Circular dichroism in the region of state produced due to vacancies in sillenite-type crystals

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The gyrotropy of pure and doped sillenite crystals ($Bi_{12}SiO_{20}$, $Bi_{12}GeO_{20}$, and $Bi_{12}TiO_{20}$) was investigated. It was found that silicon, germanium, and titanium vacancies contribute significantly to circular dichroism. This contribution disappears upon doping with aluminum, which is associated with filling of vacancies.

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The investigation of gyrotropy induced in electronic states of impurity centers is emerging as one of the methods for studying the structure of solids as well as the structure and nature of the energy levels of impurities. Both chiral centers in achiral matrices as well as impurities in chiral matrices in crystals are studied.

In this work, we study the role of vacancies in sillenite crystals, which are of great interest in technology. The gyrotropy of $Bi_{12}SiO_{20}$, $Bi_{12}GeO_{20}$, and $Bi_{12}TiO_{20}$ crystals was discovered and investigated in Refs. 1–6. The dispersion curves for optical rotation in the range 0.4–1.0 μm were measured; in the region of the fundamental absorption edge ($\lambda \sim 0.4$ μm), the rotation for bismuth silicate and bismuth germanium reaches 125°/mm. No appreciable anomalies were observed.

Sillenite crystals belong to the space group I 23. In the unit cell, the SiO_4 (GeO_4, TiO_4) tetrahedra are situated at the center and at the vertices of a cube; heptavertex BiO_7 polyhedra are located between them.[7,8]

One of the attractive properties of crystals of this type is photoconductivity. The

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appearance of photoconductivity is attributed to the presence of levels in the forbidden band which are due to silicon (germanium or titanium) vacancies and are found in the region 2.15–2.59 eV.[9–11] The presence of these vacancies has been demonstrated directly in Ref. 7, where it was demonstrated by x-ray diffraction methods that the filling factor for filling of tetrahedra by germanium atoms is 0.91.

In the absorption spectra of pure crystals, the presence of these states leads to the appearance of a broad shoulder on the fundamental absorption edge, due to a band-band transition. When the crystals are strongly doped with aluminum, the shoulder on the absorption edge disappears due to filling of silicon vacancies by aluminum.[11]

Since for a lattice described by the space group I 23 the local symmetry of possible positions is characterized by the groups C_2 and C_3, i.e., optically active groups, it is interesting to investigate the circular dichroism (CD) in the region of levels arising due to vacancies.

In this work, we measured the absorption spectra and CD of pure bismuth silicate, germanate, and titanate crystals and bismuth silicate crystals doped with aluminum. A broad shoulder, which is missing in the absorption spectra of crystals

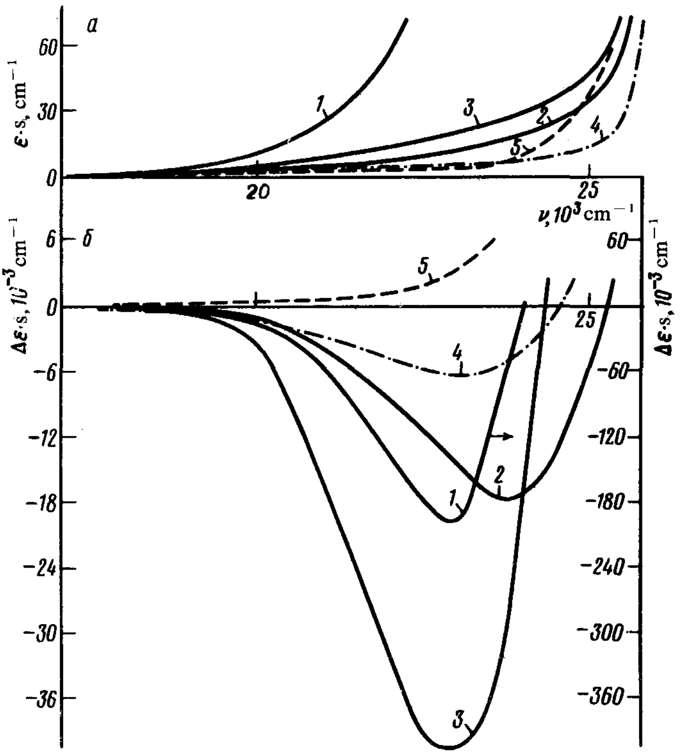

FIG. 1. a) Absorption spectra; b) circular dichroism. 1) $Bi_{12}TiO_{20}$, 2) $Bi_{12}GeO_{20}$, 3) $Bi_{12}SiO_{20}$, 4) $Bi_{12}SiO_{20}$ + 0.013% Al, 5) $Bi_{12}SiO_{20}$ + 0.03% Al.

doped with aluminum, is clearly visible in the absorption spectra of pure crystals, as in the spectra obtained in Ref. 11 (Fig. 1a). The CD spectra of these crystals show that the states arising due to silicon (germanium or titanium) vacancies are manifested as distinct bands with opposite sign in the long-wavelength edge of intense CD, due to a band-band transition (Fig. 1b). The amplitude of this band varies depending on the degree of doping of the crystal by aluminum: it is maximum in the pure crystal and disappears in a strongly doped crystal. Thus the CD spectrum carries more information than the absorption spectrum and the filling of levels, arising due to vacancies, is more clearly seen. The position of the band maximum observed in the CD spectrum differs somewhat from the position of the bend in the absorption spectrum. This is explained by the fact that the intense edge of CD, which arises in a band-band type transition, displaces the position of the extremum.

Thus, it has been demonstrated experimentally that levels which arise due to silicon (germanium or titanium) vacancies and which determine the absorption and photoconductivity in the region ~ 2.6 eV also contribute to circular dichroism in this energy range. As far as we know from the literature, the appearance of circular dichroism in the region of states related to vacancies has not been previously observed.

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