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Reexamination of the structure of opal-A: A combined study of synchrotron X-ray diffraction and pair distribution function analysis

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Abstract

The structure of opal-A was not fully understood due to its poorly crystalline nature. To better understand its structural characteristics, we have analyzed opal-AN (amorphous-network) and opal-AG (amorphous-gel) using synchrotron X-ray diffraction (XRD), pair-distribution function (PDF) analysis, and transmission electron microscopy (TEM). Opal-AN mainly exists as an aggregation of different sizes of nanospheres (<5 nm) generating banded features, whereas opal-AG displays close-packed silica nanospheres with a diameter of ~400 nm. TEM energy-dispersive X-ray spectroscopy (EDS) indicates that Na, Al, K, and Ca are present as trace elements in opal-AN and opal-AG. XRD patterns of both samples show one prominent peak at ~4.0 Å, together with broad peaks at ~2.0, ~1.45, and ~1.2 Å. Previous studies only identified the ~4.0 Å diffraction peak for the definition of opal-A. Hence, opal-A needs to be redefined by taking into account the newly observed three broad peaks. PDF patterns of opal-AN and opal-AG reveal short-range atomic pairs (<15 Å) with almost identical profiles. Both phases exhibit Si-O correlation at 1.61 Å and O-O correlation at 2.64 Å in their [SiO_4] tetrahedra. The currently accepted opal structure is disordered intergrowths of cristobalite- and tridymite-like domains consisting of six-membered rings of [SiO_4] tetrahedra. Our PDF analyses have identified additional, coesite-like nanodomains comprising four-membered [SiO_4] rings. Moreover, we have identified eight-membered rings that can be generated by twinning and stacking faults from six-membered rings. The coesite nanodomains in opal-A may be a precursor for coesite micro-crystals formed by the impact of supersonic micro-projectiles at low pressures. More broadly, our study has also demonstrated that the combined approach of synchrotron XRD/PDF with TEM is a powerful approach to determine the structures of poorly crystallized minerals.

Keywords: Synchrotron X-ray diffraction, pair distribution function analysis, transmission electron microscopy, local structure, opal-A