

Background & Aims

- Alkaline earth substituted lanthanum ferrites are good candidate cathode materials for solid oxide fuel cells (SOFCs) due to its high mixed ionic-electronic conductivity.
- Limited research has been conducted to systematically distinguish the influence of Ca, Sr and Ba substitution, while $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ has been extensively used as a cathode material.
- To investigate the influence of alkaline earth substitution on crystal structure, electrical conductivity and oxygen transport properties of $\text{La}_{0.6}\text{A}_{0.4}\text{FeO}_{3-\delta}$ (A = Ca, Sr and Ba).

Crystal structure

- Thermally stable up to 1000 °C
- Phase transition → loss of BO_6 octahedra tilt system
- According to Price *et al.*¹ LCF64 shows a sequence of $a^0a^0a^0 \rightarrow a^0a^0a^0 \rightarrow a^0a^0a^0$ during cooling, in Glazer's notation.

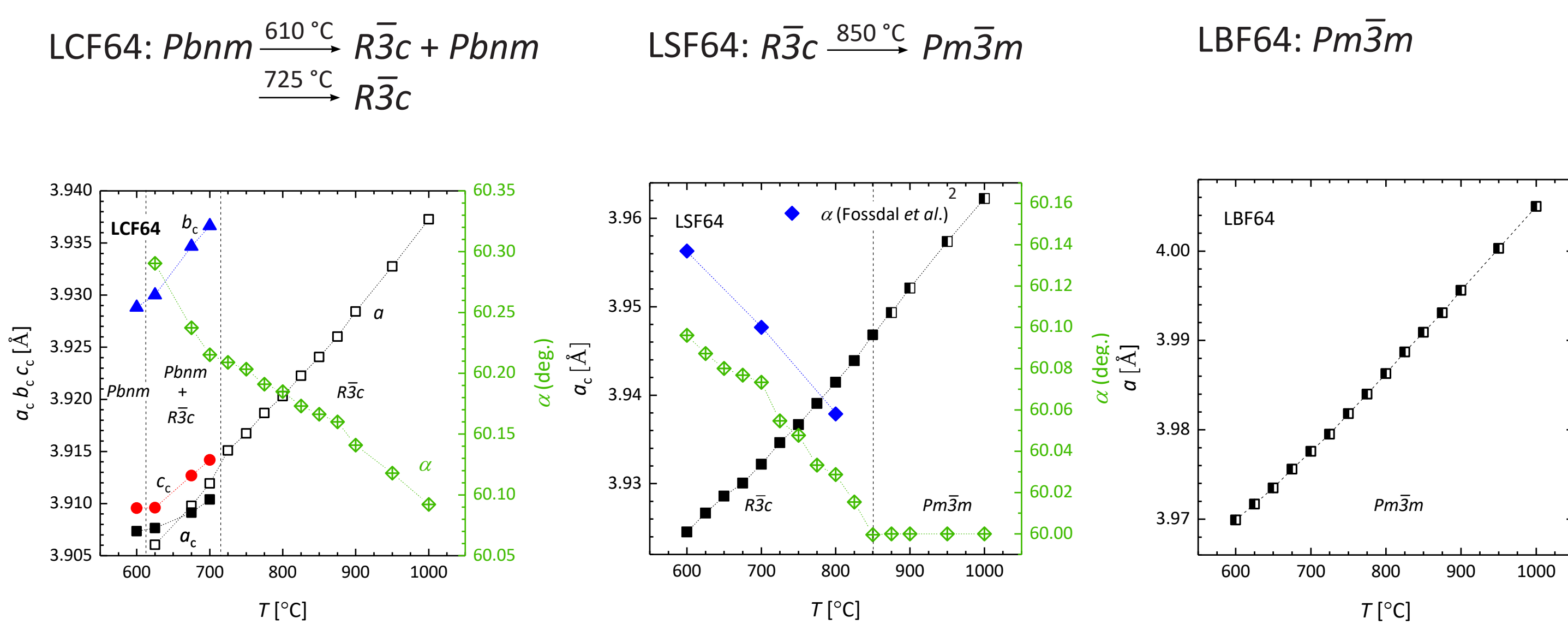
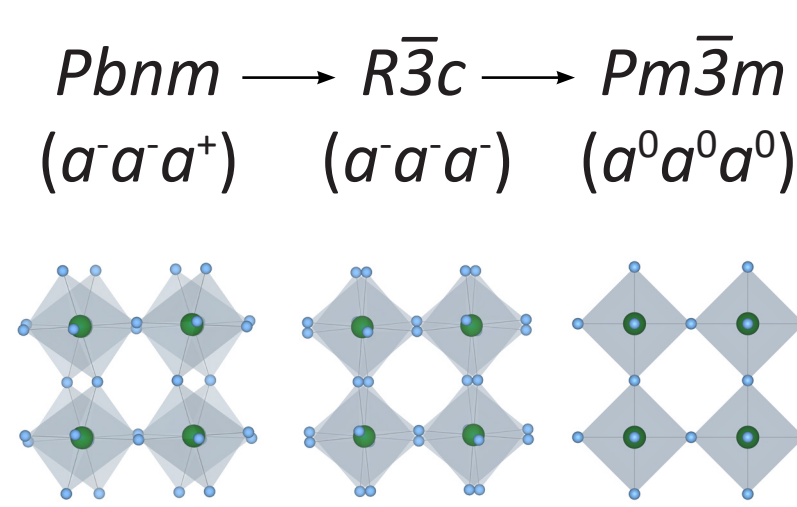


Fig. 1 Pseudo-cubic lattice parameters for LCF64, LSF64, and LBF64 as a function of temperature from Rietveld refinement of HT-XRD data recorded in the range 600-1000 °C in air.

Electrical conductivity

- In the temperature range 650-1000 °C and $p\text{O}_2 = 0.21$ bar:

$$\sigma_{\text{LSF64}} > \sigma_{\text{LCF64}} \approx \sigma_{\text{LBF64}}$$

$$\mu_p = \sigma / (N_{\text{ABO}_3} e[\text{Fe}^{\bullet}])$$

the number of unit cell per unit volume

- Mobility of the electron hole (μ_p)

$$\mu_p^{\text{LSF64}} > \mu_p^{\text{LBF64}} > \mu_p^{\text{LCF64}}$$

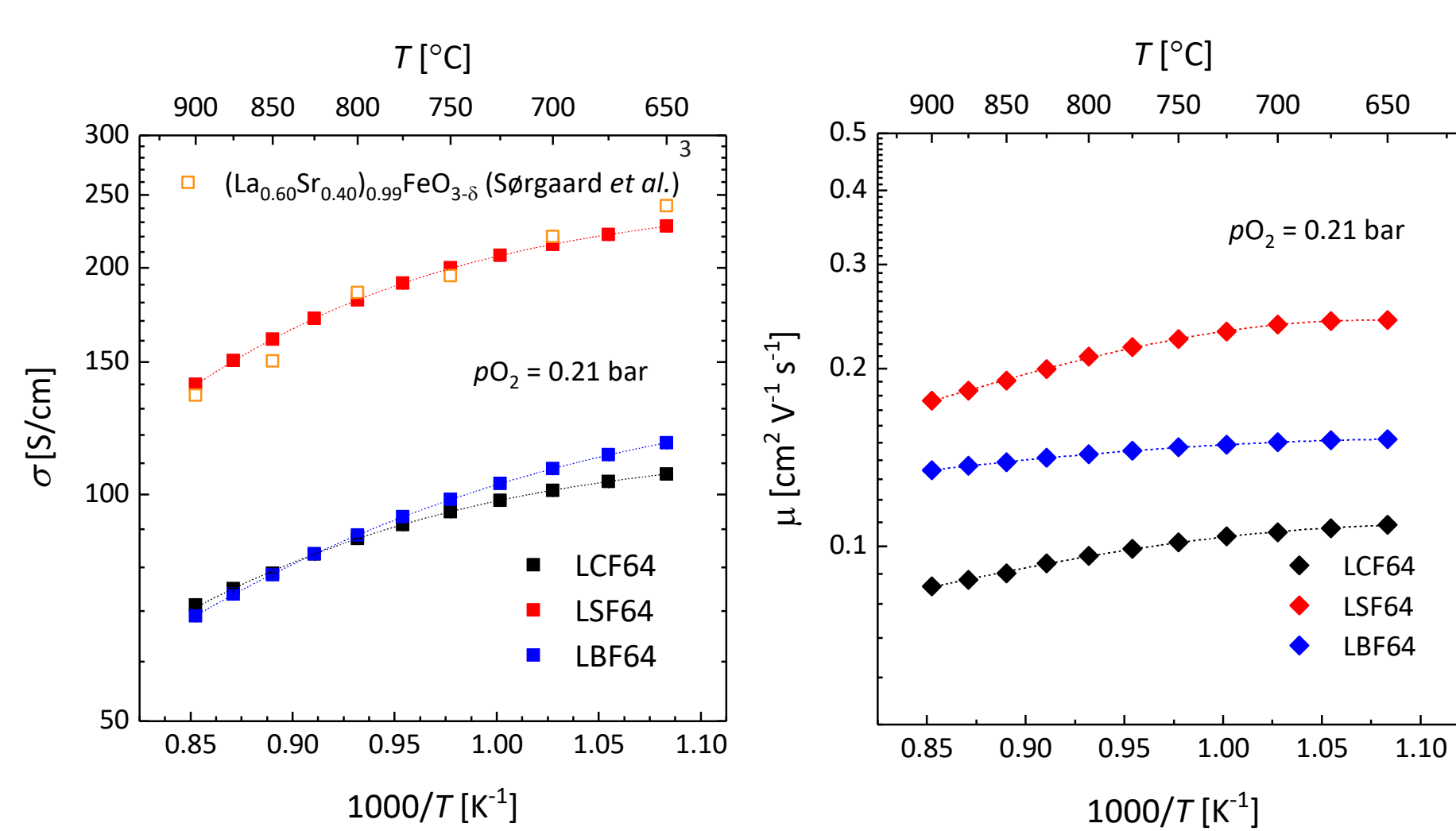


Fig. 2 Reciprocal temperature dependence of electrical conductivity (left) and charge carrier ($[\text{Fe}^{\bullet}]$) mobility (right) from 650°C to 900 °C at $p\text{O}_2 = 0.21$ bar. LSF64: good agreement is found with data from literature.²

Oxygen nonstoichiometry

- Oxygen nonstoichiometry (δ) was studied using thermogravimetric analysis (TGA) in the temperature range of 650-900 °C and $p\text{O}_2$ range of 0.045-0.9 bar

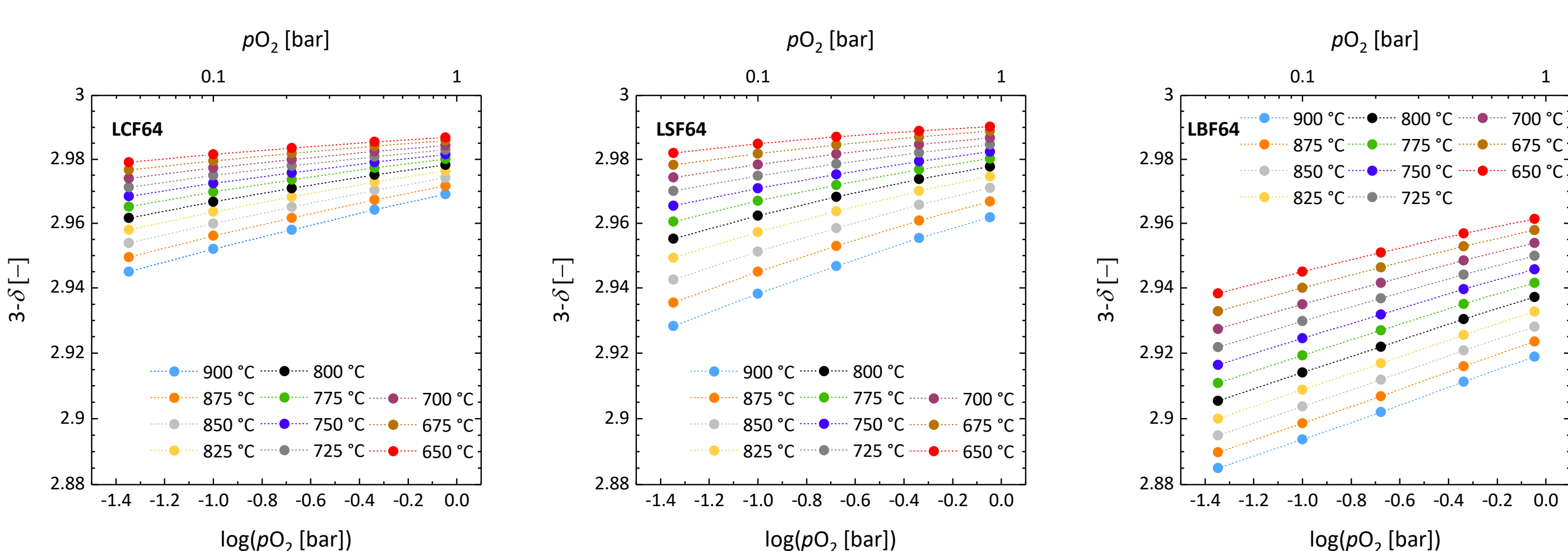
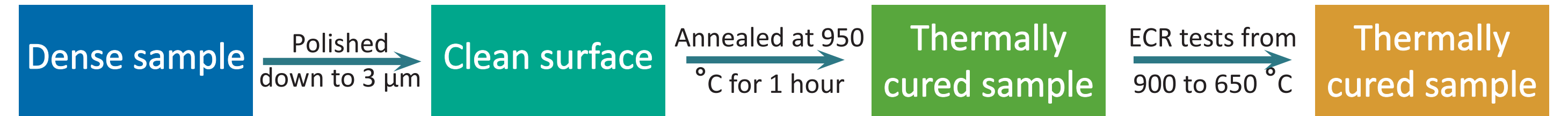


Fig. 3 Oxygen stoichiometry ($3-\delta$) of LCF64, LSF64 and LBF64 in response of $p\text{O}_2$ at different temperature.

Electrical Conductivity Relaxation (ECR)

Thermal History



- Surface exchange coefficient (k_{chem}) and chemical diffusion coefficient (D_{chem}) were derived from the nonlinear least-square fitting of ECR data.

- Significant similarities between D_{chem} values of LCF64, LSF64 and LBF64

- Activation energy of k_{chem} :

$$E_a^{\text{LCF64}} = 1.51 \pm 0.02 \text{ eV}$$

$$E_a^{\text{LSF64}} \approx E_a^{\text{LBF64}} = 0.89 \pm 0.01 \text{ eV}$$

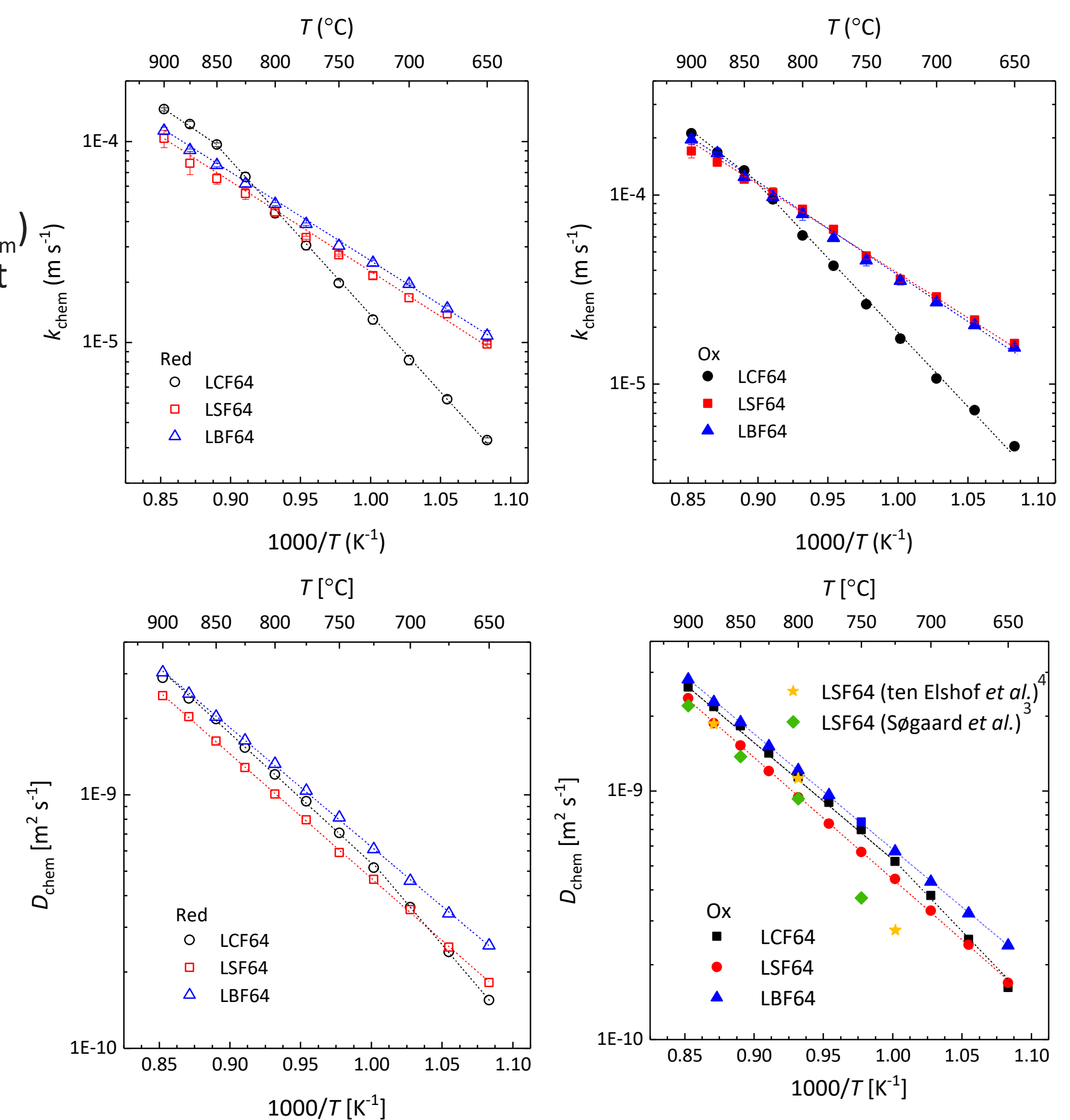


Fig. 4 Inverse temperature dependence of the surface exchange coefficient (k_{chem}) and chemical diffusion coefficient (D_{chem}) upon reduction and oxidation run for LCF64, LSF64 and LBF64 in the temperature range 650-900 °C between 0.1 and 0.21 bar.

Self-diffusion coefficient (D_s) & vacancy diffusion coefficient (D_v)

- D_s and D_v was derived by: $D_{\text{chem}} = \gamma_o D_s = \gamma_v D_v$ where γ_o, γ_v thermodynamic factors of oxygen ion, oxygen vacancy in the crystal, respectively.

$$\gamma_o = \frac{1}{2} \cdot \frac{\partial \ln(p\text{O}_2)}{\partial \ln(C_o)} = \frac{3-\delta}{2} \cdot \frac{\partial \ln(p\text{O}_2)}{\partial (3-\delta)}$$

$$\gamma_v = -\frac{1}{2} \cdot \frac{\partial \ln(p\text{O}_2)}{\partial \ln(C_v)} = -\frac{\delta}{2} \cdot \frac{\partial \ln(p\text{O}_2)}{\partial \delta} = \frac{3-\delta}{\delta} \gamma_o$$

- Significant similarities in D_s and D_v value between LCF64, LSF64 and LBF64

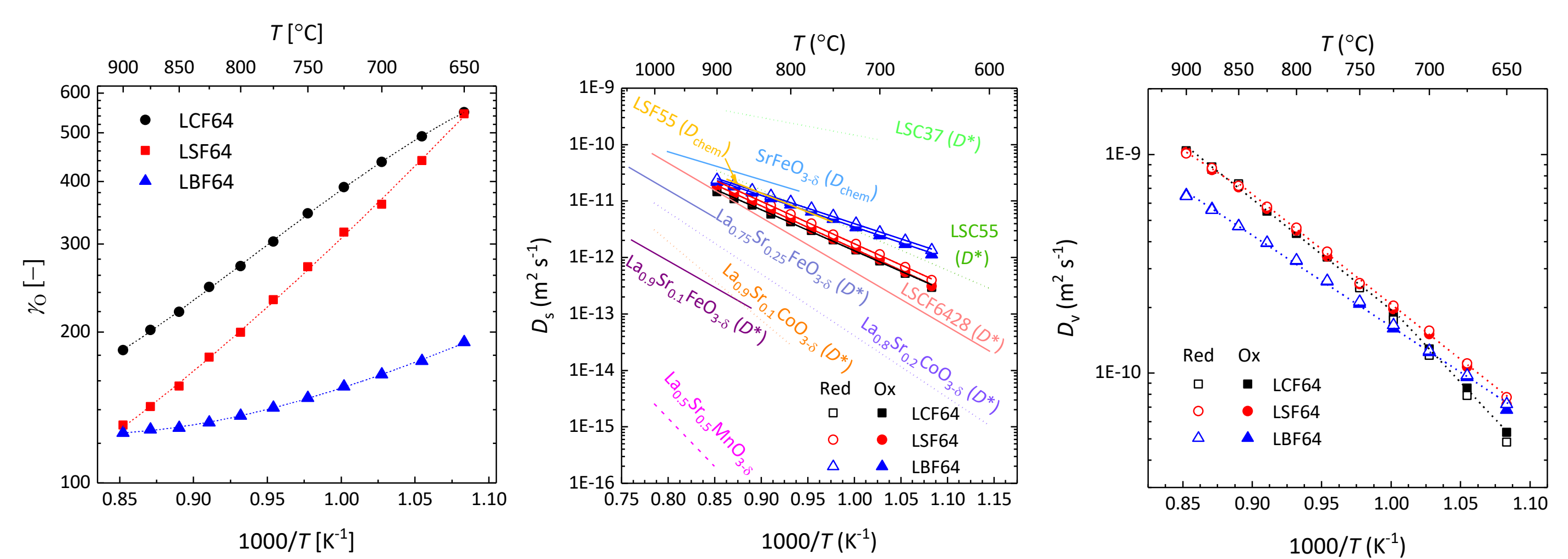


Fig. 5 Inverse temperature dependence of the oxygen ion thermodynamic factor (γ_o), self-diffusion coefficient (D_s) and vacancy diffusion coefficient (D_v) upon reduction and oxidation run for LCF64, LSF64 and LBF64. D_s values of LCF64, LSF64 and LBF64 were compared with several other compositions^{5,6,7,8,9}. D_s^* denotes the D_s value was obtained from the isotope exchange depth profiling technique and D_{chem} denotes the D_s value was derived from the data of ECR measurements.

Conclusions

- Thermal evolution of crystal structures of pure-phase LCF64, LSF64 and LBF64 were characterized by HT-XRD.
- LSF64 shows a significantly higher electrical conductivity and electron hole mobility than that of LCF64 and LBF64.
- Great similarity in the value of D_{chem} , D_s and D_v was found between LCF64, LSF64 and LBF64.

References

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