Giant Increase of Photoinduced Reflectivity in $LiNa_5Mo_9O_{30}$

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$LiNa_5Mo_9O_{30}$ single crystals are promising nonlinear optical material with excellent transparency in wide spectral range from 0,357 to 5,26 μm [1]. Previously $LiNa_5Mo_9O_{30}$ was examined in both forms as the singe crystal and polycrystalline material. To explain and understood the relation between crystal structure and electronic properties of the $LiNa_5Mo_9O_{30}$, complex approach which includes experimental studies of X-ray with photoinduced reflectance spectroscopy, and the first principles band structure techniques within a framework of electron density functional theory (DFT) were used.

Synthesis of $LiNa_5Mo_9O_{30}$ micropowders by means of sol-gel method through the citrate way was performed. The DFT band structure calculations for obtained compound were carried out. Calculations of structural, electronic and optical properties of $LiNa_5Mo_9O_{30}$ microcrystals were performed in the framework of density functional theory (DFT) using the pseudopotentials plane-wave basis set CASTEP (Cambridge Serial Total Energy Package) [2] module of Biovia Materials Studio 8.0.

It is found that maximal dispersion of band structure is observed for Brillouine zone (BZ) directions Γ-Z and X-Y both for LDA and GGA functional. The top of the valence band is situated in the point Γ(0;0;0) of the BZ. Generally, dispersion $E(k)$ is higher for the conduction band states. Single maxima of PDOS near -60 eV and -35 eV are formed by 4s and 4p states of Mo, respectively, while its 4d electrons give contributions at -18 eV and -5 eV÷-2 eV. The oxygen is presented by two bands within -18 eV÷-15 eV (2s electrons) and within -6 eV÷0 eV (4p electrons). Following the reasons presented above one can conclude that the upper valence band is formed by bands originated from 4p(O) and 2s(Li) states and the conduction band originates from combination of the s(Li), d(Mo) and some contribution of p(O).

Following the performed calculations investigations of real and imaginary parts of the dielectric dispersion functions were carried out.

The giant increase of reflectivity was discovered for $LiNa_5Mo_9O_{30}$ crystal by illumination using the 371 nm nanosecond nitrogen laser. It was shown that the illumination at 532 nm does not cause any changes.

Basing on calculations of the optical functions we performed the photoinducing treatment of the samples near and outside the first UV spectral maximum using the radiation of photoinducing UV nanosecond laser at 337 nm and second harmonic generated 532 nm signal originated from Nd:YAG laser emitting 1064 nm radiation. The changes of reflectivity within the spectral range covering this maximum were investigated. Huge sensitivity to the wavelength of photoinducing radiation was found.

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