

Rare-earth elements in synthetic zircon: Part 2. A single-crystal X-ray study of xenotime substitution

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ABSTRACT

Zircon crystals synthesized in a Li-Mo oxide melt and doped with trivalent lanthanides and Y (REE), both with and without P, were examined by single-crystal X-ray diffraction (XRD). REE are incorporated into the Zr site in the zircon structure, and some Zr appears to be displaced to the Si site. Crystals doped with middle REE (MREE, Sm to Dy) and Y, plus P follow the xenotime substitution ($\text{REE}^{3+} + \text{P}^{5+} = \text{Zr}^{4+} + \text{Si}^{4+}$) rather closely, whereas crystals doped with heavy REE (HREE, Er to Lu) deviate from the xenotime substitution, having REE:P atomic ratios significantly greater than one. Xenotime substitution requires that P^{5+} replace Si^{4+} , but this substitution becomes limited by strain at the Si site in HREE-doped crystals. As Si sites become saturated with P^{5+} , additional charge balance in synthetic zircon crystals may be provided by Mo^{6+} and Li^+ from the flux entering interstitial sites, accounting for an additional 0.3 to 0.6 at% HREE beyond that balanced by P^{5+} ions. Heavy REE are more compatible in the zircon structure than are LREE and MREE, and HREE substitution is ultimately limited by the inability of the zircon structure to further accommodate charge-compensating elements. Thus the limit on REE concentrations in zircon is not a simple function of REE^{3+} ionic radii but depends in a complex way on structural strain at Zr and Si sites, which act together to limit REE and P incorporation. The mechanisms that limit the coupled xenotime substitution change from LREE to HREE. This change means that REE fractionation in zircon may vary according to the availability of charge-compensating elements. REE partition coefficients between zircon and melt must also depend in part on the availability of charge-compensating elements and their compatibility in the zircon structure.