

RIXS and XANES spectroscopy study of La bearing compounds and La-doped silicate glasses

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Minerals and glasses that contain rare earth elements (REE) form an exciting class of materials. They have extraordinary properties, which are related to the partially filled valence shell and have found applications in many fields relevant to applied science and industry. Most of their applications are for optical materials, ceramics, electronic materials, catalysis, bioscience and nuclear waste management. This study deals with the investigation of the electronic structure of La bearing crystalline models to understand the electronic structure and coordination of La in silicate glasses.

The electronic structure of REE may be investigated by x-ray absorption near edge spectroscopy (XANES) at the L- and M-edges. It provides information about electronic states close to the Fermi level. The main edge spectral shape arises from transitions from the $2p$ to the $5d$ orbital, which is dedicated to dipole transitions. However, normal XANES is less sensitive to the pre-edge fine structure because of the core-hole lifetime broadening. In resonant inelastic x-ray scattering (RIXS) a core-electron is promoted to an excited state just as in XANES but also the energy dependence of the scattered photon is measured, which gives additional information about the intermediate state, the final state and the pre-edge fine structure, which corresponds to $2p$ to $4f$ quadrupole transitions. Moreover, the XANES region can be studied in considerably more detail as compared to standard absorption spectroscopy because of absence of the core-hole lifetime broadening. Kvashnina et al. [3] showed a way to evaluate the measured RIXS spectra using the Missing code. The calculations take into account spin-orbit interactions and the multiplet structure that arise from the Coulomb and exchange energies interactions between $4f$ electrons, between $4f$ and $2p$ electrons and between $4f$ and $3d$ electrons.

$2p3d$ -RIXS and XANES have been collected for La_2O_3 , LaF_3 , LaCO_3 , $\text{LaN}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$, monazite and several La-doped silicate glasses at beamline W1 [1] of the Deutsche Elektronen-Synchrotron (DESY) in Hamburg and at beamline ID 26 [2] of the European Synchrotron Radiation Facility (ESRF) in Grenoble. The collected RIXS planes show for all samples weak but different pre-edge features, which are probably related to quadrupolar transitions. The preliminary results indicate that differences in the electronic structure are related to slight differences in intra-atomic multiplet splitting and thus to differences in chemical bonding. The extracted high-resolution XANES spectra of the model compounds reflect the difference in the structural environment of La. The XANES spectra of the glasses indicate differences in La-O distance depending on glass composition.

References:

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