

## Optical Spectroscopy for Studying Dynamic and Kinetic Processes

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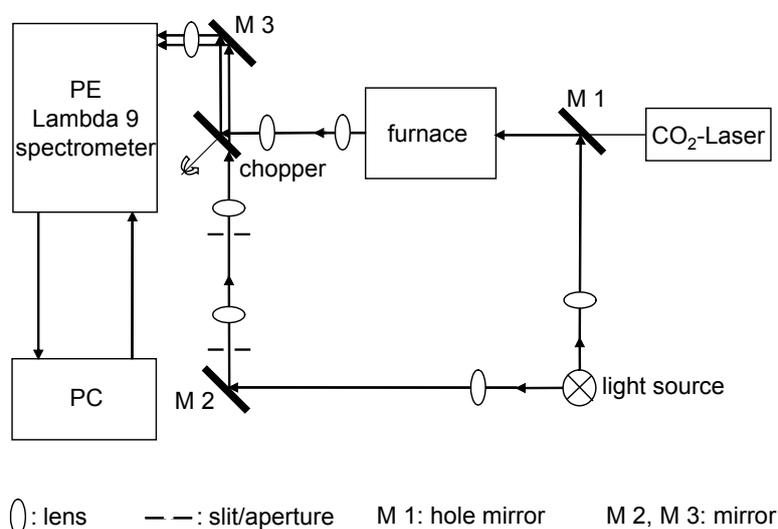
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*Presented at the Bunsen Colloquium: Spectroscopic Methods in Solid State Diffusion and Reactions  
September 24<sup>th</sup> – 25<sup>th</sup>, 2009, Leibniz University Hannover, Germany*

Optical spectroscopy is a powerful technique for studying kinetic and dynamic processes in solids. In the present contribution, in particular two properties of optical spectroscopy will be exploited:

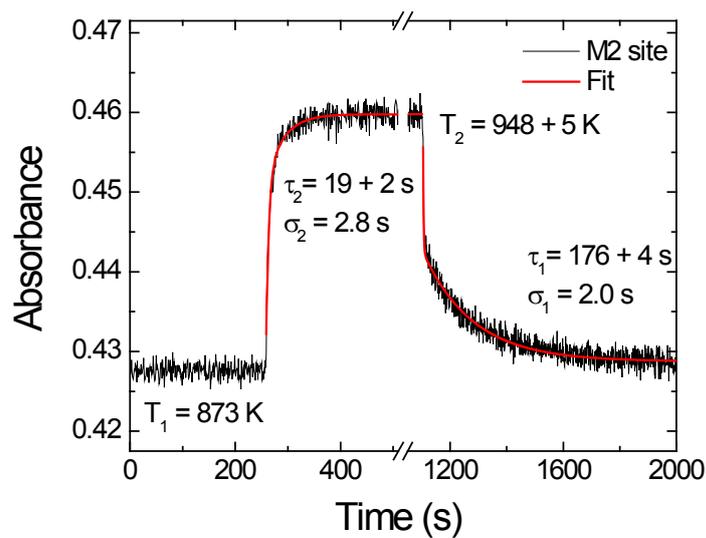
- (i) ligand field spectra of transition metal cations often can provide unique insights into the charge state of the ion under consideration as well as into their actual local coordination and the symmetry of their lattice site.
- (ii) optical absorption induced by hopping processes of small polarons reveals information on the dynamics of these processes and allows for the determination of associated small-polaron hopping energies.

Experimentally, the study of kinetic and dynamic processes in solids as a rule requires measurements to be performed at elevated temperatures under in-situ conditions and, *e.g.*, at defined oxygen partial pressures. Fig. 1 shows an experimental set-up used in some of the experiments reported below.

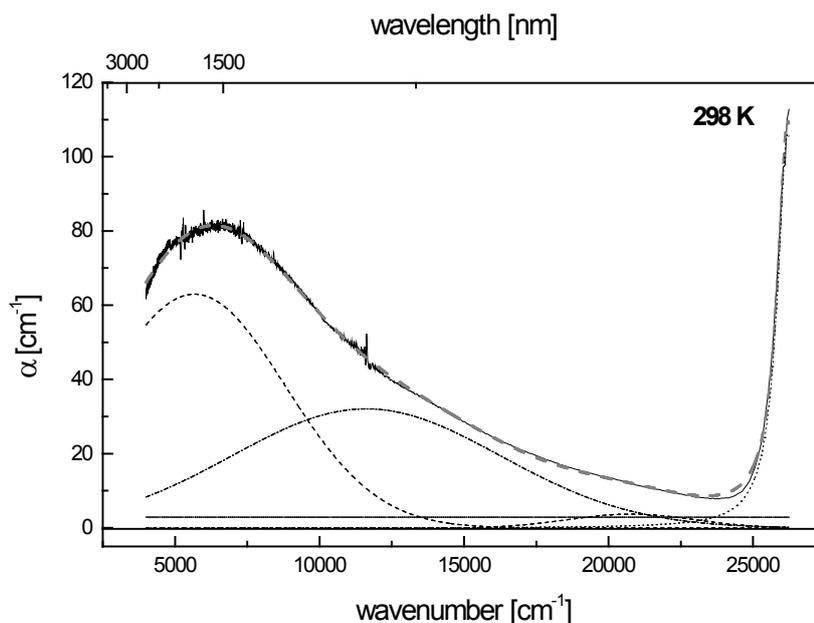


**Fig. 1** Sketch of the experimental setup for optical spectroscopy at elevated temperatures.

The kinetics of cation distributions in olivines has been one of the research fields of the last few years [1-4] of the Braunschweig Solid State Chemistry Group. Figure 2 shows how the optical absorbance  $A = \varepsilon \cdot c \cdot d$  due to  $\text{Co}^{2+}$  ions on M2 sites in  $(\text{Co}_{0.21}\text{Mg}_{0.79})_2\text{SiO}_4$  olivine changes with time upon temperature jumps between 873 and 948 K. The time evolution of absorbance – after the sudden initial changes due to the temperature dependent absorption coefficient  $\varepsilon$  – reflects the reequilibration of the cation distribution after the external perturbation. From the systematic studies performed, it has been found that the activation energy for cation redistribution is composition dependent and of the order of 200 kJ/mol. From the oxygen activity dependence of the kinetics it has been concluded that the cation site exchange processes are due to a local defect mechanism involving cation vacancies.



**Fig. 2** Temperature-jump optical relaxation experiments on M2 sites in  $(\text{Co}_{0.21}\text{Mg}_{0.79})_2\text{SiO}_4$  together with fits for temperature jumps between 873 K and 948 K. Relaxation times for the cation site-change reaction at 873 K and 948 K are 176 s and 19 s, respectively. Experiments performed in air.



**Fig. 3** Optical absorption spectrum of single crystalline blue  $\text{BaTiO}_3$  at 298 K fitted by three Gaussian peaks

Small-polaron hopping processes in BaTiO<sub>3</sub> give rise to optical absorption in the NIR region [5,6] and a close relationship has been shown to exist between the optical excitation energy  $E_{\text{opt}}$  and the associated hopping energy  $E_{\text{m}}$  of the small polarons:  $E_{\text{opt}} \approx 4E_{\text{m}}$ . As an example, Fig. 3 displays the spectrum of strongly reduced (blue) single crystalline BaTiO<sub>3</sub>. The absorption around 6000 cm<sup>-1</sup> (0.74 eV) has been associated with small-polaron hopping. Indeed, the magnitude of the hopping energy of about 0.18 eV has been confirmed by electrical conductivity and also absolute values of the optically determined conductivity agree well with the directly determined data.

### References

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