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Calculation of electronic polarizabilities and effective charges of ions in pyroelectric α-$LiIO_3$ crystals

S.N.Khrykina, A.V.Yatsenko

Taurida National University, 4 Yaltinskaya St., 95007 Simferopol, Ukraine

Electronic polarizability (EP) of ions in α-$LiIO_3$ crystal has been calculated basing on refraction coefficients of the crystal. The EP of O^{2-} ions in α-$LiIO_3$ has been shown to be described by a 2nd rank tensor. Using the data obtained, local electric fields at the ions in the crystal structure have been calculated and the stability of Li^+ ions has been considered. The probable value ranges have been determined for effective charges of I^{5+} and O^{2-} ions.

На основании анализа коэффициентов преломления кристалла α-$LiIO_3$ выполнены расчеты электронной поляризуемости (ЭП) ионов, входящих в состав кристалла. Показано, что ЭП ионов O^{2-} в α-$LiIO_3$ описывается тензором 2-го ранга. При использовании полученных данных проведены расчеты локального электрического поля на ионах в структуре этого кристалла и анализ устойчивости ионов Li^+. Определен диапазон вероятных значений эффективных зарядов ионов I^{5+} и O^{2-}.

Crystals of lithium iodate α modification (α-$LiIO_3$) are used widely in non-linear optical devices, infrared and acoustic converters, due to the favorable combination of the material pyroelectric and piezoelectric properties. A comprehensive review on the structure and properties of that crystal is presented in [1, 2]. The importance of industrial applications of the crystal is confirmed by numerous attempts to grow the single crystal samples in microgravity [3]. Many different aspects of the crystal structure ordering at $T = 293$ K as well as the transition mechanism to β and γ phases, however, are scarcely studied to date.

Recently, the computerized simulation is used widely to study crystal structures with ionic and ion-covalent bindings. The method makes it possible to supplement considerably the results obtained using the classical methods of the crystal structure analysis (inelastic neutron scattering, X-ray analysis, NMR, etc.). The method is particularly efficient when the exhaustive data on effective charges q_{eff} and electronic polarizability are available for the ions included in the object as well as on the repulsive potential parameters for ion pair interactions. The known data on q_{eff} values for ions in the α-$LiIO_3$ crystal structure are presented in the Table below. The estimation made in [4] is based on the experimental (measured by NMR) value of the main component V_{zz} of the electric field gradient (EFG) tensor at ^7Li nuclei. In those calculations, however, the dipole contribution into EFG has been not accounted for, thus, the obtained q_I and q_O values are underestimated considerably. The data of [5] also are unreliable being in contradiction with the purely ionic character of the (Li^+–O^{2-}) binding. The nearest surrounding of most ions influences not only their q_{eff} but also electronic polarizabilities (EP). The EP values for ions in

Table. Effective ion charge values in α-$LiIO_3$ crystal

q_{Li} (|e|)	q_I (|e|)	q_O (|e|)	Method
1.000	1.605	−0.868	NMR data analysis [4]
0.51	3.66	−1.39	IR mode analysis [5]