Study of wide band-gap crystal LiCaAlF₆ by IR-reflection spectroscopy and *ab initio* calculations

N.N. Novikova, S.A. Klimin, B.N. Mavrin*

Institute for Spectroscopy RAS, 108840 Troitsk, Moscow, Russia

**Abstract.** Polarized IR-reflection spectra and results of *ab initio* calculations of vibrational and electronic properties of LiCaAlF₆ single crystal are presented. It is shown that the crystal band gap is direct. Experimental and theoretical parameters are obtained for dipole-active and all phonons, respectively, including silent modes. Experimental IR-reflection and Raman spectra are well described in the frame of results obtained by *ab initio* calculations. The peculiarities are discussed concerning the structure of electronic bands, the interatomic interactions, the character of lattice vibrations, and the phonon dispersion.

Isostructural crystals with general chemical formula LiMM'F₆ (M = Ca,Ba,Sr; M' = Al, Ga) possess a very wide band gap (E₉ = 12.65 eV for LiCaAlF₆ [1]). That’s why they are perspective for applications in UV spectroscopic region. The crystal LiCaAlF₆, pure as well as doped by d- and f-ions, is intensively studied. The list of its applications includes laser emission, scintillators, visualization of neutrons, UV optical windows, etc. The phonon spectrum of LiCaAlF₆, necessary for the description of relaxation processes and vibronic spectra of f-d transitions [2], is not sufficiently studied. Raman phonons were studied in Ref. [3]. In this work, we present results of IR spectroscopic study as well as of *ab initio* calculations of LiCaAlF₆.

Crystal structure of LiCaAlF₆ is trigonal [4], Li₂ZrF₆ type, space group is P31c (D₃d, No. 163), z=2. Irreducible representations of phonon modes are classified as following Г_vib = 3A₁g + 5A₂g + 8E_g + 4A₁u + 6A₂u + 10E_u [3], A₁g and E_g being Raman active, A₂u and E_u – IR-active, A₂g and A₁u – silent modes.

Reflectivity spectra were registered using Brucker IFS66 fourier-spectrometer. *Ab initio* calculations were performed by two methods. Phonon properties in the center of Brillouin zone were calculated in the DFT-LCAO approximation with the use of CRYSTAL 14 code [5] and B3LYP hybrid pseudopotential [6]. Calculations of phonon and electronic dispersions across Brillouin zone were performed in the basis of plane waves using the code QUANTUM ESPRESSO [7].

Experimental reflectivity spectra of LiCaAlF₆ are presented in Fig.1 by symbols. The experimental parameters of IR phonons were obtained by fitting the spectra in the code RefFIT [8] using Drude-Lorentz model for dielectric constant. Model spectra with the best fit are presented for comparison in Fig. 1 by grey curves. The following TO frequencies (cm⁻¹) for IR active modes were obtained: 131, 284, 299, 400, 588 (A₃u modes), 122, 190,

* Corresponding author: mavrin@isan.troitsk.ru

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197, 269, 324, 360, 417, 451, 575 \((E_u)\). We have to note that weak phonon modes (marked by arrows in Fig. 1) were reliably identified after \textit{ab initio} calculation performed.

Calculated by both \textit{ab initio} methods structural parameters coincide with experimental ones \[9\] within 1 \% accuracy. Partial densities of electronic states and dispersion of electronic states was obtained, according to which, LiCaAlF\(_6\) is a direct band-gap isolator. Theoretically obtained phonon frequencies are in good agreement with experimental ones, both IR and Raman active. The energies (in cm\(^{-1}\)) of silent phonon modes were also obtained (LCAO gives 244, 275, 406, 579 \((A_{1u})\) modes), 31, 237, 305, 488, 726 \((A_{2g})\). Calculated IR reflectivity spectra (black curves at the bottom of Fig. 1) describe well experimental results. Analysis of TO-LO splittings was performed. One inverted phonon was found \((E_u\) mode 451 cm\(^{-1}\)). Due to the interaction of weak phonon, falling into the TO-LO gap of the strong mode, with the last one, its TO-LO splitting inverts \[10-13\].

The phonons with energies higher than 500 cm\(^{-1}\) are separated by a gap from low-frequency ones. The analysis of atomic displacement in normal modes revealed predominantly stretching character of vibrations for high-frequency gapped modes. Phonon density of states calculated is also characterized by a gap in the 470-540 cm\(^{-1}\) spectral region. Phonon dispersion curves demonstrates strong softening (up to 3-5 cm\(^{-1}\)), close to A-point of the Brillouin zone, for two phonon modes, namely, for the lowest-energy phonons with symmetry \(A_{2g}\) (98 cm\(^{-1}\)) and \(E_g\) (132 cm\(^{-1}\)). This can be interpreted as quasi-doubling of primitive cell along \(z\) axis.

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**References**