MYSTERY OF NON-EQUIVALENT CENTERS IN CONGRUENT AND STOICHIOMETRIC $LiNbO_3$ AND $LiTaO_3$

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Lithium Niobate (LN) and Lithium Tanatalate (LT) doped with transition and rare-earth ions are of great interest for both fundamental science and advanced applications. According to the Rutherford back scattering data [1], all trivalent ions substitute for Li and should create similar centers. However, more than 11 different centers were distinguished by site-selective spectroscopy in congruent LN:Er [2]. Electron Paramagnetic Resonance, EPR and Electron Nuclear Double Resonance, ENDOR provides additional information about characteristics of impurity centers and their structures. Our EPR/ENDOR study has shown that transition and rare-earth ions create unexpected variety of completely different non-equivalent centers in both stoichiometric and lithium deficient congruent crystals. Four Nd^{3+}, two Er^{3+}, and nine Yb^{3+} centers were found and described in LN. Dominated Nd_1 center has C_3 point symmetry (axial center), whereas three others have lowest C_1 symmetry. Distant defects create small distortions of crystal field at the impurity site, which cause a line broadening, but do not change the C_3 symmetry. Defects in the near neighborhood can lower center symmetry from C_3 to C_1. We concluded that Nd_1 has distant charge compensation, whereas the charge excess in low-symmetry Nd(Li) centers is compensated by near lithium or niobium vacancies. Both Er^{3+} centers have C_1 symmetry. Since no axial centers were found, models with cation vacancies do not describe our experimental data. The Yb^{3+} ions create three C_3 and six C_1 centers. The ENDOR observations of Nb nuclei for dominated axial Yb_1 center gave us direct evidence that there are no defects in its surrounding. One axial and one C_1 centers are self compensated Yb(Li)-Yb(Nb) pairs. Six other centers are different complexes of Yb^{3+} and intrinsic defects. In high quality congruent LN and LT crystals, only the Fe^{3+} ions substituted for Li^+ were observed (Fe1 centers with the C_3 symmetry, the distant charge compensation by intrinsic defects in cation sublattice). In stoichiometric samples of LN and LT the additional C_3 symmetry centers (Fe2-Fe4) were discovered. The ENDOR has shown that the Fe^{3+} ions in Fe2-Fe4 centers substitute for Nb^{5+} or Ta^{5+}. The determination of the lattice sites and charge compensators of non-isovalent impurities are vital for both defect structure calculation and defect engineering for tailoring material properties for various applications. The work was supported by NSF.

References

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