Lead diffusion in CaTiO₃: A combined study using Rutherford backscattering and TOF-SIMS for depth profiling to reveal the role of lattice strain in diffusion processes

Christopher Beyer[1,*], Ralf Dohmen[1], Detlef Rogalla[2], Hans-Werner Becker[2], Katharina Marquardt[3], Christian Vollmer[4], Ulrich Hagemann[5,6], Nils Hartmann[5,6,7], and Sumit Chakraborty[1,2]

[1]Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum, 44801 Bochum, Germany
[2]RUBION, Ruhr-Universität Bochum, 44801 Bochum, Germany
[3]Bayerisches Geoinstitut, Universität Bayreuth, 95447 Bayreuth, Germany
[4]Institut für Mineralogie, Westfälische Wilhelms-Universität Münster, 48149 Münster, Germany
[5]Interdisciplinary Centre for Analytics on the Nanoscale, Universität Duisburg-Essen, 47057 Duisburg, Germany
[6]Centre for Nanointegration Duisburg-Essen (CENIDE), Universität Duisburg-Essen, 47057 Duisburg, Germany
[7]Fakultät für Chemie, Universität Duisburg-Essen, 47057 Duisburg, Germany

Abstract

We present experimental data on the diffusivity of Pb in CaTiO₃ perovskite, which is commonly used for dating kimberlites and carbonatites. Experiments were performed on oriented synthetic and natural CaTiO₃ single crystals. The Pb-source was either a laser deposited $(Ca_{0.83}Pb_{0.07})Ti_{1.05}O_3$ thin film or a $(Ca_{0.9}Pb_{0.1})TiO_3$ powder reservoir. The crystals were annealed in a high-temperature furnace between 736 and 1135 °C and for durations from 2 to 283 h. The diffusion profiles were measured with Rutherford backscattering and time-of-flight secondary ion mass spectrometry in the depth-profiling mode. The concentration profiles measured on the same samples with the two analytical methods are in agreement. The measured concentration profiles show two regions—a steep gradient at the diffusion interface that transitions sharply (at ~50 to 150 nm from the surface) to a low concentration tail that penetrates deeper into the crystal. This diffusion behavior could be modeled best using diffusion coefficients that are a function of the Pb concentration, with a different set of diffusion coefficient for the high and the low concentration region of the profile, respectively. The diffusion coefficients extracted from the thin film and powder source experiments are similar within uncertainties. Pb diffuses slower at concentrations between 8.5 and 0.6 wt% and 1.6 to 2.6 log units faster below ~0.5 wt% Pb. Temperature dependency for each region is discussed in the text, and the Arrhenius relation for the fast diffusion regime that is most relevant for natural samples is

$$D_{Pb}^{fast} = 2.5 \times 10^{-13} \times \exp\left(-158(24)\,kJ/mol/RT\right)\,m^2/s \ .$$

We found a distinct change in the structure of CaTiO₃ in the surface region of the single crystal that is coincidental with the change in diffusivity. This initial region is dominated by planar defects. We propose that Pb is trapped in planar defects that have formed due to the high strain introduced into the perovskite structure caused by the mismatch in the ionic radius between Ca^{2+} and Pb^{2+}. The activation energies obtained here yield closure temperature for Pb in CaTiO₃ between 300 and 400 °C for a range of different cooling scenarios if diffusive resetting of Pb in CaTiO₃ occurs at all. At typical cooling rates of hours to days for ascending kimberlite, the age of crystal growth is preserved, with closure temperatures similar to the magma temperature.

Keywords: Perovskite, diffusion, experimental, lattice strain, closure temperature, U/Pb chronometry