

The aperiodic states of zircon: an ab initio molecular dynamics study

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ABSTRACT

We theoretically investigated the local structure of the aperiodic states of zircon (ZrSiO_4) using ab initio quantum mechanical calculations. The low and high density liquid and solid glassy phases were obtained by constant volume Car-Parrinello molecular dynamics simulations, using the molar volume of metamict and crystalline zircon, respectively. As in naturally metamict zircons, the polymerization of Si units, the segregation of Zr atoms, and an overall decrease of the Zr coordination were observed. However, the local ordering of our theoretical glasses differs from that of the natural amorphous samples. In the theoretical glasses, the Zr-O distances in the first coordination polyhedra are significantly more distributed and five- and six-coordinated Si species were observed. The relaxation of the glass structure on a time scale exceeding the possibility of molecular modeling is a possible explanation for these discrepancies. The dielectric and ^{29}Si NMR responses of the glassy phases were computed, providing new constraints for the analysis of experimental data recorded from metamict zircons. The calculated NMR spectra are in good agreement with the experimental NMR spectra in the four-coordinated Si region. Our results show that the usual regular systematic decrease of the ^{29}Si chemical shift as a function of the polymerization of Si units (Q^n species) cannot be used to interpret the ^{29}Si NMR spectrum of amorphous zircon. In particular, whereas the empirical scale would indicate an average polymerization of Q^3 , the average polymerization of $Q^{1.5}$ observed in the low density zircon glass can account for the experimental data. In a non-uniform model of the structure of metamict zircon, this lower average polymerization is consistent with a clustering of cations limited to few coordination polyhedra.