

Charge disproportionation in the iron(IV) oxide $\text{Sr}_3\text{Fe}_2\text{O}_7$

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Perovskite-related oxides with iron in the high oxidation state +4 are an interesting class of materials for studying correlations between chemical composition, crystal structure, electronic states, magnetism and electrical transport behavior. This subject is currently of great interest in oxomanganates revealing the colossal magnetoresistance effect. The interplay of strongly covalent Fe(3d)–O(2p)–Fe(3d) interactions, electron-electron correlation and electron-lattice coupling lead to unusual electronic properties of Fe^{IV} oxides. Examples are the distorted perovskite CaFeO_3 and the Ruddlesden-Popper type phase $\text{Sr}_3\text{Fe}_2\text{O}_7$ where ^{57}Fe Mössbauer spectroscopy revealed a charge disproportionation of Fe^{IV} , which is frequently formulated as $2\text{Fe}^{\text{IV}} \rightarrow \text{Fe}^{\text{III}} + \text{Fe}^{\text{V}}$. Both materials are semiconductors. We have investigated how the electronic properties of $\text{Sr}_3\text{Fe}_2\text{O}_7$ are influenced first by cation substitutions and second by high pressure in order to understand the factors which favor a charge disproportionation of Fe^{IV} .

In the course of substitution studies the phases $\text{Sr}_{2.7}\text{Ba}_{0.3}\text{Fe}_2\text{O}_{\sim 7}$, $\text{Sr}_{2.6}\text{La}_{0.4}\text{Fe}_2\text{O}_7$, and $\text{Sr}_3\text{Fe}_{2-x}\text{Ti}_x\text{O}_{7-y}$ ($0.2 \leq x \leq 1.5$, $0.05 \leq y \leq 0.33$) were prepared from the oxides, annealed at O_2 pressures up to 70 MPa and characterized by X-ray powder diffraction, ^{57}Fe Mössbauer spectroscopy, magnetic susceptibility and electrical resistance measurements. All samples crystallize in the tetragonal crystal structure

of $\text{Sr}_3\text{Fe}_2\text{O}_7$ (space group $I4/mmm$) the main structural motif of which are two-dimensional double-layers of corner-sharing FeO_6 octahedra. In $\text{Sr}_{2.7}\text{Ba}_{0.3}\text{Fe}_2\text{O}_{\sim 7}$ and $\text{Sr}_3\text{Fe}_{1.8}\text{Ti}_{0.2}\text{O}_{\sim 7}$ oxygen deficiency was small and the formal oxidation state of Fe is approximately +4. Similar as for $\text{Sr}_3\text{Fe}_2\text{O}_7$ the Mössbauer spectra of the magnetically ordered phases of these compounds (Fig. 1) are characterized by two sextets with an intensity ratio of approximately 1:1 and considerably different isomer shifts and magnetic hyperfine splittings. This is evidence for a charge disproportionation of Fe^{IV} .

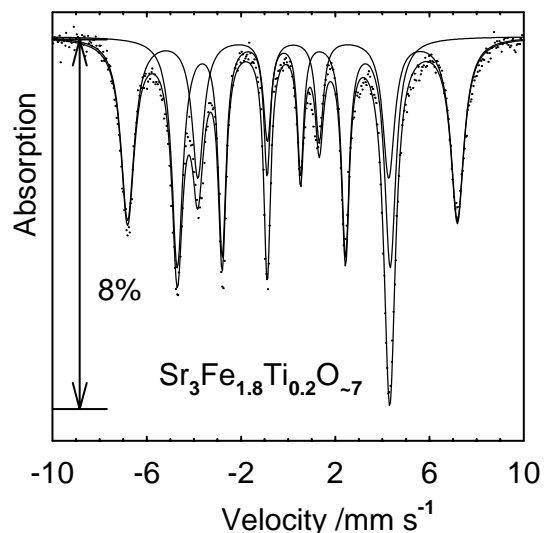


Figure 1: Mössbauer spectrum of the magnetically ordered phase of $\text{Sr}_3\text{Fe}_{1.8}\text{Ti}_{0.2}\text{O}_{\sim 7}$ at 4 K. Solid lines correspond to a fit of the data with two sextets.

Table 1. Mössbauer parameters of $\text{Sr}_3\text{Fe}_2\text{O}_{\sim 7}$ and cation substituted phases; $\Delta\delta$ and ΔB correspond to the differences in isomer shifts and hyperfine fields of the two sextets, respectively. In the last two columns the area fractions of the Fe^{III} like sites in the Mössbauer spectra and the Fe^{III} fractions derived from sample composition are given.

compound	$\Delta\delta$ [mm s ⁻¹]	ΔB [Tesla]	Area(Fe^{III}) [%]	Fe^{III} fraction [%]
$\text{Sr}_3\text{Fe}_2\text{O}_{\sim 7}$	0.33	13.5	52	5
$\text{Sr}_{2.7}\text{Ba}_{0.3}\text{Fe}_2\text{O}_{\sim 7}$	0.34	13.4	48	5
$\text{Sr}_3\text{Fe}_{1.8}\text{Ti}_{0.2}\text{O}_{\sim 7}$	0.38	15.3	49	6
$\text{Sr}_{2.6}\text{La}_{0.4}\text{Fe}_2\text{O}_7$	0.32	14.5	50	20
$\text{Sr}_3\text{FeTiO}_{6.84}$	0.46	19.6	40	33
Reference data for $\text{Fe}^{\text{III}}/\text{Fe}^{\text{V}}$	0.81	33		

Some results from the evaluation of the Mössbauer spectra are given in Table 1. The differences $\Delta\delta$ and ΔB in isomer shifts and magnetic hyperfine fields of the two sextets, which reflect the differences in the charge- and spin-densities between the two sites in the charge disproportionation phase, are much smaller than expected from Fe^{III} and Fe^{V} reference data. This suggests that the charge disproportionation in $\text{Sr}_3\text{Fe}_2\text{O}_7$ corresponds to a collective electronic state involving a charge- and spin-density wave. The values of $\Delta\delta$ and ΔB for $\text{Sr}_{2.7}\text{Ba}_{0.3}\text{Fe}_2\text{O}_{\sim 7}$ are nearly the same as for $\text{Sr}_3\text{Fe}_2\text{O}_7$, but they are larger for $\text{Sr}_3\text{Fe}_{1.8}\text{Ti}_{0.2}\text{O}_{\sim 7}$. This is attributed to a stronger spin- and charge- separation due to the disturbance of the electron-transfer pathways when Fe^{IV} ions are replaced by Ti^{IV} ions. From the Mössbauer data it is concluded that a collective charge disproportionation state is also retained in $\text{Sr}_{2.6}\text{La}_{0.4}\text{Fe}_2\text{O}_7$, formally a mixed-valence material with 80% Fe^{IV} and 20% Fe^{III} . On the other hand, larger degrees of Ti substitution introduce considerable oxygen deficiency and a concomitant reduction of Fe^{IV} to Fe^{III} . In $\text{Sr}_3\text{FeTiO}_{6.84}$ (33% Fe^{III}) the area fractions in the Mössbauer spectra roughly correspond to the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{IV}}$ ratio expected from sample composition. Probably the stronger disturbance of the electron-transfer pathways in $\text{Sr}_3\text{FeTiO}_{6.84}$ leads to a stronger localization of the electronic system and the formation of a $\text{Fe}^{\text{III}}/\text{Fe}^{\text{IV}}$ mixed-valence state.

The magnetism of the materials is governed by a competition between ferro- and antiferromagnetic exchange interactions which give rise to overall antiferromagnetic ordering for $\text{Sr}_{2.7}\text{Ba}_{0.3}\text{Fe}_2\text{O}_{\sim 7}$ and $\text{Sr}_3\text{Fe}_{1.8}\text{Ti}_{0.2}\text{O}_{\sim 7}$ and to spin-glass behavior for $\text{Sr}_{2.6}\text{La}_{0.4}\text{Fe}_2\text{O}_7$ and $\text{Sr}_3\text{FeTiO}_{6.84}$. All cation substitutions result in a decrease of electrical conductivity in comparison with $\text{Sr}_3\text{Fe}_2\text{O}_7$.

High-pressure Mössbauer studies of $\text{Sr}_3\text{Fe}_2\text{O}_7$ reveal that the charge disproportionation of Fe^{IV} disappears between 10 and 20 GPa. Optical reflectivity spectra of $\text{Sr}_3\text{Fe}_2\text{O}_7$ were measured between 0.6 and 4 eV for pressures up to 37 GPa (Fig. 2).

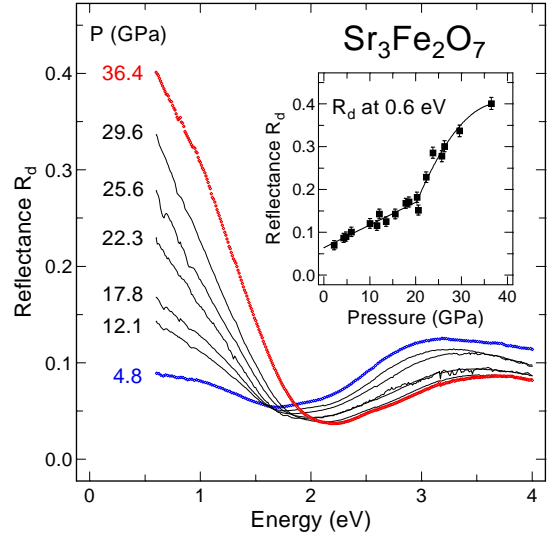


Figure 2: Reflectivity spectra of $\text{Sr}_3\text{Fe}_2\text{O}_7$ at room temperature and different pressures. The absolute reflectivity R_d refers to that measured at the sample-diamond interface. The inset shows the pressure dependence of R_d at 0.6 eV.

The spectra show a continuous increase in the near-infrared (NIR) reflectivity with pressure which is most pronounced above 20 GPa. This suggests that the optical excitation gap diminishes under pressure and finally an insulator-metal transition occurs. In order to correlate the changes in electronic properties with structural changes the pressure dependence of the crystal structure of $\text{Sr}_3\text{Fe}_2\text{O}_7$ was investigated up to 45 GPa by angle-dispersive powder X-ray diffraction using synchrotron radiation and image plate detection. The structural data reveal no anomalies in the whole pressure range. This is seen for instance from the pressure dependence of the lattice parameter a (Fig. 3) as $a/2$ basically corresponds to the Fe–O1 distances in the iron-oxygen planes of the crystal structure. Also the ratio c/a does not show a significant pressure dependence (inset of Fig. 3).

The electronic behavior of Fe^{IV} oxides may be qualitatively rationalized by considering the width w_σ of the σ^* conduction band arising from the e electrons of the t_{2g}^1 electronic configuration of Fe^{IV} in relation to the electron-electron correlation energy, U . As the nearly regular FeO_6 octahedra in the crystal structure of $\text{Sr}_3\text{Fe}_2\text{O}_7$ are not in favor of a Jahn-Teller effect expected for localized e electrons, it is reasonable to consider the σ^* electrons as collective electrons.

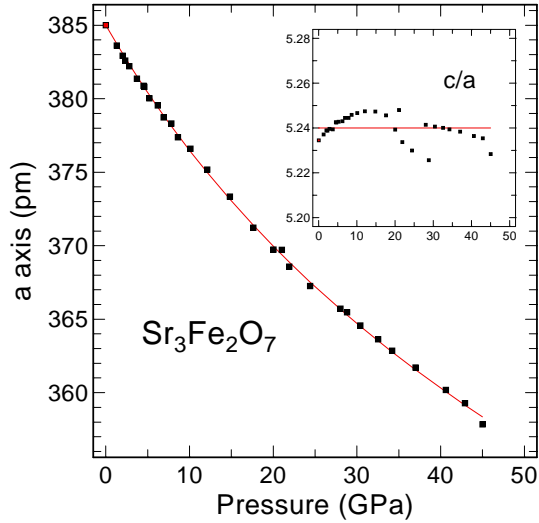


Figure 3: Pressure dependence of the lattice parameter a and of the ratio c/a (inset) for $Sr_3Fe_2O_7$ at room temperature. The solid line corresponds to a Birch-Murnaghan type of fit to the experimental data. Since the a parameter of the sample at ambient pressure is close to that reported for $Sr_3Fe_2O_{7.00(5)}$ we use stoichiometric formula for discussing the high-pressure properties.

In the metallic limit ($w_\sigma > U$) the σ^* band would be quarter-filled. It is suggested that in a certain range of w_σ/U ratios in the vicinity of the insulator-metal transition a collective charge disproportionation state is stabilized.

The ferromagnetic interactions in $Sr_3Fe_2O_7$ and related materials are attributed to a pronounced tendency to delocalize the σ^* electrons, which are, however, coupled to the more localized t_2 electrons, similar to the double-exchange mechanism in oxomanganates. The absence of discontinuities in the structural parameters of $Sr_3Fe_2O_7$ as a function of pressure indicates that the main effect of pressure is a shortening of the Fe–O distances and thus a strengthening of the Fe–O–Fe interactions. The resulting increase in the ratio w_σ/U leads to the disappearance of the charge disproportionation between 10 and 20 GPa and most likely to an insulator-metal transition above 20 GPa. In contrast to $CaFeO_3$ there is no pressure-induced high-spin to low-spin transition.