EXAFS Investigation of \( \text{Sr}_3\text{Mo}_{1.5}\text{Zn}_{0.5}\text{O}_{7-x} \) at the Mo - K edge

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Ternary strontium transition metal oxides with perovskite structure or with perovskite-like layer structures derived thereof have been investigated in the past fifteen years in numerous ways, due to their electric and magnetic properties and their structural similarity to the cuprate superconductors. Of particular interest in this context were the Ruddlesden-Popper phases, with the general formula \( \text{A}_{n+1}\text{B}_n\text{O}_{3n+1} \), initially described in the system \( \text{Sr}/\text{Ti}/\text{O} \) [1] which are characterized by a regular sequence of rock-salt layers (AO) and perovskite layers (ABO\(_3\)). Compounds with perovskite \( (n = \infty) \) and \( \text{K}_2\text{NiF}_4 \) structure \( (n = 1) \) [2] may also be grouped in this series. The new layered perovskite phase \( \text{Sr}_3\text{Mo}_{1.5}\text{Zn}_{0.5}\text{O}_{7-x} \) [3] was synthesised by solid-state reaction starting from \( \text{SrO}, \text{MoO}_3, \text{Mo} \) and a \( \text{Zn}/\text{ZnO} \) oxygen buffer separated in space.

The crystal structure was refined by the Rietveld method from X-ray powder diffraction data. The compound crystallizes in the space group \( \text{I}4/\text{mmm} \) (No. 139) with the lattice parameters \( a = 3.9631(1) \) Å and \( c = 20.5830(4) \) Å. The chemical analysis of a powder sample of \( \text{Sr}_3\text{Mo}_{1.5}\text{Zn}_{0.5}\text{O}_{7-x} \) results in mass fractions of \( \text{Sr} \) 46.45 ± 0.11 %, \( \text{Mo} \) 25.18 ± 0.26 %, \( \text{Zn} \) 6.30 ± 0.02 %, \( \text{O} \) 19.61 ± 0.38 %, leading to molar ratio \( \text{Sr} : \text{Mo} : \text{Zn} : \text{O} = 2.98(1) : 1.48(2) : 0.54(1) : 6.9(1) \). Furthermore, the oxygen content of the compound was determined by oxidation analysis by means of DTA/TG in airflow to a temperature of \( T = 1273 \) K. Assuming that molybdenum would completely oxidize to \( \text{Mo}^{4+} \), an oxygen deficit of \( x \approx 0.25 \) was established. This indicates the presence of a mixed-valent compound \( (5/6 \text{Mo}^{4+}, 1/6 \text{Mo}^{6+}) \). The oxygen deficit of \( x \approx 0.25 \) leads to an effective valence of +4.3.

In order to obtain data on electronic states of Mo in \( \text{Sr}_3\text{Mo}_{1.5}\text{Zn}_{0.5}\text{O}_{7-x} \), X-ray absorption spectroscopy was applied. For this purpose, XANES investigations at the Mo – K edge were carried out. The measurements were performed at the beamline X1 in transmission geometry. The experimental setup (Si(111) monochromator) and the simultaneous measurement of the sample and the standard (Mo foil) permit a resolution of 1 eV. Figure 1 shows the normalized Mo – K edge of elementary molybdenum (Mo foil; applied as a standard), of \( \text{Mo}^{4+} \) (\( \text{MoO}_2 \)), \( \text{Mo}^{6+} \) (\( \text{MoO}_3 \)), and a mixture of \( \text{Mo}^{4+} \) and \( \text{Mo}^{6+} \) (50 % \( \text{MoO}_2 \) / 50 % \( \text{MoO}_3 \)) compared with the Mo – K edge of \( \text{Sr}_3\text{Mo}_{1.5}\text{Zn}_{0.5}\text{O}_{7-x} \). \( \text{MoO}_3 \) and the mixture containing \( \text{MoO}_3 \) show a clearly visible pre-edge peak, which is characteristic for a \( 1s \) (Mo) -> 4d (Mo) transition [4]. The main-edge position taken at 50 % of the complete edge-jumps at \( 20000 \) eV (Mo), \( 20007.4 \) eV (\( \text{MoO}_3 \)), \( 20008.3 \) eV (\( \text{Sr}_3\text{Mo}_{1.5}\text{Zn}_{0.5}\text{O}_{7-x} \)), \( 20008.6 \) eV (\( \text{MoO}_2 / \text{MoO}_3 \)) and \( 20009.8 \) eV (\( \text{MoO}_3 \)) may be attributed to the excitation of a Mo \( 1s \) electron onto the \( 5p \) level. The position of the absorption edge of \( \text{Sr}_3\text{Mo}_{1.5}\text{Zn}_{0.5}\text{O}_{7-x} \) in comparison to the absorption edge positions of \( \text{MoO}_3 \) and \( \text{MoO}_3 \) and the mixture of 50 % \( \text{MoO}_2 \) and 50 % \( \text{MoO}_3 \) clearly indicates the presence of \( \text{Mo}^{4+} \) and \( \text{Mo}^{6+} \) in \( \text{Sr}_3\text{Mo}_{1.5}\text{Zn}_{0.5}\text{O}_{7-x} \). Whereby the amount of \( \text{Mo}^{4+} \) is definitely larger as that of \( \text{Mo}^{6+} \), which correlates well with the electron counting (see text above). Since the evaluation of the spectra was made at the limits of device resolution, a quantitative estimation of the \( \text{Mo}^{4+} \) and \( \text{Mo}^{6+} \) fractions was not attempted.
Figure 1: Normalized Mo – K edge of elementary molybdenum, MoO₂, MoO₃, and a mixture of 50 % MoO₂ / 50 % MoO₃ compared with the Mo – K edge of Sr₃Mo₁.₅Zn₀.₅O₇₋ₓ.

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References