ISSN 1063-7745, Crystallography Reports, 2010, Vol. 55, No. 2, pp. 272–275. © Pleiades Publishing, Inc., 2010.
Original Russian Text © V.I. Burkov, V.N. Makhov, 2010, published in Kristallografiya, 2010, Vol. 55, No. 2, pp. 286–289.

PHYSICAL PROPERTIES OF CRYSTALS

Reflection Spectra of $NaClO_3$, $NaBrO_3$, and $LiIO_3$ Gyrotropic Crystals in the Vacuum UV Region

V. I. Burkov and V. N. Makhov

Moscow Institute of Physics and Technology, Dolgoprudnyĭ, Moscow oblast, 141700 Russia
e-mail: optikcentr@mail.mipt.ru
Lebedev Physical Institute, Russian Academy of Sciences, Leninskiĭ pr. 53, Moscow, 119991 Russia

Received March 23, 2009

Abstract—The reflection spectra in the fundamental-absorption region, 5–25 eV (250–40 nm), of optically active crystals with cubic symmetry ($NaClO_3$, $NaBrO_3$) and uniaxial optically active crystal ($LiIO_3$) have been investigated. It is shown that the reflection spectra of cubic crystals have a similar structure, which is determined by the electronic transitions in the XO_3 group. The comparison of these spectra with the corresponding spectrum of lithium iodide made it possible to determine the type of transition in the spectra of cubic crystals. Using the projection operator method, it was shown that the sign of optical rotation of cubic crystals with symmetry T is independent of the screw axis sign. Possible reasons for the unprecedentedy large optical rotation of lithium iodide crystal in the optical axis direction are considered.

DOI: 10.1134/S1063774510020197

INTRODUCTION

The optical activity of $NaClO_3$ and $NaBrO_3$ crystals has been repeatedly discussed in the literature. In particular, it was noted that the optically active sodium chloride and sodium bromide crystals of cubic symmetry (sp. gr. $P2_13$ (T^4)) with identical absolute configuration, which are transparent in the spectral range of 230–3000 nm, have an optical rotation of a different sign in this spectral range [1–3]. The optical rotatory dispersion of these crystals was measured in [4, 5], and the results obtained were generalized in [6].

The optical rotation in the transparency range of the optically active crystals under study (in our case, in the range of 230–3000 nm) is determined by the sum of partial contributions from the electronic transitions in the crystals, which lie at $\lambda < 220$ nm. For this reason the difference in the optical rotation sign may be related to the difference in the structure of electronic states of sodium chloride and sodium bromide.

At the same time, the change in the rotation sign can be caused by the features (maybe insignificant) in the lattice structure. In view of some new possibilities, we tried to study the spectroscopic characteristics of these crystals in detail using the results following from an analysis of the reflection spectra measured near the fundamental absorption edge of the crystals. The reflection spectra in the range of 5–25 eV (250–40 nm) were obtained using synchrotron radiation on the SUPERIJJML system at the Synchrotron Radiation Laboratory HASYLAB (Hamburg, Germany) [7]. The spectra were measured at the direction of beam incidence close to normal ($\alpha \sim 17°$) at 9 K.

RESULTS AND DISCUSSION

A study of the absorption spectra of the crystals showed that the absorption edges of sodium chloride and sodium bromide lie near 220 and 260 nm, respectively. An inflection is observed at the absorption edge of the former near $\lambda \sim 238$ nm. A similar inflection is observed in the spectra of sodium bromide and lithium iodide crystals at $\lambda \sim 270$ and 330 nm, respectively [6]. These transitions barely manifest themselves in the circular dichroism (CD) spectra, whereas the CD signal sharply increases near the fundamental absorption edge.

The measurement of absorption and CD spectra does not yield data on the position of excited electronic states of the crystals (more specifically, on the energies of excited states of ClO_3^- and BrO_3^- chromophores) due to the strong absorption. At the same time, the sign of CD spectra near the absorption edge indicated that the crystals studied had the same absolute configuration. The results of measuring the optical rotation sign confirmed this conclusion. For this reason we investigated the spectra of mirror reflection of the crystals in the energy range of 5–25 eV (250–40 nm) to determine the differences in their electronic structure.

The reflection spectra of $NaClO_3$ and $NaBrO_3$ crystals (Figs. 1, 2) differ only slightly. In fact, a difference is observed only in the band positions: the corresponding bands in the reflection spectrum of sodium chloride lie at higher energies. This can be explained by the higher energies of ClO_3^- molecular ion orbitals due to the higher energy of the atomic orbitals in the central atom.

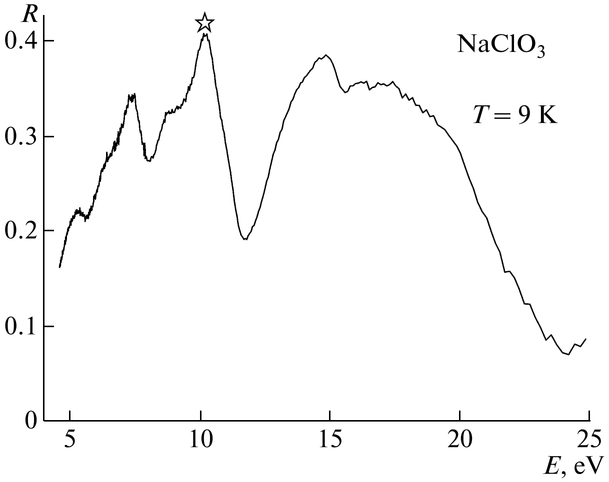

Fig. 1. Reflection spectrum of NaClO$_3$ crystal at 9 K.

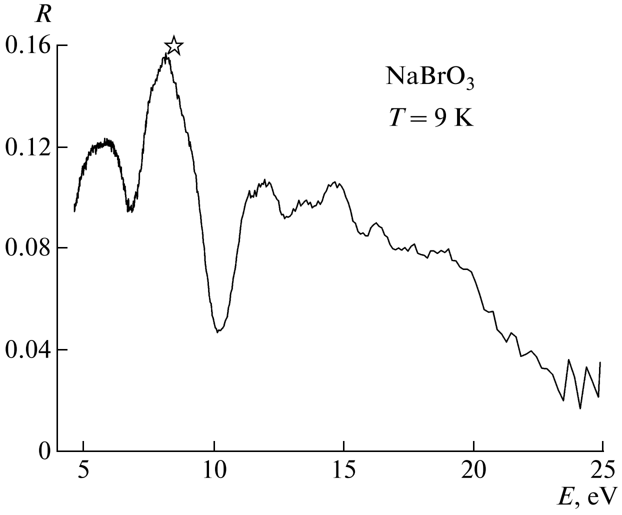

Fig. 2. Reflection spectrum of NaBrO$_3$ crystal at 9 K.

Since the positional symmetry of the XO_3^- molecular group in the lattice is C$_3$, both $A \rightarrow A$ and $A \rightarrow E$ transitions are possible (they are symmetry-allowed in the electric and magnetic dipole approximations). These transitions can be active not only in the absorption spectra, but also in the CD spectra. For the first type of transitions, the rotatory strength tensor $R_{M,0j}$ of an ensemble of equally oriented molecules with symmetry C_3 has the form [8]:

$$R_{M,0j} \sim \begin{vmatrix} \mu_z m_z & 0 & 0 \\ 0 & \mu_z m_z & 0 \\ 0 & 0 & \mu_z m_z \end{vmatrix}, \qquad (1)$$

where μ_z and m_z are the projections of the electric and magnetic moments of the transition on the Z axis of the molecular coordinate system, which coincides with the molecular symmetry axis.

In the second case, the rotatory strength tensor for the transitions to degenerate E states may contain off-diagonal terms, because the mutual orientation of the transition moments is not determined by the symmetry conditions for molecules with C_n or D_n symmetry.

According to [9], the rotatory strength tensor of A–E transitions for the above-mentioned ensemble of molecules has the form

$$R_{M,0j} \sim \begin{vmatrix} \mu_y m_y & -\mu_x m_y & 0 \\ -\mu_y m_x & \mu_x m_x & 0 \\ 0 & 0 & \mu_x m_x + \mu_y m_y \end{vmatrix}, \qquad (2)$$

where $\mu_x m_x$ are the projections of the electric and magnetic moments of transition on the X axis of the coordinate system.

It follows from expressions (1) and (2) that the directions of the electric and magnetic moments of electronic transitions are not determined by the symmetry conditions; hence, the rotatory strength sign can be arbitrary.

According to the X-ray diffraction data, the ClO_3^- and BrO_3^- groups in these crystals of cubic symmetry are located at the points of positional symmetry C_3, which are linked in the lattice by a threefold screw axis. To calculate the rotatory strength R_k of electronic transitions in a crystal with symmetry T, composed of molecular ions with symmetry C_3 in the absence of any interaction between them, it is necessary to average expressions (1) and (2) over the operations of T group symmetry using the projection operator method [10]:

$$R_k = \eta R_{M,0j}.$$

For the point group T, the projection operator

$$\eta = 1/12\{|\mathbf{E}|^2 + |\mathbf{C}_3|^2 + |\mathbf{C}_3^-|^2 + |\mathbf{C}_2|^2\},$$

where

$$|\mathbf{E}|^2 = |\mathbf{E}| \times |\mathbf{E}|$$
$$|\mathbf{C}_3|^2 = |\mathbf{C}_3| \times |\mathbf{C}_3|$$
$$|\mathbf{C}_3^-|^2 = |\mathbf{C}_3^-| \times |\mathbf{C}_3^-|$$
$$|\mathbf{C}_2|^2 = |\mathbf{C}_2| \times |\mathbf{C}_2|$$

are direct products of matrices, has the form

$$\eta \sim \begin{vmatrix} 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \end{vmatrix}. \qquad (3)$$

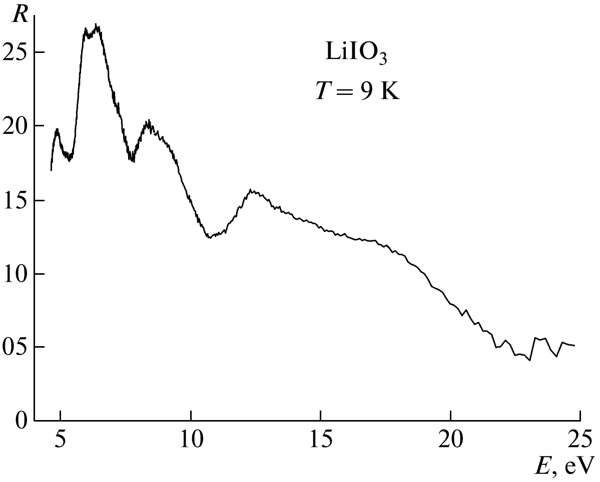

Fig. 3. Reflection spectrum of LiIO$_3$ crystal at 9 K.

As a result of averaging of tensor (1), we have

$$R_{k,0j} \sim \begin{vmatrix} \mu_z m_z & 0 & 0 \\ 0 & \mu_z m_z & 0 \\ 0 & 0 & \mu_z m_z \end{vmatrix}. \quad (4)$$

Furthermore, averaging of tensor (2) gives

$$R_{k,0j} \sim \begin{vmatrix} \mu_x m_x + \mu_y m_y & 0 & 0 \\ 0 & \mu_x m_x + \mu_y m_y & 0 \\ 0 & 0 & \mu_x m_x + \mu_y m_y \end{vmatrix}. \quad (5)$$

Expressions (4) and (5) show that the rotatory strength sign for a specific electronic transition in crystal (as well as in a molecule, see (1) and (2)) and, therefore, the sign of partial contribution to the optical rotation within a particular enantiomorphic modification of optically active crystal are not determined by the left- or right-handedness of the crystalline modification but depend on both the value and mutual orientation of the electronic moments $\langle p \rangle$ and $\langle m \rangle$ of transition, which can be arbitrary within the specific molecular symmetry.

In other words, the CD spectrum of a cubic crystal of symmetry T with a right-handed screw axis may exhibit bands with both a positive and negative sign; in a number of cases, some bands in these spectra may have a close-to-zero intensity [10]. In the CD spectrum of the same crystal but of another enantiomorphic modification, the signs of CD bands change to their opposite. This situation can easily be understood by taking into account the change in the polar vector direction to its opposite and the conservation of the axial vector direction upon reflection in the plane oriented perpendicularly to the screw axis. The optical rotation in the transparency range of crystals is determined by the sum of partial Drude contributions of all transitions that are active in the CD spectrum, each of which can be positive or negative. Due to this, the optical rotation sign in the transparency range of crystal may either coincide with the screw axis sign or be opposite.

In particular, in the CD spectrum of the well-known uranium sodium acetate crystal [10], some A–E transitions, which are responsible for strong bands in the absorption spectrum, are barely observed. In turn, other vibronic transitions to the next-in-energy doubly degenerated state E (of the $A \to E$ type) are active both in the absorption and CD spectra. These totally symmetric vibronic bands in the CD spectrum have the same sign as the totally symmetric CD bands of the "fluorescent" series ($A \to A$ transitions). At the same time, a series of asymmetric low-intensity vibronic CD bands have the opposite CD sign. In the range of transparency ($\lambda > 500$ nm), the sign of optical rotation is determined by the sign of the total contribution of the transitions that have a high intensity in the CD spectrum.

As was mentioned above, the bands in the reflection spectra of NaClO$_3$ and NaBrO$_3$ crystals are determined by the $A \to A$ and $A \to E$ transitions in the XO^{3-} molecular ion. However, it is impossible to determine the transition type from experimental data. To obtain additional information about the transition type, we investigated the reflection spectrum of a plate of uniaxial optically active LiIO$_3$ crystal, cut perpendicularly to the optical axis, at a close-to-normal incidence of light (17°) (Fig. 3). LiIO$_3$ groups in the lattice of this crystal (spatial group $P6_3(C_6^6)$) occupy the symmetry positions IO$_3^-$ in such a way that the threefold axis of these molecular ions is parallel to the optical axis of the crystal [11]. In this geometry only the A–E transitions are active in the reflection spectrum of the crystal. As one would expect, the reflection spectrum of this crystal is shifted to longer wavelengths with respect to the spectra of sodium chloride and sodium bromide and differs significantly from the spectra of the latter both in the number of bands and their intensity. Comparing the spectra of all three crystals, we selected the bands in the spectrum of cubic crystals that are absent or weak in the spectrum of lithium iodide. We assigned these bands to the A–A transitions; they are denoted by the "☆" sign in Figs. 1 and 2.

In summary, we should note that the reflection spectrum of lithium iodide contains fewer bands than the spectra of the two other crystals. According to the symmetry conditions, these bands can be active in the axial CD spectrum and, therefore, contribute to the dispersion and optical rotation in the crystal transparency range (300–3000 nm). When $A \to E$ transitions make contributions of the same sign to the optical rotation of this crystal and there are no contributions of $A \to A$ transitions of the opposite sign to the optical rotation toward the axis direction, the rotation magnitude can be very large. It is well known that optical rotation toward the optical axis of lithium iodide crystal has a record value and exceeds the corresponding values for sodium chloride and sodium bromide crystals by more than an order of magnitude. The rotation values in the latter are determined by the contributions of both $A \to A$ and $A \to E$ transitions. If the contributions of the above-mentioned transitions have opposite signs, this circumstance can apparently explain the relatively small optical rotation and the large difference in the values of the optical rotation of these cubic crystals and the uniaxial lithium iodide crystal.

CONCLUSIONS

We investigated the reflection spectra of optically active cubic $NaClO_3$ and $NaBrO_3$ crystals and uniaxial $LiIO_3$ crystal in the vacuum UV region at $T = 9$ K for the first time. It is noted that the spectra of the first two crystals are similar and differ from that of the third crystal. It is shown by the projection operator method that the sign of optical rotation in cubic crystals of symmetry T in the transparency region with the same absolute configuration and the same sign of screw axes can be arbitrary within one enantiomorphic configuration. A comparison of the spectra of cubic crystals with that of lithium iodide allowed us to select reflection bands that can be attributed to $A \to A$ transitions. The causes of the record optical rotation in lithium iodide crystals are discussed.

ACKNOWLEDGMENTS

We are grateful to G. Zimmerer and his team (University of Hamburg) for their help with synchrotron radiation measurements.

REFERENCES

1. G. Beurskens-Kerssen, F. Groon, H. J. Endeman, et al., *Crystallography and Crystal Perfection* (Academic, New York, 1963), p. 225.
2. J. M. Bijvoet, Acta Crystallogr. **13**, 1100 (1960).
3. J. M. Bijvoet, *Crystallography and Crystal Perfection* (Academic, New York, 1963), p. 236.
4. G. N. Ramachandran, Proc. Indian. Acad. Sci. **33A**, 309 (1951).
5. I. A. Kizel', Yu. I. Krasilov, and V. N. Shamraev, Opt. Spektrosk. **17**, 863 (1964).
6. V. A. Kizel' and V. I. Burkov, *Gyrotropy of Crystals* (Nauka, Moscow, 1980) [in Russian].
7. G. Zimmerer, Radiat. Meas. **42** (4–5), 859 (2007).
8. J. Snir and J. Shellman, J. Phys. Chem. **77** (13), 1653 (1973).
9. R. Hochstrasser, *Molecular Aspects of Symmetry* (Benjamin, New York, 1966; Mir, Moscow, 1968).
10. V. I. Burkov, Neorg. Mater. **32** (12), 1415 (1996).
11. J. L. de Boer, van F. Bolhuis, R. Olthof-Hazehamp, et al., Acta Crystallogr. **21**, 841 (1966).

Translated by A. Grudtsov