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Role of ilmenite micro-inclusion on Fe oxidation state of natural sapphires

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The blue color of the blue sapphire is caused by the Fe-Ti pairs. Recently, the oxidation states of Fe and Ti on high-quality blue sapphire were found as Fe³⁺ and Ti⁴⁺. However, the oxidation state of Fe on natural sapphire with some inclusions was reported as mixing of Fe²⁺ and Fe³⁺ using the x-ray absorption near edge structure spectroscopy (XANES). Generally, there are mineral inclusions on natural sapphire related to Fe such as hematite (Fe₂O₃) and ilmenite (FeTiO₃). In this study, we investigate the micro-inclusions on natural sapphires by the electron probe micro analyzer (EPMA). The oxidation states of Fe and Fe-O bond length were analyzed by x-ray absorption spectroscopy (XAS). The Fe K-edge EXAFS fitting results focused on the first shell of Fe atoms on high-quality natural sapphires were shown that the Fe-O bond length on α -Al₂O₃ was fitted well with Fe-O bond length on Fe₂O₃ presenting Fe³⁺. However, the Fe-O bond length on natural sapphires with ilmenite micro-inclusion was fitted with Fe-O bond length on Fe₃O₄ showing Fe²⁺ and Fe³⁺. As the result, the Fe²⁺ on natural sapphires was caused by the ilmenite micro-inclusion.

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