Intervalence charge transfer in aluminum oxide and aluminosilicate minerals at elevated temperatures

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ABSTRACT

Single-crystal optical spectra of corundum (Al₂O₃) and the Al₂SiO₅ polymorphs andalusite, kyanite, and sillimanite, containing both Fe²⁺-Fe³⁺ and Fe²⁺-Ti⁴⁺ intervalence charge transfer (IVCT) absorption bands were measured at temperatures up to 1000 °C. Upon heating, thermally equilibrated IVCT bands significantly decreased in intensity and recovered fully on cooling. These trends contrast with the behavior of crystal field bands at temperature for Fe, Cr, and V in corundum, kyanite, and spinel. The effects of cation diffusion and aggregation, as well as the redistribution of band intensity at temperature, are also discussed. The loss of absorption intensity in the visible and near-infrared regions of the spectrum of these phases may point to a more general behavior of IVCT in minerals at temperatures within the Earth with implications for radiative conductivity within the Earth.

Keywords: Intervalence charge transfer, temperature dependence, corundum, andalusite, kyanite, sillimanite