

Internal stress-induced recrystallization and diffusive transport in CaTiO₃-PbTiO₃ solid solutions: A new transport mechanism in geomaterials and its implications for thermobarometry, geochronology, and geospeedometry

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ABSTRACT

We conducted a series of high-temperature experiments where single crystals of CaTiO₃ were embedded in PbTiO₃ powder for durations of 4 to 502 h at temperatures between 753 and 1207 °C. Combined with results from a previous study (Beyer et al. 2019), these experiments allow us to explore the influence of chemical potential gradients on the mechanisms of incorporation of Pb in CaTiO₃. Unlike in the previous study where Pb diffused into CaTiO₃, here we find that the rims of the CaTiO₃ crystals recrystallize to form a polycrystalline aggregate of [Pb_xCa_(1-x)]TiO₃ solid solutions. The width of the recrystallized front increases with run duration, and the contact to the single crystal becomes progressively wavy. The concentration of Pb decreases within the recrystallized front toward the interior of the single crystal, and the newly formed crystals are of different chemical compositions and orientations and are themselves chemically zoned. There is a discontinuous jump in Pb-concentration at the contact of the recrystallized front with the single crystal (termed “the migrating interface”). The development of chemical concentration gradients, combined with the fact that the width of the front grows as the square-root of time indicates a role of diffusion in the process; the formation of new crystals with different composition and no orientation relation to the precursor, and the jump in concentration at the boundary between the newly formed crystals and the single crystal indicates a dissolution-precipitation type process. Thus, this is a novel mechanism where diffusion, as well as dissolution-precipitation (in the sense that the structure of the single crystal is destroyed and replaced by new crystals), occurs simultaneously in a coupled manner and neither is rate-determining. The observations in this experimental study provide several insights into the mechanisms of chemical transformation in such non-metallic materials: (1) chemical differences can trigger mechanical deformation, which in turn can control chemical fluxes; (2) newly formed crystals, even at the high temperatures of the experiments, evolve continuously in chemistry and are not of an equilibrium composition; (3) the activation energy of the overall process (~70 kJ/mol) is lower than that for diffusion and provides a more effective means of chemical transformation, even though diffusion plays a central role in the process; and (4) it underscores the role of surface/interface free energy in the evolution of the transformation process. These results have important consequences for the reading of the petrological and geochemical signatures of the rock record—notably, in addition to knowing when a phase becomes chemically stable, it is also important to know when a particular crystal of the phase begins to exist. Some possible implications for thermobarometry, isotopic dating, and geospeedometry/diffusion chronometry are discussed.

Keywords: Diffusion, recrystallization, lattice strain, kinetics, perovskite