Quasiharmonic Lattice Dynamics Calculations of Energy Balances in the Thermal Expansion of SiO_2-TiO_2 Glass

JAMES R. RUSTAD[1]

[1]University of California, Davis, One Shields Avenue, Davis, CA 95616 james.rustad@gmail.com

The lithography transition to 13.5 nm places stringent requirements on ultra-low expansion glasses used as lenses in extreme ultraviolet lithography tools. To improve current materials, such as titania-silicate glasses, it is useful to understand the mechanisms by which thermal expansion is suppressed. Quasiharmonic lattice dynamics calculations are carried out on SiO_2-TiO_2 glass mixtures, (TiO_2 less than or equal to 20 weight percent) with model empirical interaction potentials show that the addition of TiO_2 systematically lowers the thermal expansion of high purity fused silica. Adding ten weight percent titania lowers the thermal expansion coefficient by approximately 0.5 ppm/K in rough agreement with observations. The driving force for lowering the thermal expansion coefficient in the model system is broken down into mode-by-mode contributions. Despite the fact that the model does predict a significant number of 5-fold coordinated Ti^{4+} ions in the structure, the driving force is distributed broadly across the frequency spectrum and is not localized into particular frequency ranges that can be associated with the coordination structure of Ti^{4+} in the simulated glass. While there is a region of low-frequency negative mode-Grueneisen parameters associated with transverse Ti-O-Si vibrations (reputed to be the origin of the ULE effect), their contributions are not significantly different than Si-O-Si vibrations in pure SiO_2 and, at least in the model system, in no way "cause" the ultra-low expansion of SiO_2-TiO_2 glasses. These results obviate the necessity of having to call on localized phenomena such as double-well potentials or peculiar Ti-O-Si transverse vibrations to explain the effect of TiO_2 on the thermal expansion of silica glass. The observation that there at least can be a collective response to TiO_2 addition that pervasively lowers the modal contributions to the coefficient of thermal expansion supression is unexpected and useful for thinking further about mechanisms.