], and the coherence lengths were calculated from the refractive indices.

The dependence of the quadratic-susceptibility tensor components χ_{ij} of the LN and SBN crystals on the wavelength λ of the converted radiation is shown
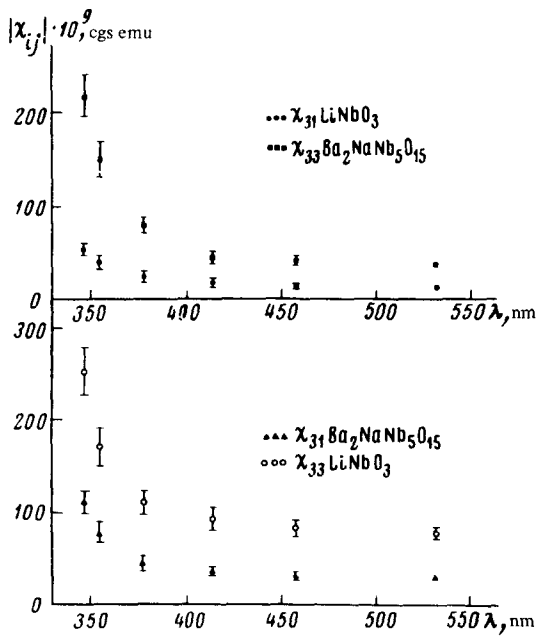
FIG. 1.

in Fig. 1. The values of χ_{ij} obtained by us for $\lambda = 532$ nm coincide within the limits of the measurement errors with the values given in[3,4].

3. The quadratic optical susceptibility of the niobate crystals is governed mainly by the nonlinear polarizability β of the Nb—O bonds, which are considered here as one-dimensional electron distributions with $\beta = \beta_\parallel \gg \beta_\perp$.[4] Knowing the direction cosines n_k of the kth Nb—O bond in a unit cell of volume V_0 and assuming β_k to be macroscopic quantities, we can set up for the LN and SBN crystals the following equations:

$$\chi_{ij} = V_o^{-1} \sum_k \beta_k n_{ki} n_{kj}^2 ; i = 3, j = 1. 3. \tag{1}$$

The frequency dispersion of χ_{ij} will then be determined by the dispersion of the effective nonlinear polarizability β of the individual Nb—O bonds and their geometric factors.

With the aid of the simplest model describing the motion of the electrons of the Nb—O bond as motion in a one-dimensional potential well,[5] we can show that the stronger dispersion of should be observed for bonds with larger length L: for $L_2 > L_1$ we have

$$\frac{\beta(L_2, \lambda'')}{\beta(L_2, \lambda')} > \frac{\beta(L_1, \lambda'')}{\beta(L_1, \lambda')} \quad \text{at} \quad \lambda'' < \lambda'. \tag{2}$$

This situation does indeed take place, for example, in LN crystals, and in the long-wave approximation, in accordance with[6], we have

$$\kappa_{pq}(\lambda) \equiv \frac{\beta(L_p, \lambda)}{\beta(L_q, \lambda)} = \left(\frac{L_p}{L_q}\right)^\sigma, \tag{3}$$

where $p = 2$, $q = 1$, $\sigma = 2$.

Separating in the LN crystals two groups of Nb—O bonds with length L_1 $= 1,889 \pm 0,003$ Å and $L_2 = 2.112 \pm 0.004$ Å, and in the SBN crystals three groups of Nb—O bonds with $L_3 = 1.815 \pm 0.028$ Å, $L_4 = 1.975 \pm 0.011$ Å, and $L_5 = 2.214 \pm 0.029$ Å we obtain, using the x-ray structure data[7,8] and equations (1), that $\chi_{31}(\lambda)/\chi_{33}(\lambda)$ is given by

$$\frac{1.11\,\kappa_{21}(\lambda) - 1.10}{1.80\,\kappa_{21}(\lambda) - 0.64}$$

in the case of LN and by

$$\frac{0.14\,\beta(L_4, \lambda)}{0.75\,\beta(L_5, \lambda) - 0.74\beta(L_3, \lambda)} < \frac{0.14\,\kappa_{53}(\lambda)}{0.75\,\kappa_{53}(\lambda) - 0.74}$$

in the case of SBN. From these equations and from the inequality $\kappa_{pq}(\lambda'') > \kappa_{pq}(\lambda')$ at $\lambda'' < \lambda'$, which is equivalent to the inequality (2), it follows that for LN crystals the value of the component χ_{31} should be smaller, and its relative change with wavelength should be larger than for the component χ_{33}, whereas for the SBN crystals the value of the component χ_{31} itself and its relative change with wavelength should be less than for the component χ_{33}. This conclusion also agrees fully with the experimental values of $\chi_{ij}(\lambda)$ (see Fig. 1).

We note that the change of the parameter κ_{pq} with change of wavelength of the converted radiation λ can be described by relation (3) with a coefficient σ that depends on λ, and according to the experimental data for LN the value of $\sigma(\lambda)$ increases monotonically, approximately from two to three in the range λ $= 532-347$ nm. Using formulas (1) and (3) with these values of $\sigma(\lambda)$, we have calculated $\chi_{ij}(\lambda)$ of the SBN crystals. Comparison of the values of $\chi_{ij}(\lambda)$ obtained in this manner for SBN with their experimental values shows that this approach gives fully satisfactory results, although we are considering only the effective quadratic polarizabilities of the bonds, which include factors of the local field.

Thus, allowance for the crystal structure of LN and SBN and for the dependence of $\beta(\lambda)$ of the Nb—O bonds on their length explains well the observed experimental features of the dispersion of the components of the tensor of the quadratic optical susceptibility of these ferroelectrics near the electron absorption bands.

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