

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

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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 ($E_g = 12.65$ 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 $P31c$ (D^2_{3d} , No. 163), $z=2$. Irreducible representations of phonon modes are classified as following $\Gamma^{vib}=3A_{1g}+5A_{2g}+8E_g+4A_{1u}+6A_{2u}+10E_u$ [3], A_{1g} and E_g being Raman active, A_{2u} and E_u – IR-active, A_{2g} and A_{1u} – silent modes.

Reflectivity spectra were registered using Bruker 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 (A_{2u} modes), 122, 190,

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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 *ab initio* calculation performed.

Calculated by both *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, LiCaAlF₆ 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].

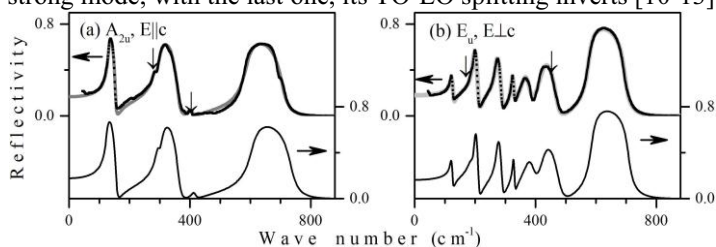


Fig. 1. Experimental (symbols), model (grey curves), and calculated *ab initio* (black curves at the bottom) reflectivity spectra of LiCaAlF₆ for (a) A_{2u} and (b) E_u vibrational modes. Arrows point to weak phonons

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

1. M. Kirm et al., Nucl. Instrum. Methods Phys. Res. A **537**, 291 (2005)
2. V.N. Makhov et al., J. Lumin. **132**, 418 (2012)
3. P. Daniel, J.Y. Gesland, M. Rousseau, J. Raman Spectrosc. **23**, 197 (1992)
4. G. Brunton, Acta Crystallogr. B **29**, 2294 (1973)
5. R. Dovesi et al., Int. J. Quantum Chem. **114**, 1287 (2014)
6. A.D. Becke, J. Chem. Phys. **98**, 5648 (1993)
7. <http://www.quantum-espresso.org>
8. A.B. Kuzmenko, Rev. Sci. Instr. **76**, 083108 (2005)
9. A.C. Cefalas et al., Proc. SPIE **4766**, 171 (2002)
10. F. Gervais, Opt. Comm. **22**, 116 (1977)
11. E.A. Vinogradov et al., Phys. Usp. **52**, 290 (2009)
12. S.A. Klimin et al., Phys. Rev. B **93**, 054304 (2016)
13. T.A. Ivanova, B.N. Mavrin, Opt. Spectrosc. **119**, 816 (2015)