Single-crystal EPR and DFT studies of a boron-associated oxygen hole center (BOHC) in datolite: Implications for radiation-induced defects in borosilicate glasses

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Radiation-induced defects in borosilicate glasses have been the subject of extensive research, because they exert profound influences on these important materials for diverse applications from fiber optics to radiation dosimetry and nuclear waste disposal. However, structural models, precursors and formation mechanisms of most radiation-induced defects in borosilicate glasses remain poorly understood. In this study, we have investigated datolite $CaBSiO_4(OH)$ (Bergen Hill, New Jersey) by use of single-crystal electron paramagnetic resonance (EPR) spectroscopy at 294 K and density functional theory (DFT) calculations. Single-crystal EPR spectra reveal the formation of a boron-associated oxygen hole center (BOHC) and an atomic hydrogen center from gamma-ray irradiation. Quantitative analyses of the BOHC spectra yield the follow spin-Hamiltonian parameters: g_1=2.0457(1), g_2=2.0113(1), g_3=2.0071(1), A_1= −0.46(1) mT, A_2= −0.92(1) mT, A_3= −0.97(1) mT. The directions of the unique g and A axes (g_1 and A_1) are approximately along the B-OH bond. These experimental results suggest that this BOHC represents hole trapping on the hydroxyl-oxygen atom after the removal of the hydrogen atom: via a reaction $O_3BOH \rightarrow O_3BO^{\bullet} + H^0$, where • denotes the unpaired electron. DFT calculations (CRYSTAL06, B3PW functional, all-electron basis sets and 2x2x1 supercells) support the proposed structural model and yield the following ^{11}B hyperfine coupling constants: A_1= −0.490 mT, A_2= −0.913 mT, A_3= −0.969 mT, in excellent agreement with the experimental results.