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Rare earth elements in synthetic zircon: Part 1. Synthesis, and rare earth element and phosphorus doping

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ABSTRACT

Zircon crystals were grown from a Li-Mo flux (7.5 mol% Li_2MoO_4; 86.5 mol% MoO_3) to which equal molar proportions ZrO_2 and Li_2SiO_3 were added (3 mol% each). The crystals were initially grown undoped, but later Dy was added to the flux without any other charge-compensating species. With Dy and P added, in equal molar proportions, the zircon crystals incorporated 1.37 mol% (6.99 wt%) Dy and 1.36 mol% (1.33 wt%) P, a factor of 5.3 increase in Dy over the crystals grown without P intentionally added to the flux. The other P+REE-doped zircon crystals displayed an approximately 1000-fold increase in REE and P from La through Lu, a result of decreasing ionic radii. The incorporation of P^{5+} allowed, in a general sense, the xenotime-type coupled substitution of (REE^{3+}, Y^{3+}) + P^{5+} = Zr^{4+} + Si^{4+}. From La to Nd, however, P exceeds REE, from Sm to Gd, the REE are generally equal to P, and from Tb to Lu the REE exceed P. The Y- and P-doped zircon behaved more like middle-REE (MREE)-doped zircon than heavy-REE (HREE)-doped zircon crystals in their ability to incorporate Y (and P) and to maintain charge neutrality. To investigate the incorporation of Dy with no P added to the flux, the P to LREE excess, and the HREE to P excess in the doped zircon, secondary ion mass spectrometry (SIMS) analyses were completed on selected crystals. In the Dy-doped crystals, the SIMS analyses revealed minor amounts of P, Li, and Mo in the crystals. These elements contributed to charge balance required by the excess Dy. In REE- and P-doped zircon, the SIMS analyses detected Li and Mo, and the Li and Mo may also provide charge balance for excess REE in the HREE+P-doped crystals.