

Pb transport in CaTiO₃ controlled by diffusion and recrystallization governed by lattice strain

CHRISTOPHER BEYER¹, KATHARINA MARQUARDT²,
CHRISTIAN VOLLMER³, SUMIT CHAKRABORTY¹

1. Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum, Germany
(sumit.chakraborty@rub.de)
2. Imperial College, London, U.K.
3. Institut für Mineralogie, Münster, Germany.

Transport of Pb into oriented natural and synthetic single crystals of CaTiO₃ has been studied using different experimental setups. The source of Pb was either a laser deposited (Ca_{0.9}Pb_{0.1})TiO₃ thin film or an infinite powder reservoir of different compositions, such as (Ca_{0.9}Pb_{0.1})TiO₃ or pure PbTiO₃. The crystals were annealed in a high-temperature furnace between 735 and 1135°C between time periods of 2 to 238 hours. The samples were analyzed afterwards using different analytical methods such as SEM, EMPA, RBS, TOF-SIMS and TEM. It was found that the transport of Pb into CaTiO₃ crystals involves several processes that occur in parallel, in addition to simple lattice diffusion. Addition of the much larger cation, Pb, in the CaTiO₃ lattice causes strain that manifests itself as newly formed dislocations in the diffusion zone. The Pb atoms tend to get trapped in these dislocations, causing an inhomogeneous distribution of Pb and slowing down the transport of Pb, in spite of the presence of additional dislocations, which would normally be considered to be faster diffusion pathways. If a higher concentration gradient is imposed on the crystals (i.e. a larger driving force via a larger chemical potential gradient), the transport behavior changes. Instead of simple volume diffusion, a front of newly crystallized (Pb,Ca)TiO₃ crystals propagates into the CaTiO₃ single crystal. The behavior of this process is characteristic of diffusion (e.g. square root of time dependence), but occurs much faster than the measured volume diffusion rates. While further characterization is in progress, we speculate at this point that the recrystallization occurs when a threshold concentration of dislocations is exceeded, controlled by the magnitude of the driving force of Pb transport. The results have implications for not only the calculation of closure temperatures of Pb in CaTiO₃ (e.g. for geochronometry of kimberlites), but for the understanding of chemical transformation in non-metallic materials (silicates, oxides, titanates) in general.