

# Kinetics of Cation Site-Exchange in Complex Oxides by Optical Relaxation Spectroscopy

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In many complex ionic oxides, such as perovskites, spinels and olivines, cations are often found to occupy structurally nonequivalent sites. Information on cation distributions and their temperature dependence is scarce. The kinetics of cation site-exchange have not been studied to any greater extent up to now - despite the fact that cation site-exchange processes represent elementary atomic jumps contributing to cation diffusion in these complex structures.

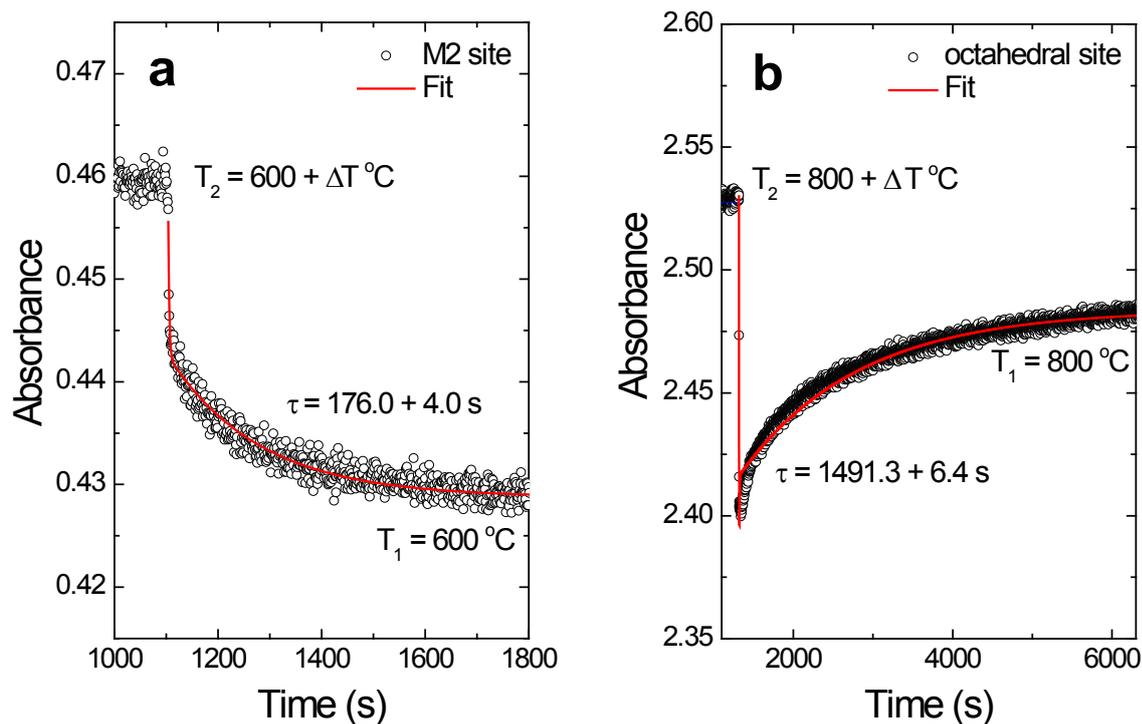
In cobalt-containing olivines,  $(\text{Co}_x\text{Mg}_{1-x})_2\text{SiO}_4$ , divalent cations occupy two nonequivalent octahedral sites, M1 and M2, with the preference of the  $\text{Co}^{2+}$  ions on the smaller M1 site mainly due to the crystal field stabilization energy and the bonding nature of ions in the sites [1]. In spinels, cations are distributed on tetrahedrally and octahedrally coordinated sublattices.  $\text{NiGa}_2\text{O}_4$  is a largely inverse spinel with about 90% of  $\text{Ni}^{2+}$  in the octahedral sites [2].

We report here experimental studies on the kinetics of cation site-exchange in complex oxides of the olivine and spinel structures by means of the combination of site- and ion-selective optical relaxation spectroscopy and temperature-jump technique. Fig. 1 shows that the time evolution of optical absorbance,  $A$ , upon temperature jumps can be modelled using the kinetic equation

$$A(t) = \varepsilon(t) \cdot c(t) \cdot d = \left[ (\varepsilon_0 - \varepsilon_\infty) \exp(-t/\sigma) + \varepsilon_\infty \right] \cdot \left[ (c_0 - c_\infty) \exp(-t/\tau) + c_\infty \right] \cdot d$$

where  $\sigma$  is the relaxation time of the absorption coefficient  $\varepsilon$  after the temperature jump, which was found from fitting to be several seconds.  $\tau$  is the relaxation time of the concentration of absorbing ions on the respective site after the temperature jump;  $d$  the thickness of the absorber.  $\varepsilon_0$ ,  $c_0$  and  $\varepsilon_\infty$ ,  $c_\infty$  are absorption coefficients and concentrations in the initial state (at time  $t = 0$ ) and final equilibrium state (at time  $t = \infty$ ).

The relaxation time for cation site-exchange from modelling the experimental data in air shown in Fig. 1 is  $176 \pm 4$  s at 600 °C for  $(\text{Co}_{0.21}\text{Mg}_{0.79})_2\text{SiO}_4$  and  $1491 \pm 6$  s at 800 °C for  $\text{NiGa}_2\text{O}_4$ , respectively.



**Fig. 1** Time dependence of the optical absorbance and fits of the relaxation course after temperature jumps: (a)  $\text{Co}^{2+}$  in M2 octahedral sites for  $(\text{Co}_{0.21}\text{Mg}_{0.79})_2\text{SiO}_4$  olivine and (b)  $\text{Ni}^{2+}$  in octahedral sites for  $\text{NiGa}_2\text{O}_4$  spinel.

The temperature- and composition-dependent kinetics of the cation exchange processes can be described within the framework of a vacancy mechanism for cation site-exchange and provide insights into details of cation diffusion in complex oxides [3,4].

## References

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