Crystal chemistry and thermodynamics of apatite for iodine incorporation

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Apatite structure provides a great potential for incorporating long-lived radioactive iodine from nuclear waste streams. Because of its chemical durability and high iodine content, apatite waste forms can reduce iodine release rate and minimize the waste volume. This study focuses on the crystal chemistry of apatite (A5(BO4)3I) using Artificial Neural Network (ANN) and first-principles calculations. A total of 92 apatite compositions were compiled and 47 were used to train ANNs and 45 were used to test the performance the trained network. The results show that the performances of the ANNs are satisfied for unit cell parameter a and c and the channel size in the structure. The trained and tested ANNs were used to predict iodine apatite with unknown compositions. With a crystal chemistry concern, chemical compositions that lead to matching the channel size to iodine were then predicted. A number of new apatite compositions were predicted to be able to incorporated iodine ion in the structural channel. In order to estimate if the predicted compositions are energetically stable, first-principles calculations were carried out. The calculated crystal structure and bonding distances were used to compare with available experimental results as a benchmark for the quality of the calculations. The electronic structure, charge density, and electron overlap were used to understand iodine bonding environment. Phonon density of states was calculated using the linear response theory and finite-difference approach, which was used to calculate free energy of the formation of $A_5(BO_4)_3I$. These results can be used to understand the thermodynamic stability of the apatites with respect to their decomposed phases. The results provide important clues to design experiments to synthesize new apatite compositions. The goal is to provide a fundamental understanding how iodine is incorporated in apatite crystal structure. This understanding can provide important insights for apatite waste design by optimizing the chemical composition and synthesis procedure.

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