

Ultra-Thin Sections - Illuminating the Spectra of Highly Opaque Minerals

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It is no surprise that transmission spectroscopy has been very rarely applied to opaque minerals. By definition, opacity is the lack of light passage. Hence, collecting the information gathered by optical and Near IR wavelengths passing through a highly opaque mineral sample is rather counterintuitive. However, many of the most abundant mineral phases both on the surface and in the deep earth are opaque due to photon absorbing mechanisms such as Inter-Valance Charge Transfer (IVCT) and magnetic enhanced d-d transitions. both suspected to decrease dramatically in high temperatures such as those found in the deeper earth. In our work, we demonstrate how ultra-thin samples (0.15 nm - 2 μm) open a window to unexplored optical absorbance features in highly opaque samples. Here we present the first-ever collected absorbance spectra of magnetite (150 nm thick), ilmenite ($\sim 1 \mu\text{m}$), and hematite ($\sim 1 \mu\text{m}$) at temperatures ranging from ambient to 1100 $^{\circ}\text{C}$. We used both synthetic and natural samples and achieved the minute thicknesses required for transparency using two different methods. Thin film specimens ($< 500 \text{ nm}$) were synthesized through Molecular-Beam Epitaxy (MBE) at the Schlom Lab at Cornell. Natural samples were manually thinned to 200 μm and further thinned to single digit μm thickness using a Dimpler TEM sample prepping apparatus.

Initial ambient temperature results agree with proposed mechanisms for the opacity of the measured phases, near-IR centered wide Inter-Valance Charge Transfer (IVCT) peak for the magnetite (~ 1250) and the ilmenite ($\sim 1300 \text{ nm}$ in agreement with previous work [3]), and magnetically enhanced d-d transition bands for the hematite [4]. Despite their thinness, both synthetic and natural samples proved to be stable enough for the investigation of the temperature dependence of both mechanisms up to 1100 $^{\circ}\text{C}$. IVCT absorption bands have been previously shown to decrease at high temperatures in phases possessing diluted (non-stoichiometric) IVCT sites. Our results show for the first time that the intensity IVCT absorption bands fall dramatically upon heating in stoichiometric IVCT minerals. In hematite, the magnetically enhanced spin-forbidden absorption has been investigated beyond the curie temperature of hematite ($> 680 \text{ }^{\circ}\text{C}$) and has shown a decrease in d-d transition absorption suggesting a breakdown in magnetic enhancement. We believe that ultra-thin sections are a yet to be widely utilized very attainable tool that holds the power to elucidate the darkest of minerals and shed light on their electronic outlay, their trace components, and their crystallographic defects, in a quantitative and orientation specific manner.

References:

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