

Termická analýza a kalorimetrie oxidových materiálů



VŠCHT
Praha

David Sedmidubský

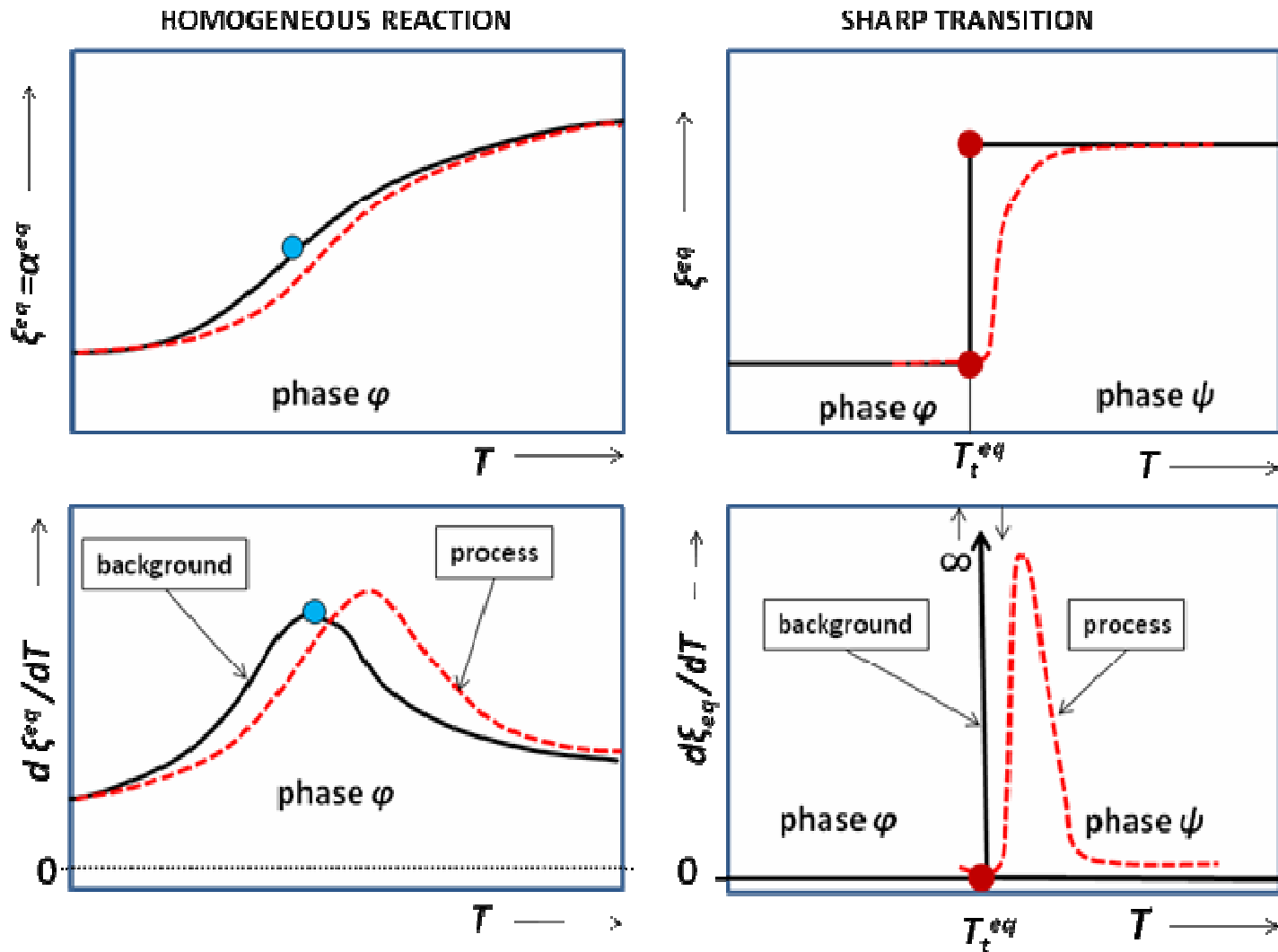
*Vysoká škola chemicko-technologická v Praze
Ústav anorganické chemie*



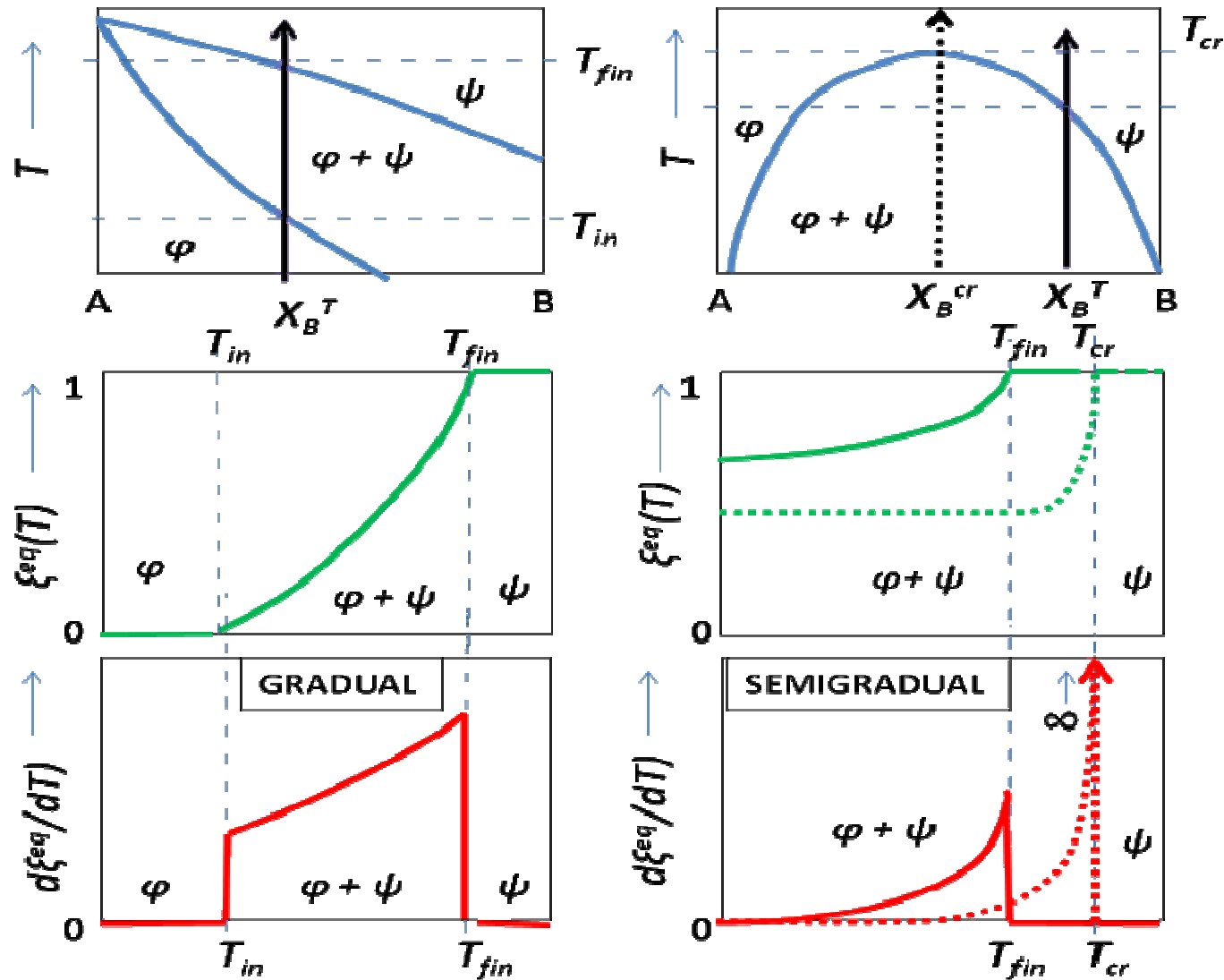
Termická analýza a kalorimetrie oxidových materiálů

- Termická analýza a konstrukce fázových diagramů
- Fenomenologie fázových přechodů
- Kalorimetrické stanovení základních termodynamických veličin
- $\Delta_f H$, $C_p(T)$: experiment vs. teorie
- Fázové diagramy T - x - p_{O_2}
- Oxidová x kovová tavenina a chování v okolí kritického bodu
- Tepelná kapacita za konstantní aktivity kyslíku – saturační příspěvek
- Vliv nestechiometrie na C_p
- Nestechiometrie a další materiálové vlastnosti (α_p , β_T)

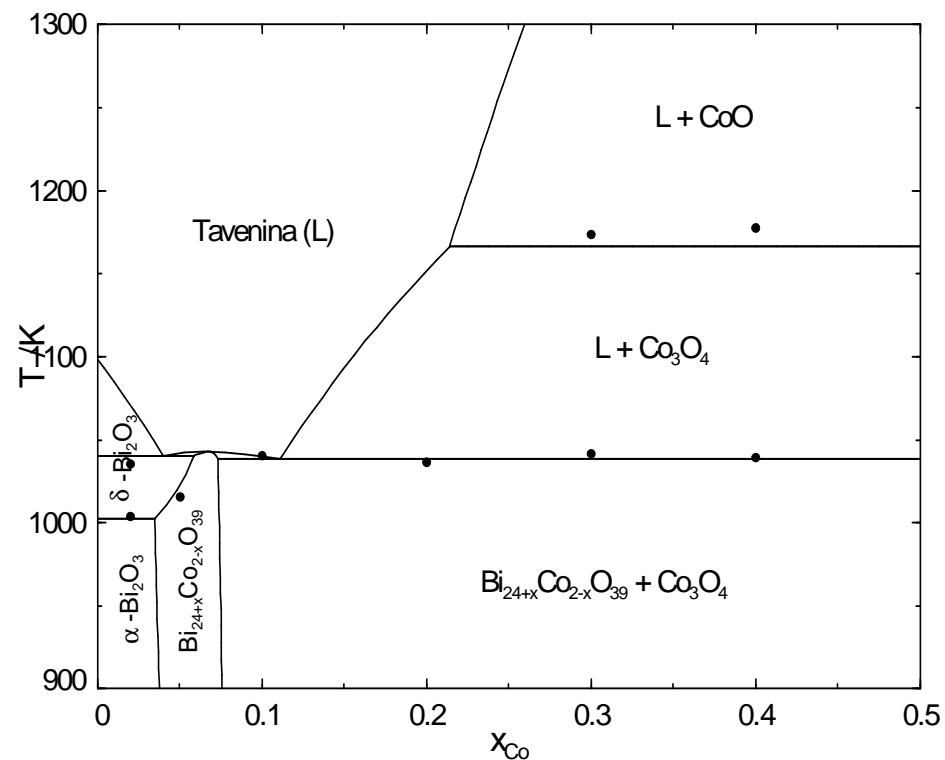
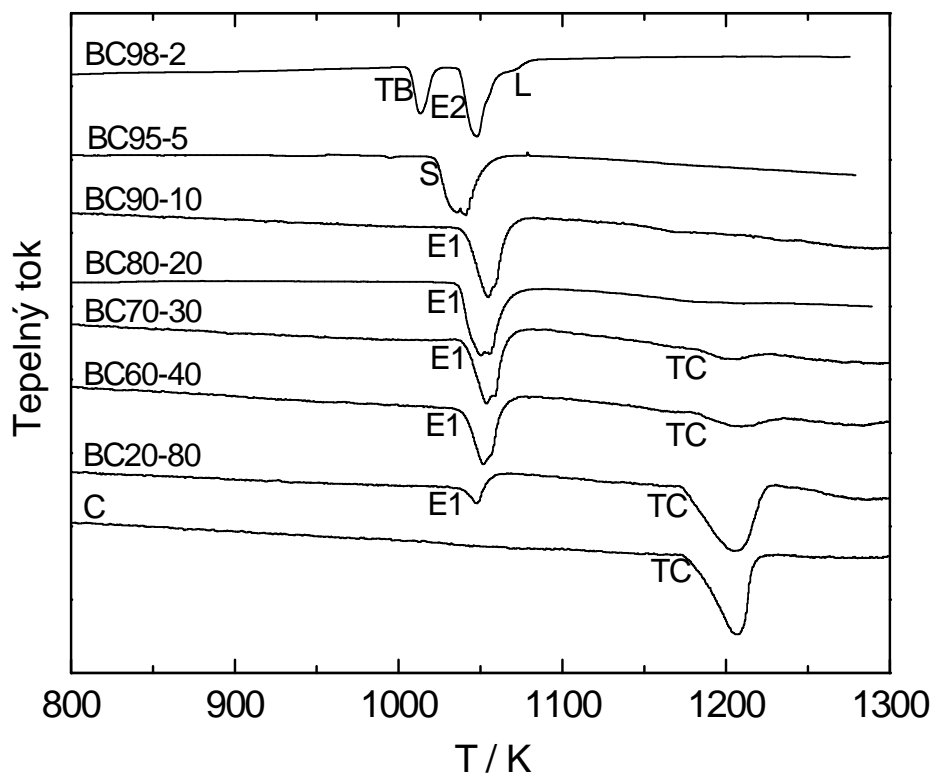
Termická analýza a klasifikace fázových přechodů



Termická analýza a klasifikace fázových přechodů



DTA/DSC – experimentální fázové diagramy, slučovací entalpie z rovnovážných dat

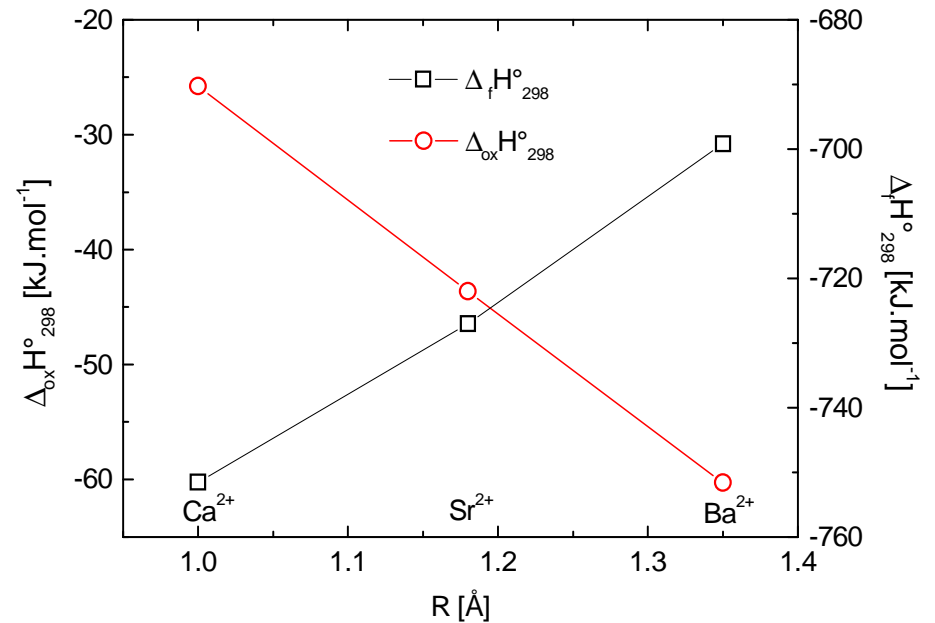
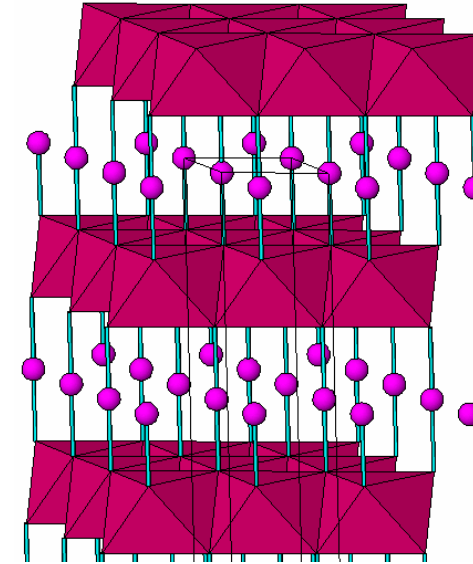
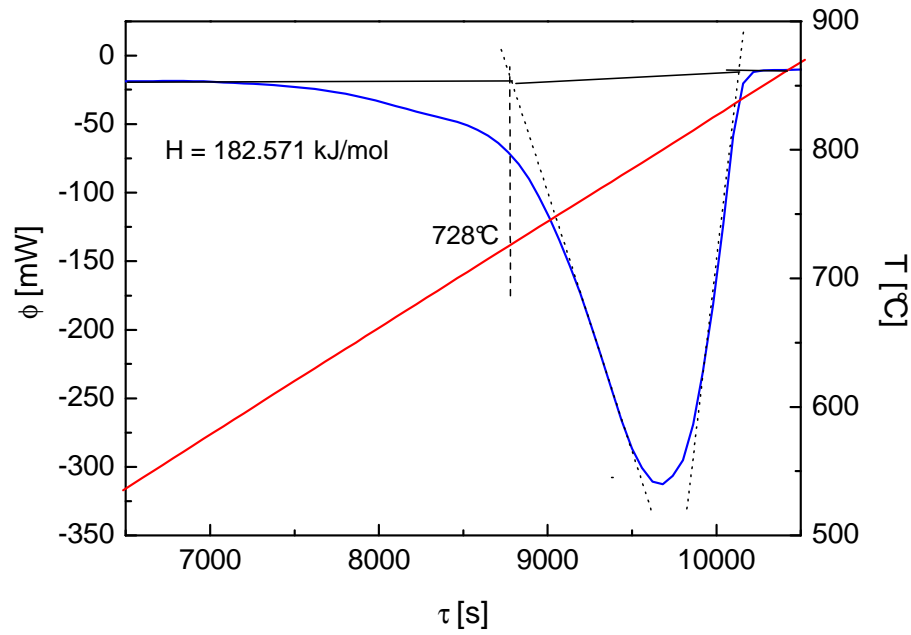


O.Jankovský, D.Sedmidubský, Z.Sofer
 Phase Diagram of the Pseudobinary System Bi-Co-O
 Journal of the European Ceramic Society 33 [13-14] (2013) 2699-2704

DSC – entalpie fázových přechodů

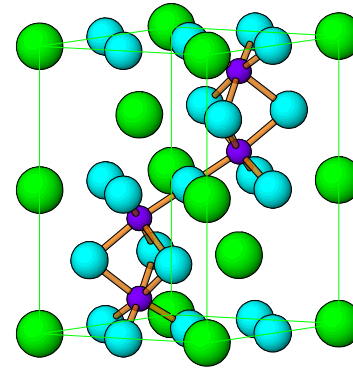
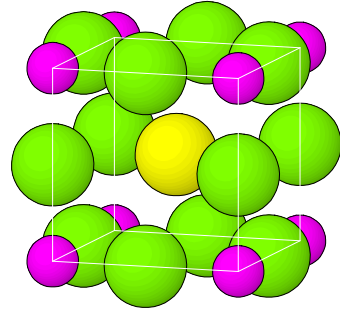


AE = Ca, Sr, Ba

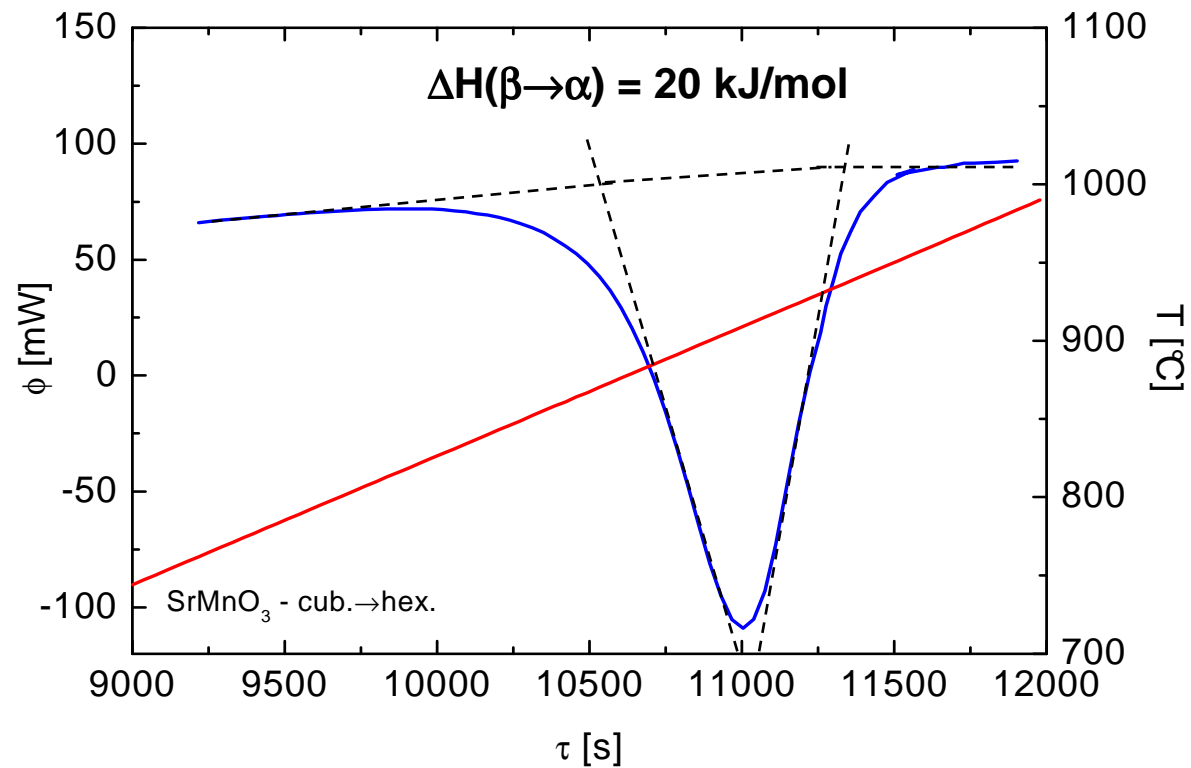


DSC – entalpie fázových přechodů

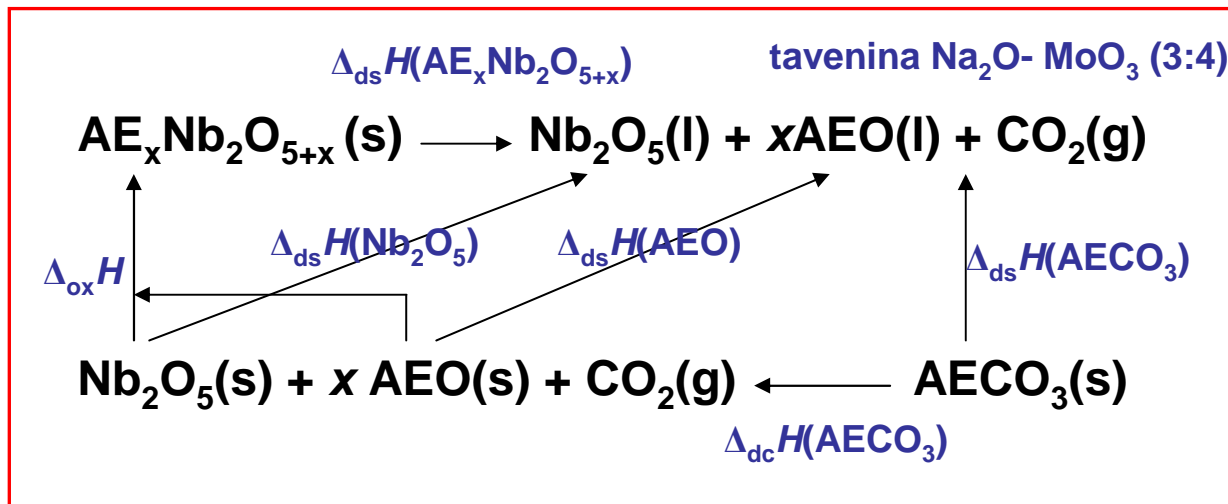
β -SrMnO₃
Pm3m



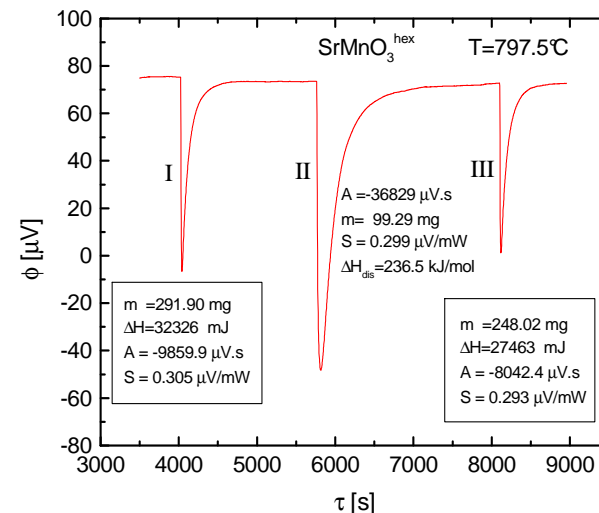
α -SrMnO₃
P6₃/mmc



Vhazovací kalorimetrie – měření rozpouštěcího tepla



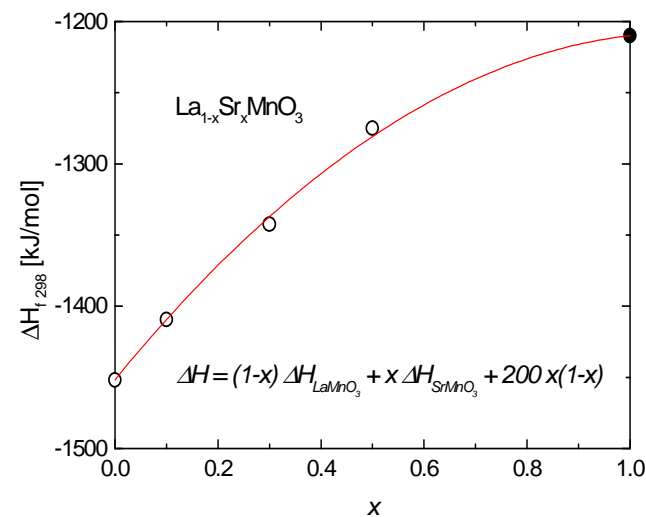
tavenina $PbO-B_2O_3$ (2:1)



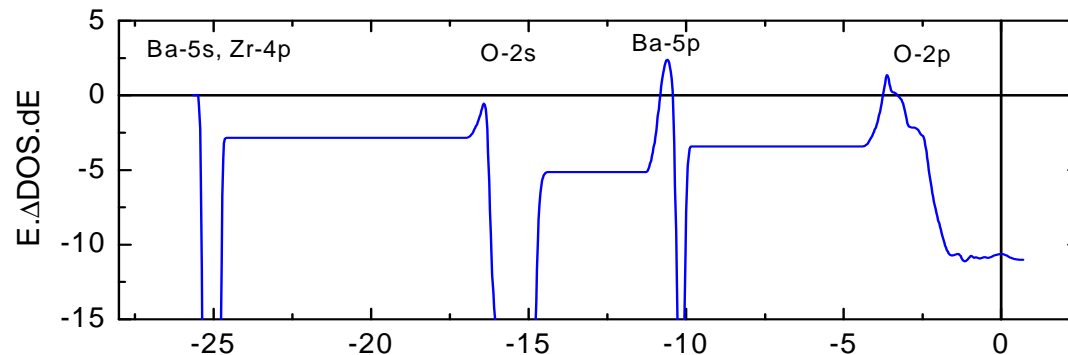
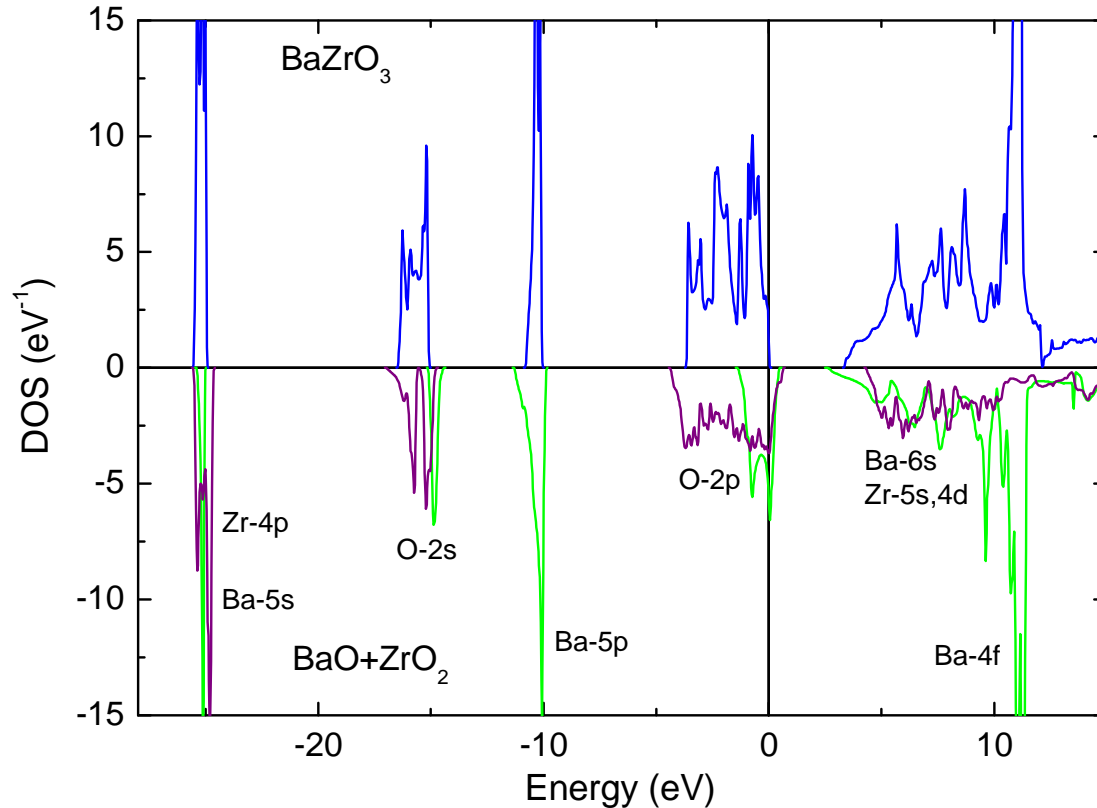
$$\Delta_{ox}H = x\Delta_{ds}H(AEO) + \Delta_{ds}H(Nb_2O_5) - \Delta_{ds}H(AE_xNb_2O_5)$$

$$\Delta_{ds}H(AEO) = \Delta_{ds}H(AECO_3) - \Delta_{dc}H(AECO_3)$$

Substance	T (K)	$\Delta_{ds}H$ (kJ mol ⁻¹) ^{a)}	$\Delta_{ox}H(298\text{ K})$ DC	$\Delta_{ox}H(298\text{ K})$ ab-initio	$\Delta_{ox}H(298\text{ K})$ Lit
CaNb ₂ O ₆	1073	196.8 ± 20.7 (8)	-132 ± 24	-316	-159.8 ^{c)} -130.1 ^{d)}
Ca ₂ Nb ₂ O ₇	1073	195.7 ± 27.8 (8)	-208 ± 32	-405	-147.3 ^{c)} -177.5 ^{e)}
SrNb ₂ O ₆	1073	180.50 ± 15.7 (4)	-168 ± 19	-318	-325.0 ^{f)}
Sr ₂ Nb ₂ O ₇	1073	167.54 ± 34.7 (4)	-289 ± 37	-475	-367.4 ^{f)}



Slučovací entalpie směrných oxidů: ΔH_{ox}



$$\frac{\Delta \int \rho(\mathbf{r}) V(\mathbf{r}) d\mathbf{r}}{\text{Ry}}$$

Ba - 0.196

Zr + 0.146

O + 0.646

Int. + 0.410

Σ + 1.006

$$\frac{\Delta \sum_i E_i}{\text{Ry}}$$

Val. - 0.840

Cor. - 0.249

Σ - 1.089

ΔH_{ox} - 0.083 Ry

- 110 kJ/mol

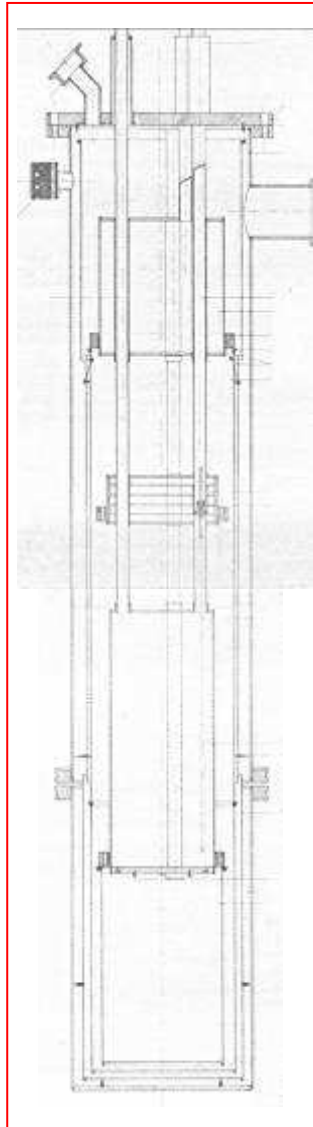
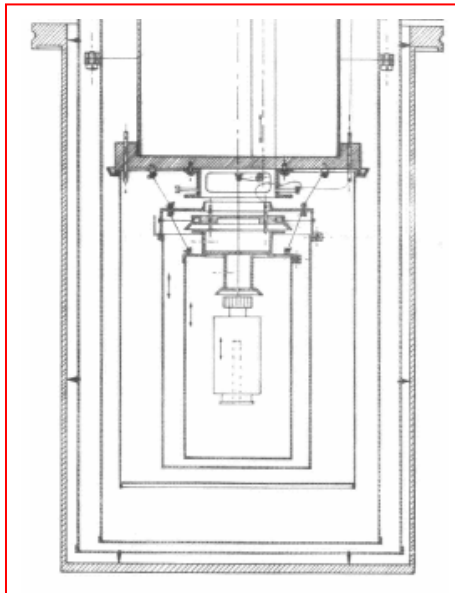
Tepelná kapacita za nízkých teplot

Adiabatická kalorimetrie

$$C_p = Q/\Delta T$$

Teplotní rozsah: 4.2 - 340 K

Chladicí kapaliny: He, N₂



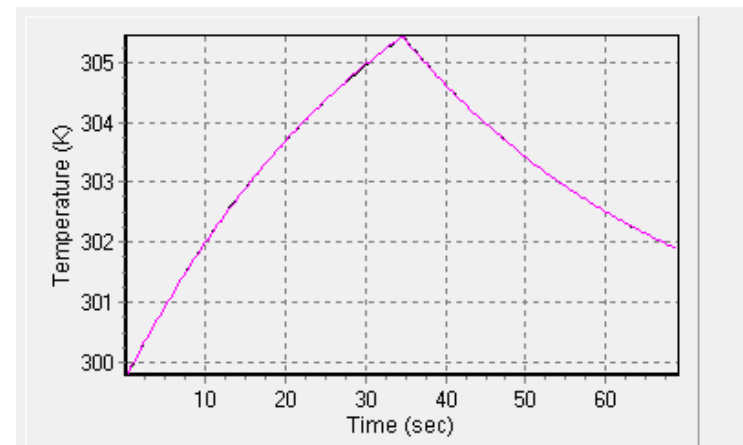
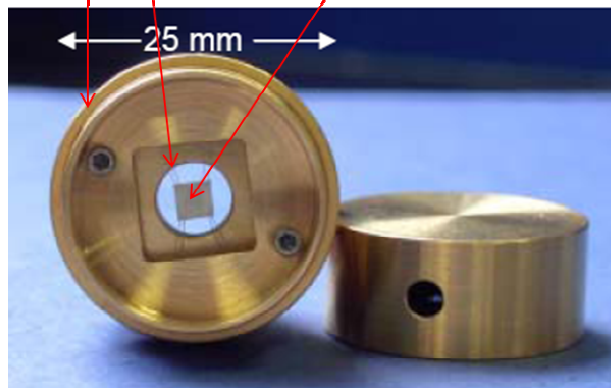
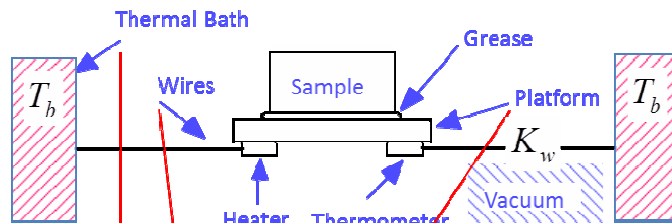
Tepelná kapacita za nízkých teplot

Relaxační metoda / PPMS

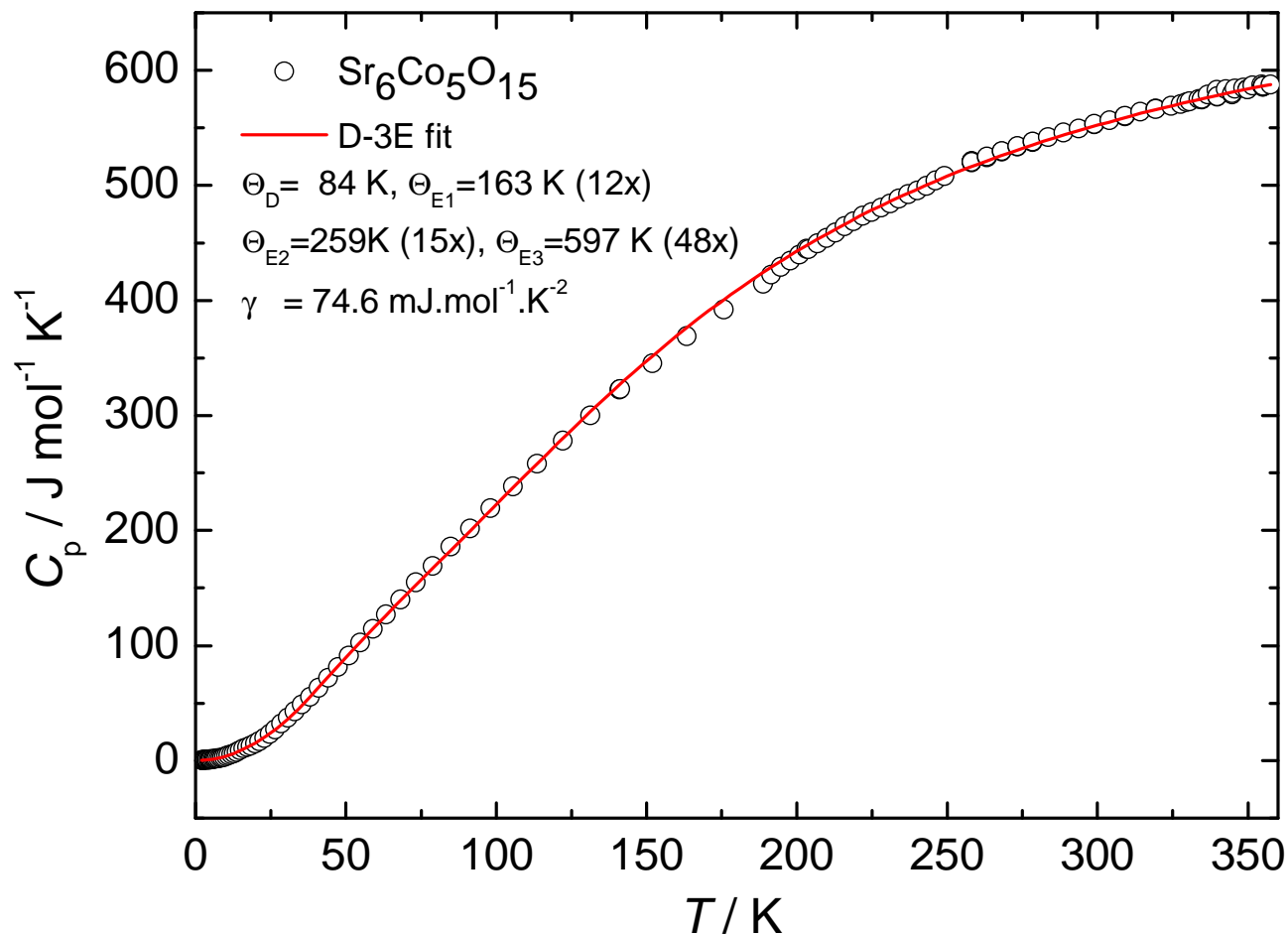
Teplotní rozsah: 1.8 - 400 K

Chladicí kapalina: He

$$C = \frac{P \cdot \tau}{T_{\max} - T_b}$$



Tepelná kapacita za nízkých teplot – Debyeův-Einsteinův model



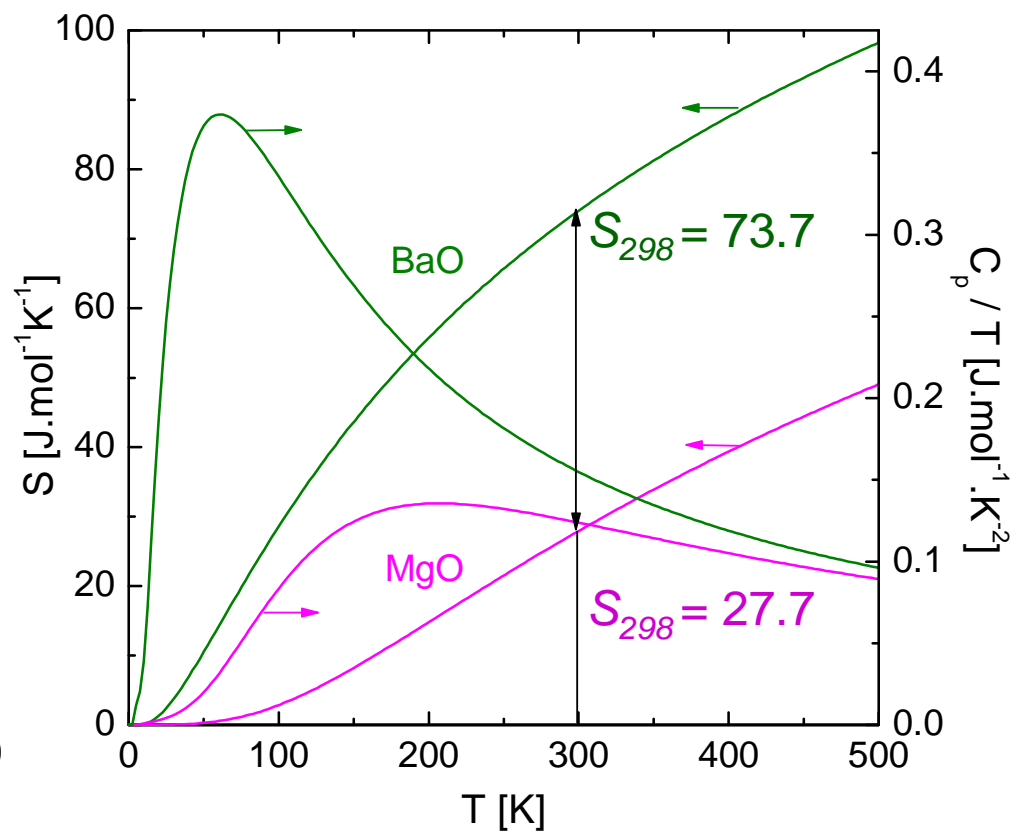
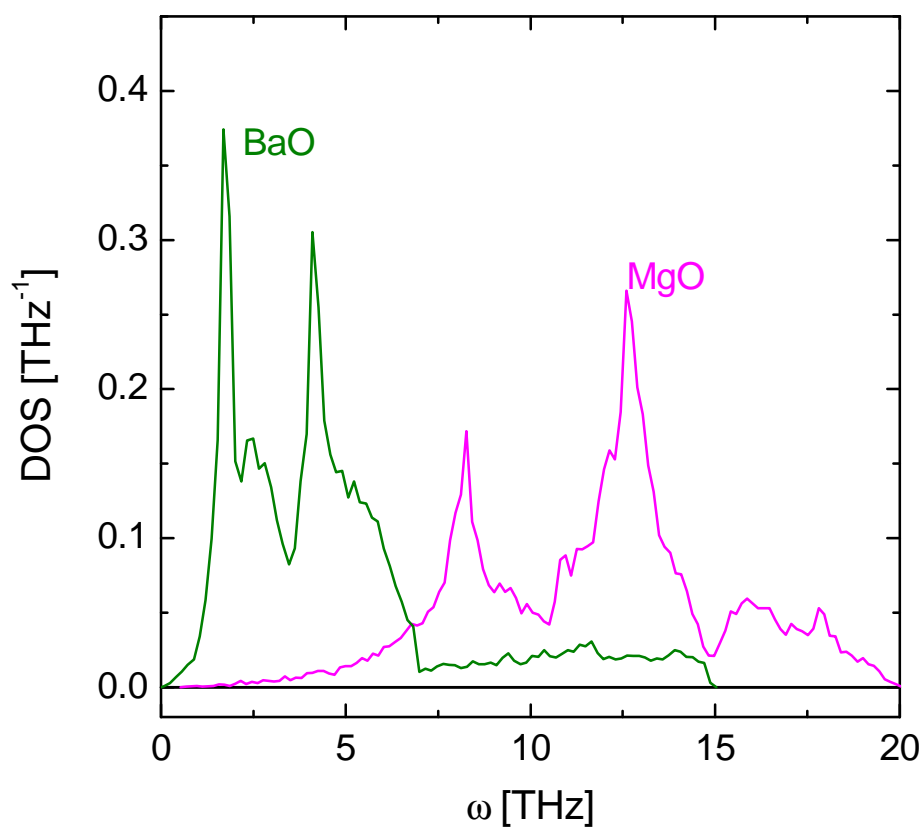
$$C_{\text{phD}} = 9R \left(\frac{T}{\Theta_D} \right)^3 \int_0^{x_D} \frac{x^4 \exp(x)}{[\exp(x) - 1]^2} dx$$

$$C_{\text{phE}i} = R \frac{x_{Ei}^2 \exp(x_{Ei})}{[\exp(x_{Ei}) - 1]^2}$$

$$C_{\text{el}} = \gamma T$$

$$C_p = C_{\text{el}} + C_{\text{phD}} + \sum_{i=1}^3 g_i C_{\text{phE}i}$$

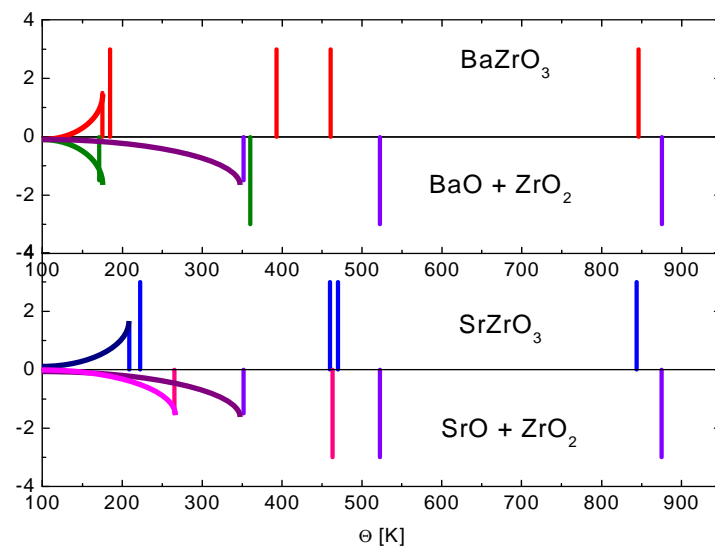
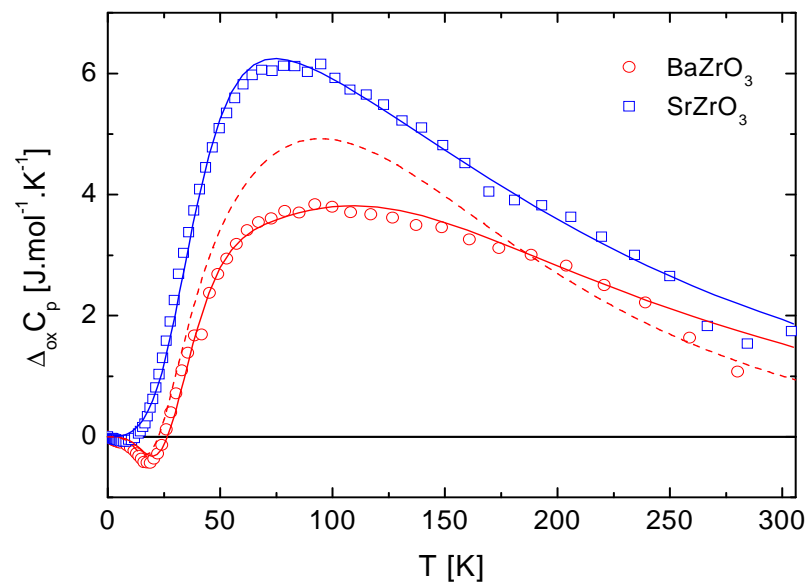
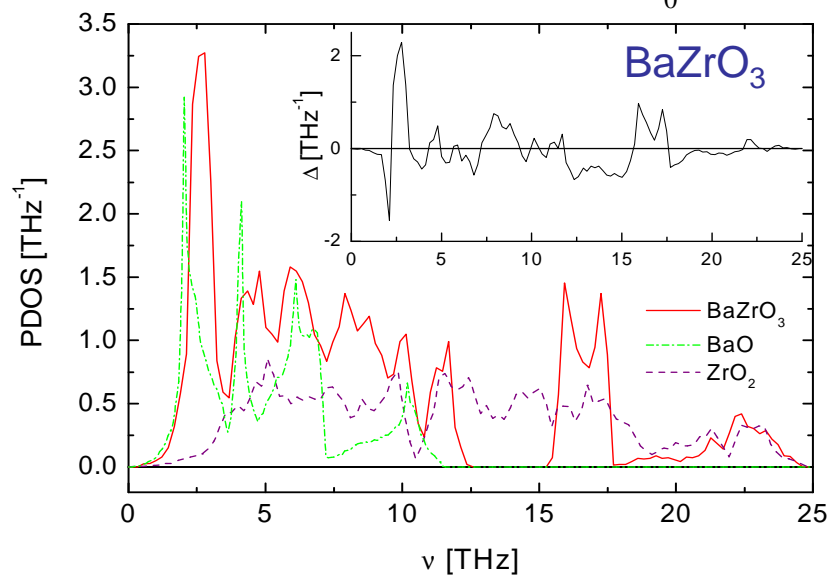
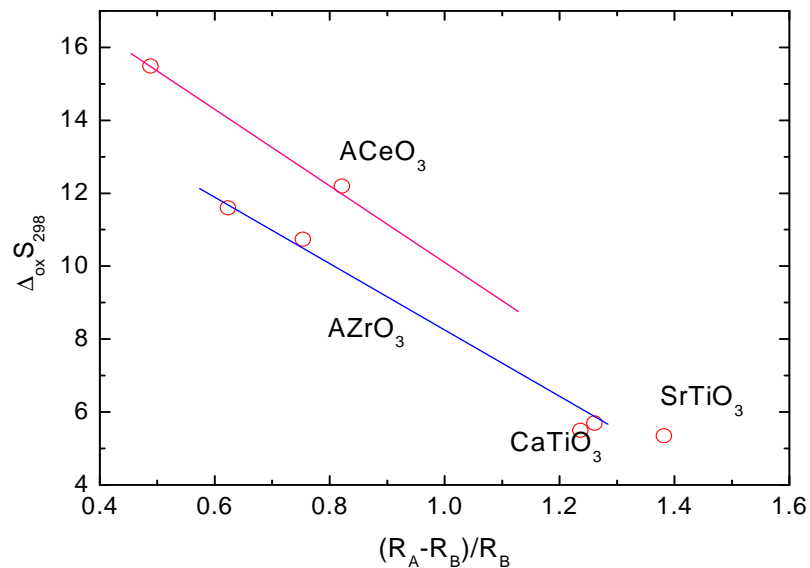
Entropie a nízkoteplotní C_p – vliv hmotnosti atomů a silových konstant: MgO vs. BaO



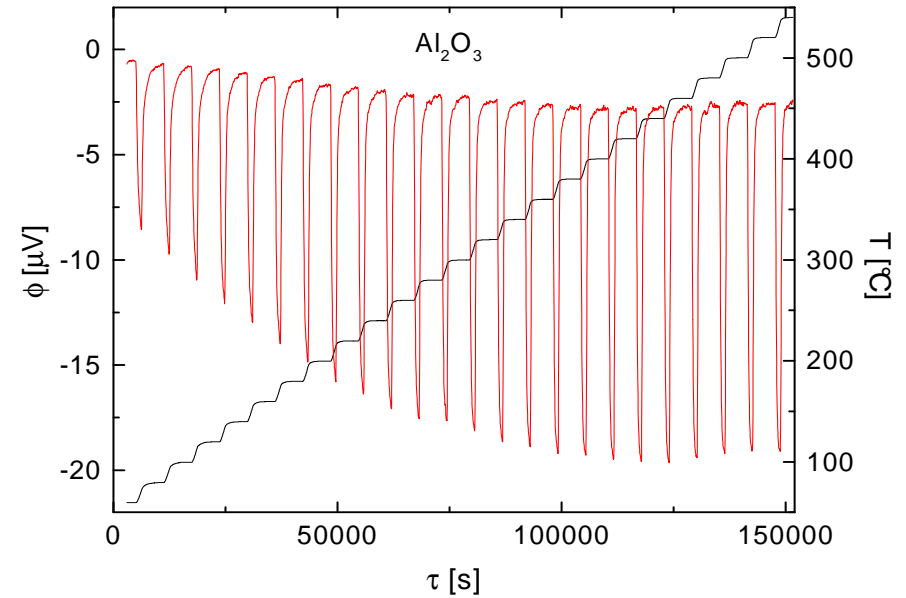
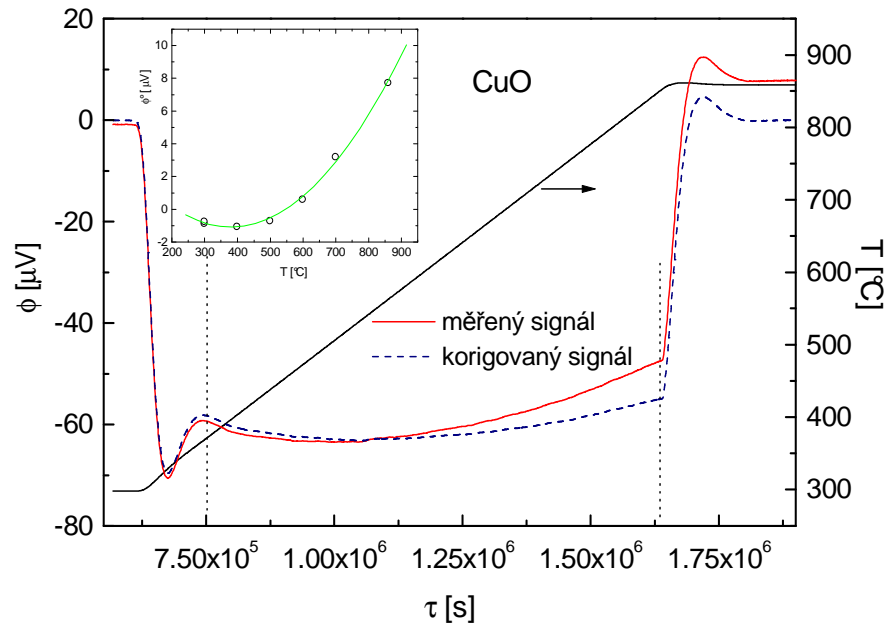
Entropie a nízkoteplotní C_p směsných oxidů

$$\Delta S_{ox} = S(ABO_3) - S(AO) - S(BO_2)$$

$$\Delta_{ox} S_{298} = \int_0^{298} \frac{\Delta_{ox} C_p}{T} dT$$



HF-DSC – dynamická vs. inkrementální metoda



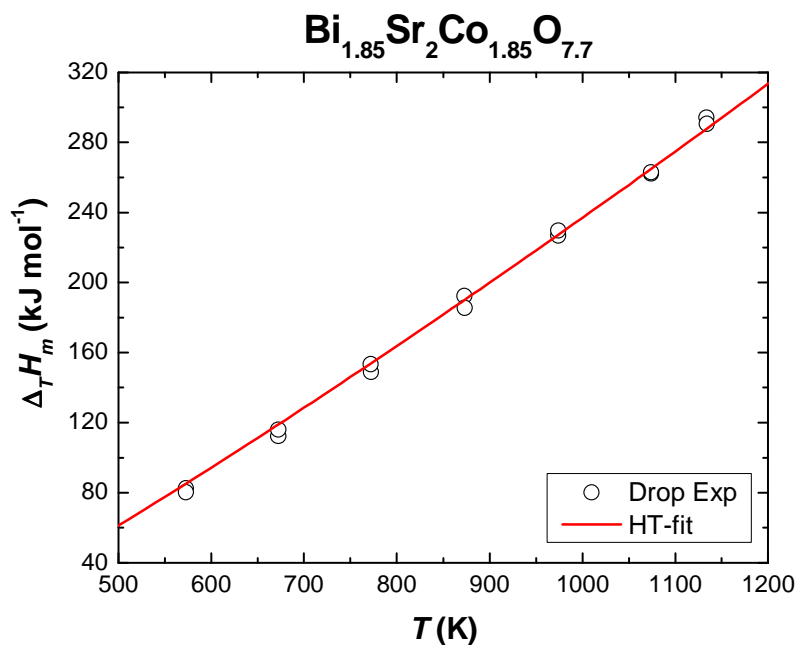
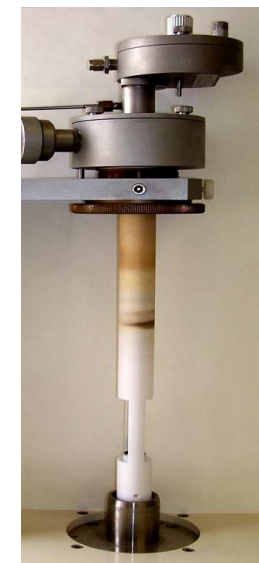
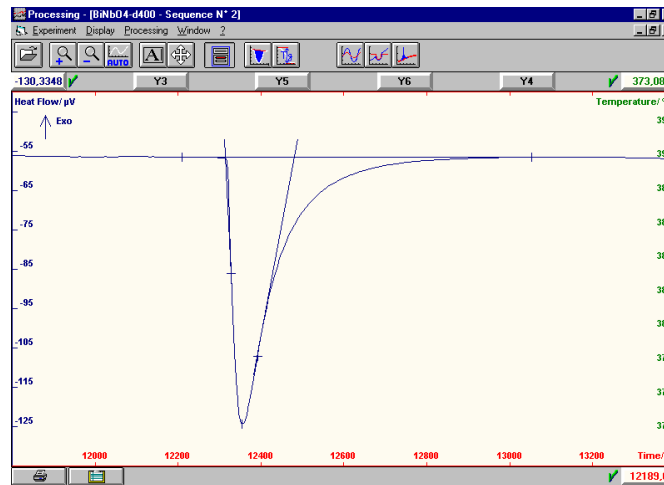
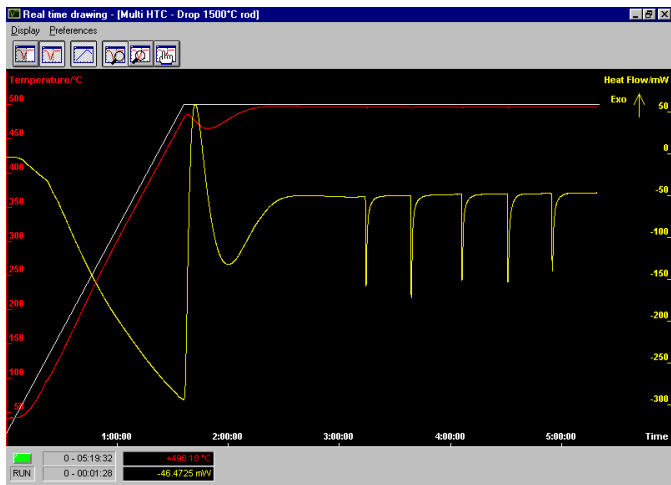
$$C_{pm}(T) = \frac{\Phi_S(T) - \Phi_B(T)}{S(T) \cdot r(T)} \frac{M_S}{m_S}$$

$$S(T) = \frac{\Phi_R(T) - \Phi_B(T)}{C_{pR}(T) \cdot r(T)} \frac{M_R}{m_R}$$

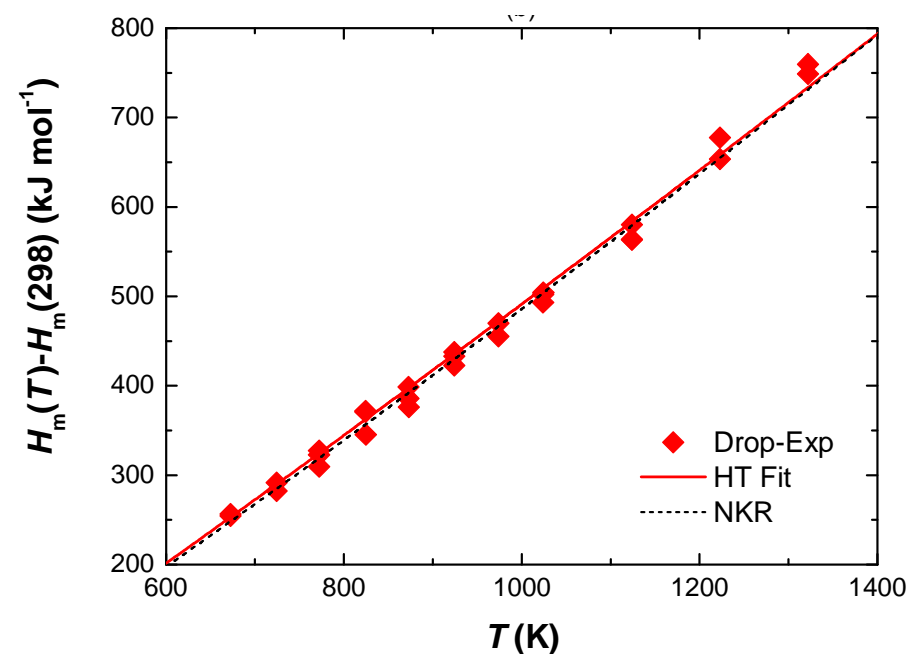
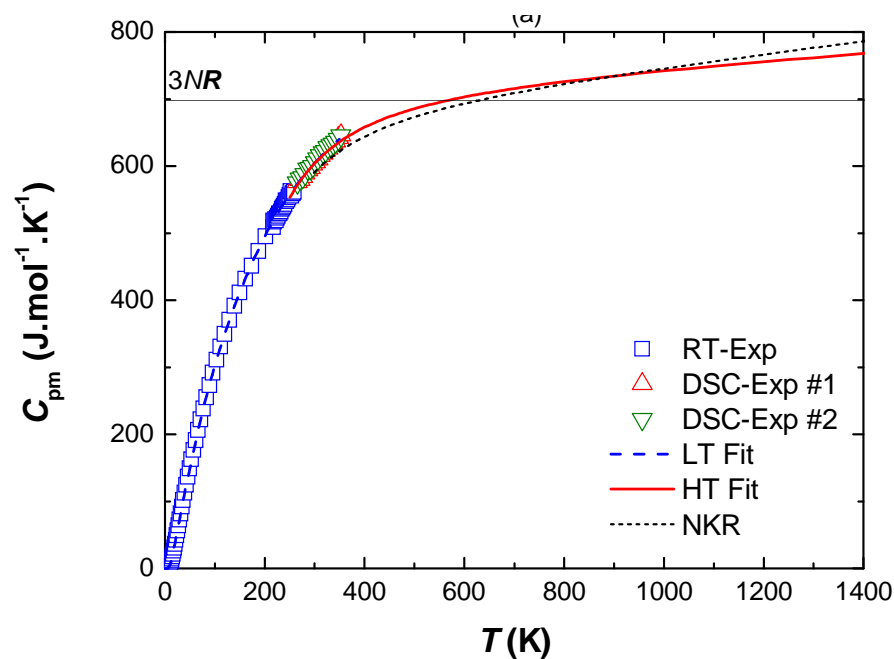
$$C_{pm}\left(\frac{T_1+T_2}{2}\right) = \frac{\Delta H}{T_2 - T_1} \frac{M_S}{m_S}$$

$$\Delta H = \frac{\int \phi_S d\tau - \int \phi_B d\tau}{S} \quad S = \frac{\int_{T_1}^{T_2} \phi_R d\tau - \int \phi_B d\tau}{\int_{T_1}^{T_2} C_{pmR} dT} \frac{M_R}{m_R}$$

Vhazovací kalorimetrie – stanovení relativních entalpií



Simultánní analýza dat LT- C_p , HF-DSC a vhazovací kalorimetrie



$$C_{pm} = A + BT + C/T^2$$

$$\Delta H_m(T) = H_m(T) - H_m(T_0) = \int_{T_0}^T C_{pm} dT = A(T - T_0) + B(T^2 - T_0^2)/2 - C(1/T - 1/T_0)$$

$$F = \sum_{i=1}^{N(C_p)} w_i^2 [C_{pm,i} - A - BT_i - C/T_i^2]^2 + \sum_{j=1}^{N(\Delta H)} w_j^2 [\Delta H_{mj} - A(T_j - T_{0,j}) - B(T_j^2 - T_{0,j}^2)/2 + C(1/T_j - 1/T_{0,j})]^2 \rightarrow \min$$

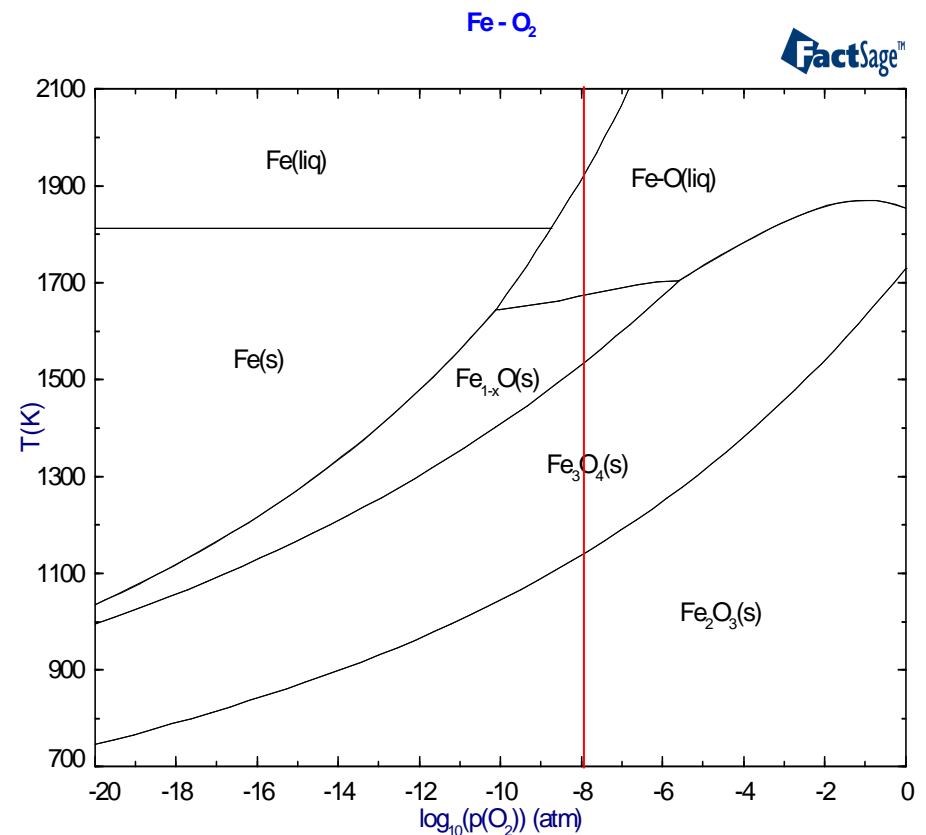
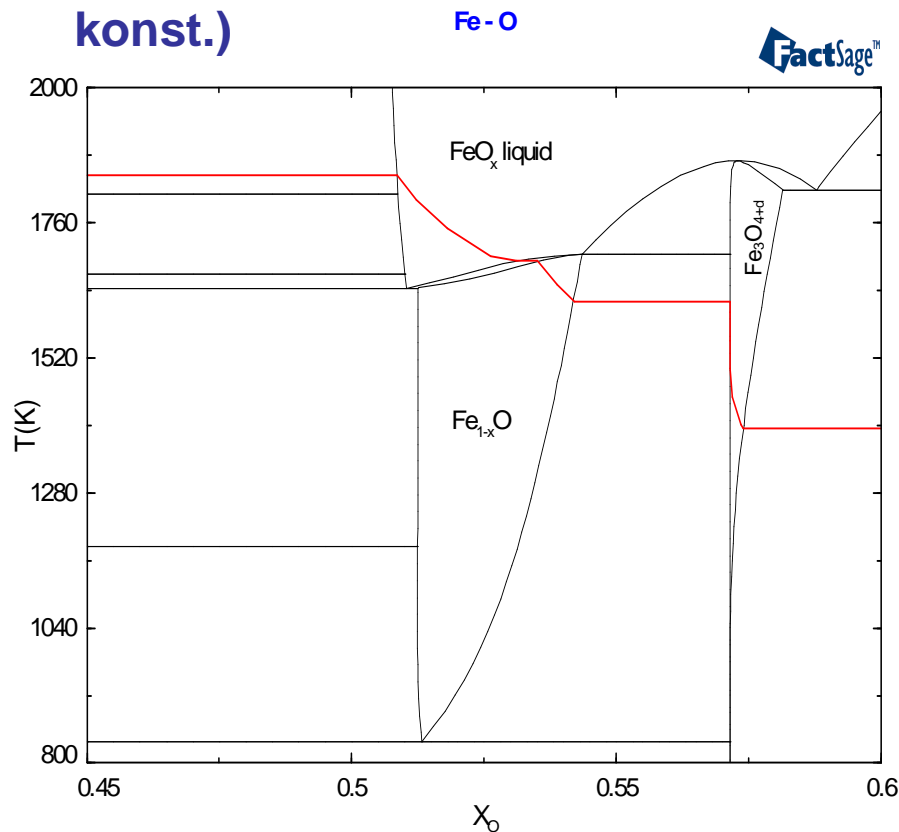
J. Leitner, V. Jakeš, Z. Sofer, D. Sedmidubský, K. Růžička, P. Svoboda
Heat capacity, enthalpy and entropy of ternary bismuth tantalum oxides
J. Solid State Chem. 184 (2011) 241–245

Kyslíková nestechiometrie v oxidových systémech

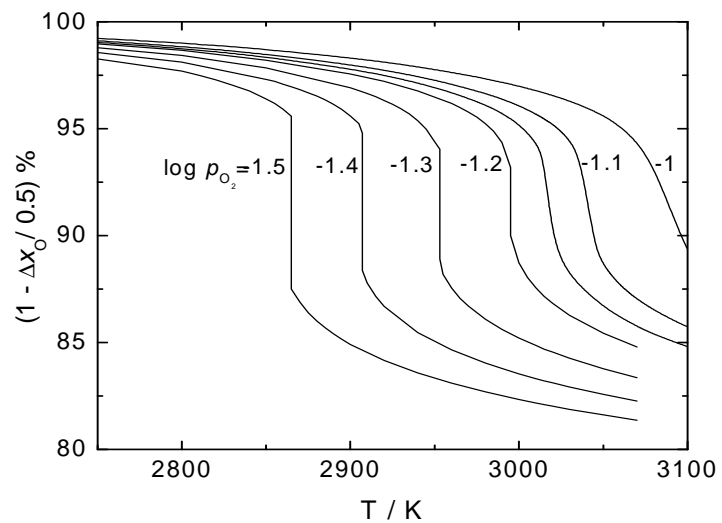
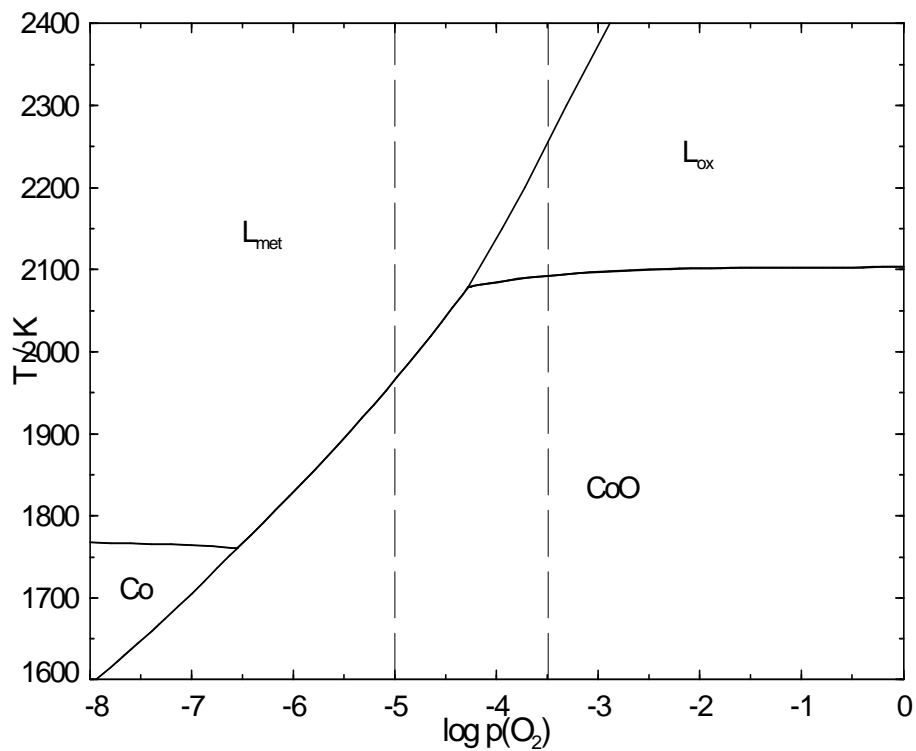
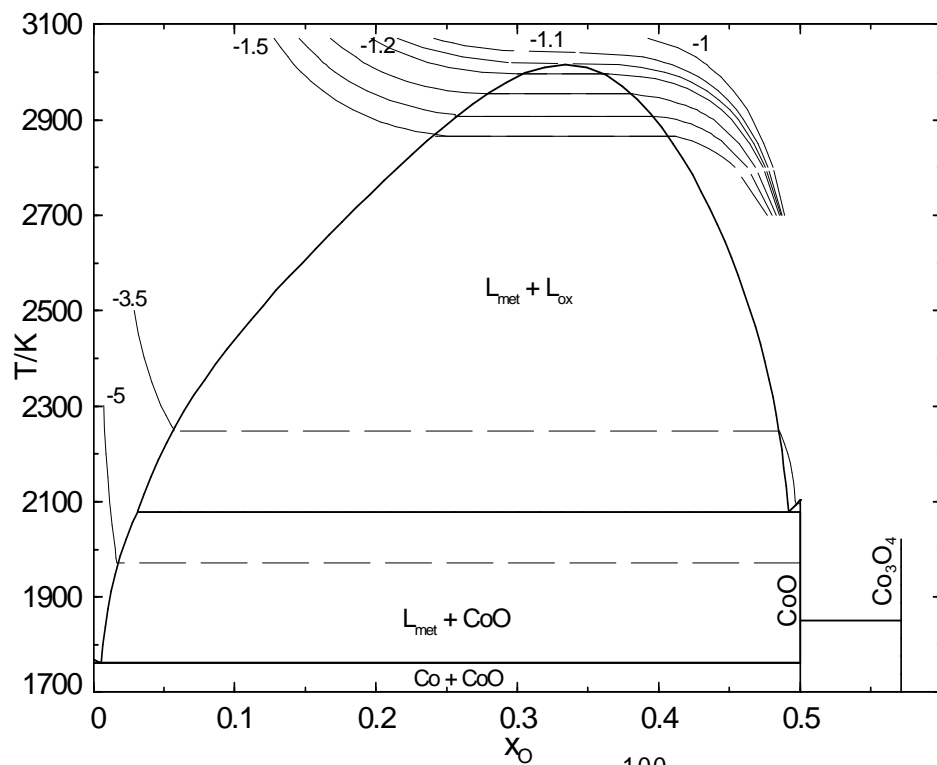
Látky vyměňující s okolím jednu či více složek : nestechiometrické oxidy, hydridy, hydráty, oxykarbonáty, sulfidy, ...

Obsah volné složky (kyslíku) v systému je určen její aktivitou

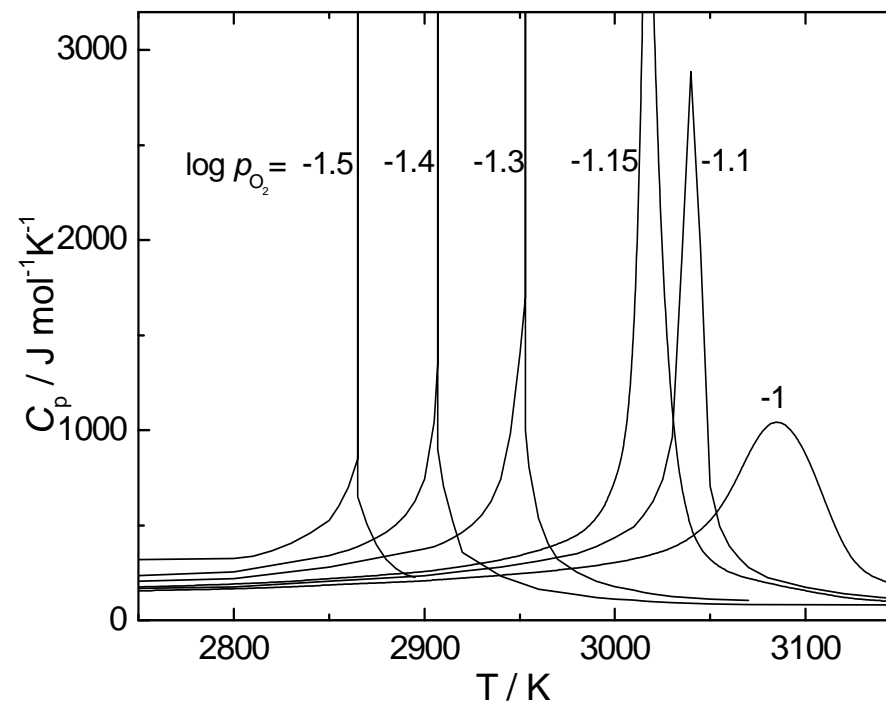
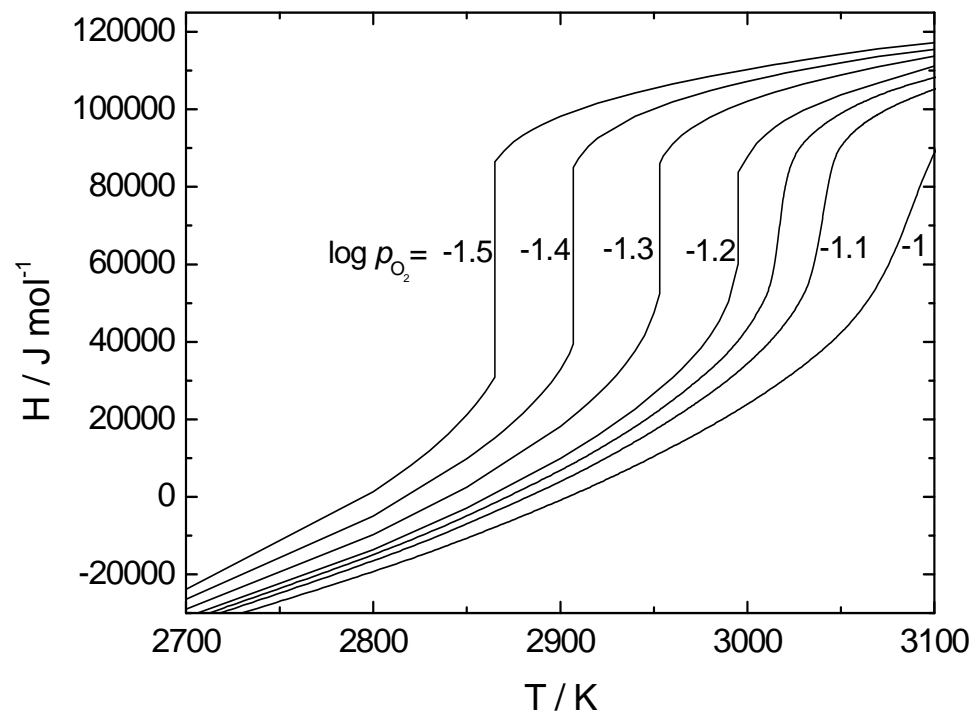
Nastavení aktivity volné složky – řízená dynamická atmosféra ($p_{O_2} = \text{konst.}$)



System Co-O: odmíšení a kritický bod

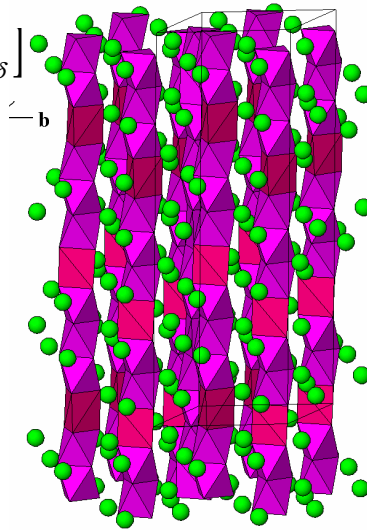
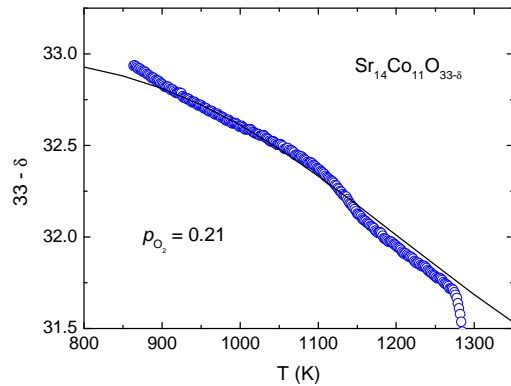
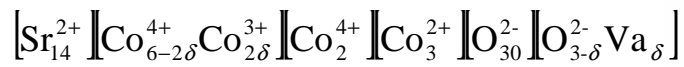


System Co-O: admixture and critical point



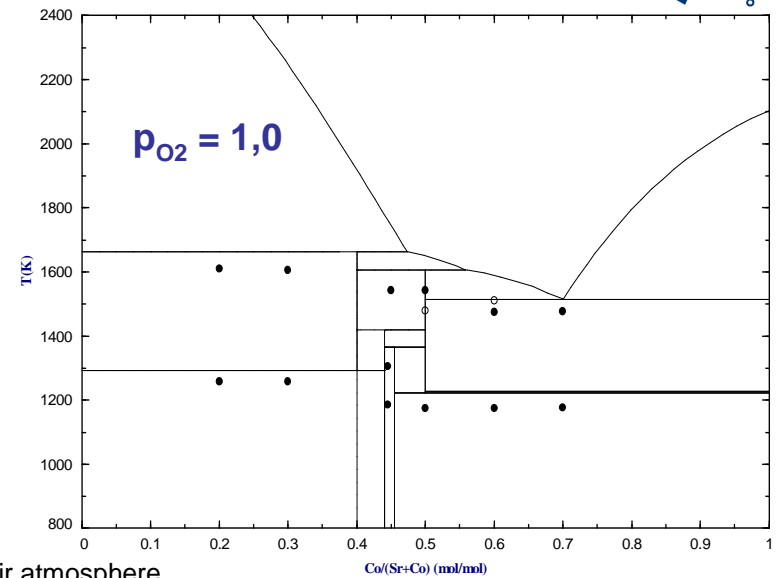
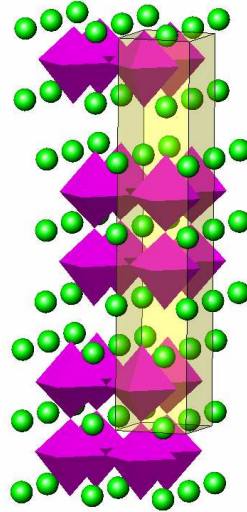
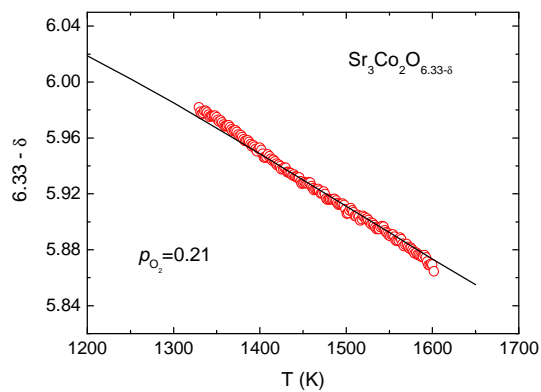
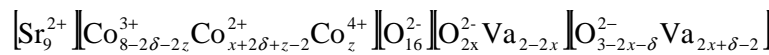
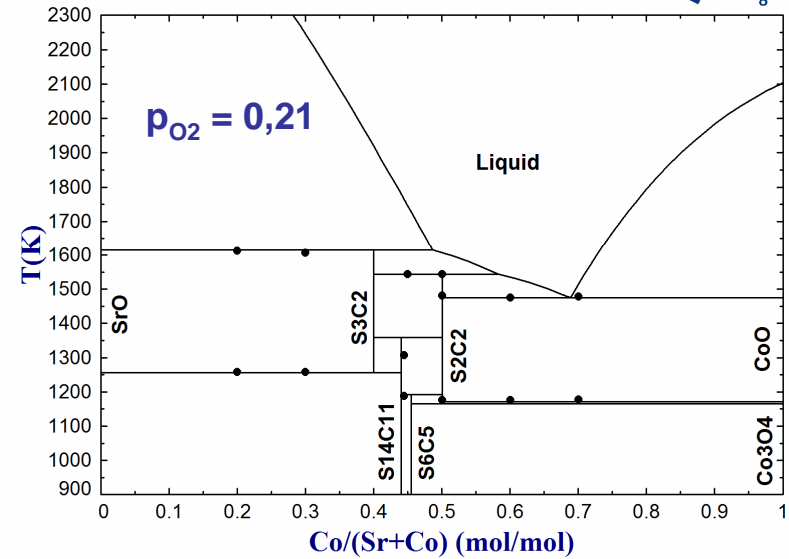
Fázové diagramy částečně otevřených systémů

System Sr-Co-(O)



Sr - Co - O₂
 $p(\text{O}_2) = 0.21 \text{ atm}, 1 \text{ atm}$

FactSage™



O.Jankovský, D.Sedmidubský, J.Vítek, Z. Sofer, Phase equilibria in Sr-Co-O system in air atmosphere

Journal of the European Ceramic Society 35 (2015) 935-940

Podmínky rovnováhy v částečně otevřených systémech

Hypervolná energie:

$$Z = G - \sum_{f=1}^F \mu_f n_f = H - TS - \sum_{f=1}^F \mu_f n_f$$

oxydy: $Z = G - n_O G^\circ_{O_2} / 2 - RT \ln(a_{O_2}) / 2$

$$Z = \sum \mu_j n_j - (n_f^\circ + \delta) \mu_f = \sum (\mu_j^\circ + RT \ln a_j) n_j - (n_f^\circ + \delta) (\mu_f^\circ + RT \ln a_f)$$

$$n_j = \nu_{jO} + \sum \nu_{jr} \lambda_r + \nu_{jf} \delta$$

intrinzické krystalochemické reakce:

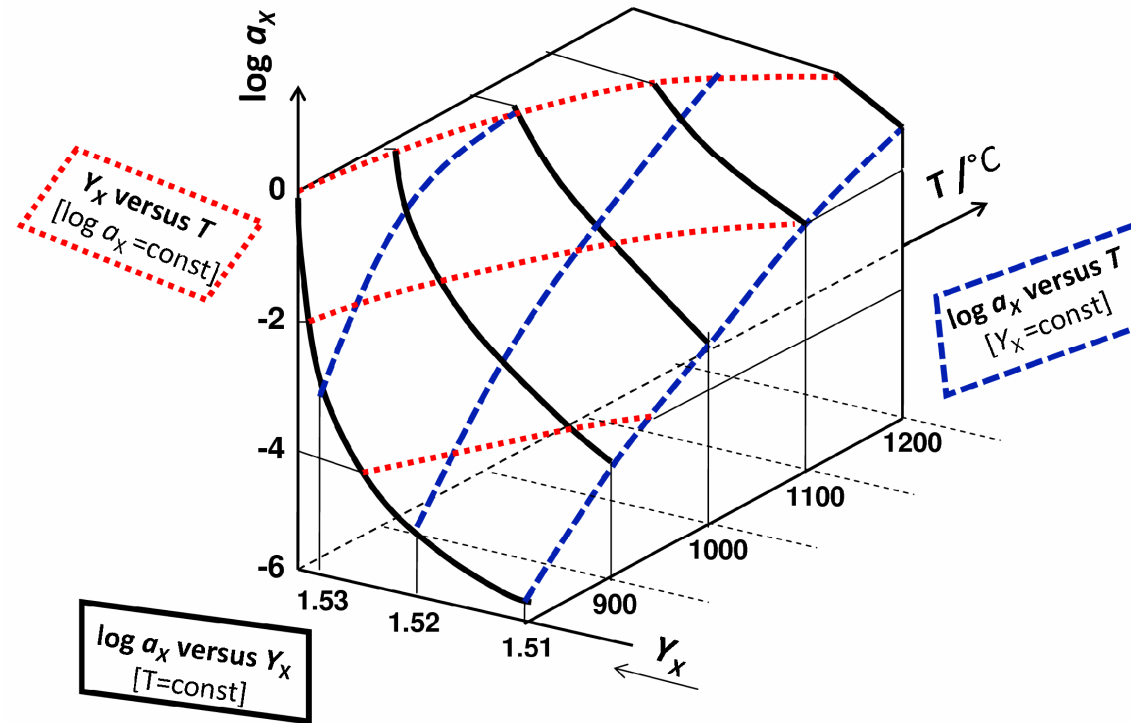
$$\lambda_{r,eq}: \quad (\partial Z / \partial \lambda_r)_{\delta, T, P} = \sum_j \nu_{jr} (\mu_j^\circ + RT \ln a_j) = \Delta G_r^\circ + RT \ln K_r = 0$$

inkorporační reakce:

$$\delta_{eq}: \quad (\partial Z / \partial \delta)_{T, P, \lambda_r} = \sum_j \nu_{jf} (\mu_j^\circ + RT \ln a_j) - \mu_f^\circ + RT \ln a_f = \Delta G_{If}^\circ + RT \ln K_{if} = 0$$

$$(\partial Z / \partial \delta)_{T, P} = (\partial Z / \partial \delta)_{T, P, \lambda_r} + \sum_r (\partial Z / \partial \lambda_r) (\partial \lambda_r / \partial \delta) = \Delta G_{If}^\circ + \sum_r \Delta G_r (\partial \lambda_r / \partial \delta) = 0$$

Nestechiometrie jako funkce T a $\log a_f$



vlastní plutabilita:

$$K_{ff} = \left(\frac{\partial Y_f}{\partial \ln a_f} \right)_{T,p}$$

TGA, coulometrická titrace

teplotní ftochabilita:

$$K_{fT} = - \left(\frac{\partial Y_f}{\partial T} \right)_{a_f,p}$$

TGA

relativní parc. mol. entalpie:

$$\Delta \bar{H}_f = R \left(\frac{\partial \ln a_f}{\partial (1/T)} \right)_{Y_f,p}$$

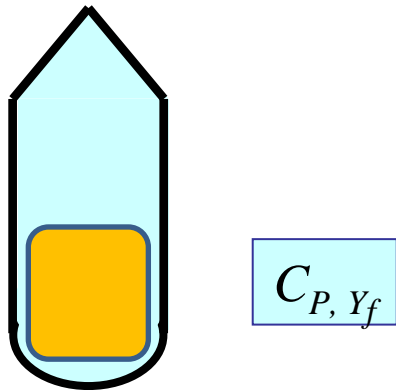
EMF galvanických článků

Nestechiometrie a tepelná kapacita

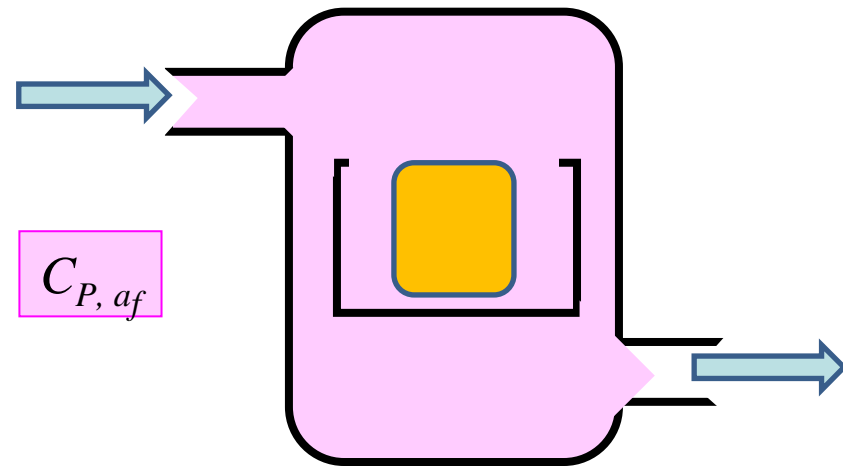
Izochorická: $C_V = \left(\frac{\partial U}{\partial T} \right)_V$

Izobarická: $C_p = \left(\frac{\partial H}{\partial T} \right)_p = C_V + TV_m \frac{\alpha^2}{\beta}$

Izopletní:



Izodynamická: konstantní aktivita volné složky



$$A_n X_{m+\delta} = n A_1 X_y$$

Molální zlomek $Y_f = (m+\delta)/n = y$

$$a_f = p_f/p_f^o$$

$$C_{p, a_f} = C_{p, Y_f} + \Delta_{sat} C_p$$

Saturační příspěvek k izodynamické kapacitě

$$C_{p,a_f} = \left(\frac{\partial H}{\partial T} \right)_{p,a_f} = \left(\frac{\partial H}{\partial T} \right)_{p,Y_f} + \left(\frac{\partial H}{\partial N_f} \right)_{p,T} \left(\frac{\partial N_f}{\partial Y_f} \right) \left(\frac{\partial Y_f}{\partial T} \right)_{p,a_f} = C_{p,Y_f} - \bar{H}_f \kappa_{fT}$$

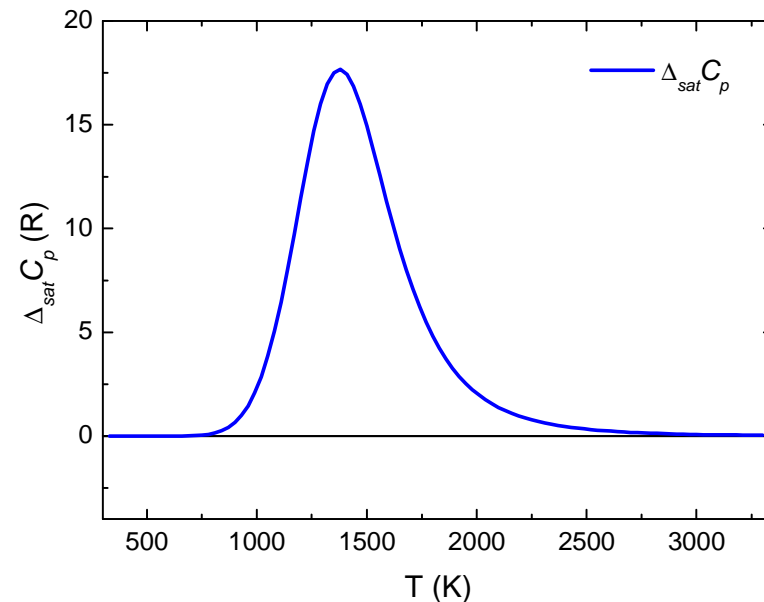
= 1 pro $A_1 X_y$

$$\Delta_{sat} C_p = -\bar{H}_f \kappa_{fT} = -(\bar{H}_f^\circ + \Delta \bar{H}_f) \kappa_{fT} = (\bar{H}_f^\circ + \Delta \bar{H}_f) \left(\frac{\Delta \bar{H}_f}{RT^2} \right) \kappa_{ff}$$

Nestechiometrický oxid $MO_{n-\delta}$

$$\delta = \frac{nK_o}{p_{O_2}^{1/2} + K_o} \quad \ln K_o = -\frac{\Delta \bar{H}_o}{RT} + \frac{\Delta \bar{S}_o}{R}$$

$$\Delta_{sat} C_p = -\bar{H}_o \left(\frac{\partial \delta}{\partial T} \right) = \bar{H}_o \frac{\Delta \bar{H}_o}{RT^2} \frac{np_{O_2}^{1/2} K_o}{(p_{O_2}^{1/2} + K_o)^2}$$



Deviační příspěvek k C_p v důsledku nestechiometrie

$$\Delta_{dev} C_p = C_{p,Y_f} - C_{p,Y_f^\circ} = \int_{Y_f^\circ}^{Y_f} \left(\frac{\partial C_p}{\partial Y_f} \right) dY_f = \int_{Y_f^\circ}^{Y_f} \left(\frac{\partial \bar{H}_f}{\partial T} \right) dY_f = \int_{Y_f^\circ}^{Y_f} \left(C_f^\circ + \frac{\partial \Delta \bar{H}_f}{\partial T} \right) dY_f$$

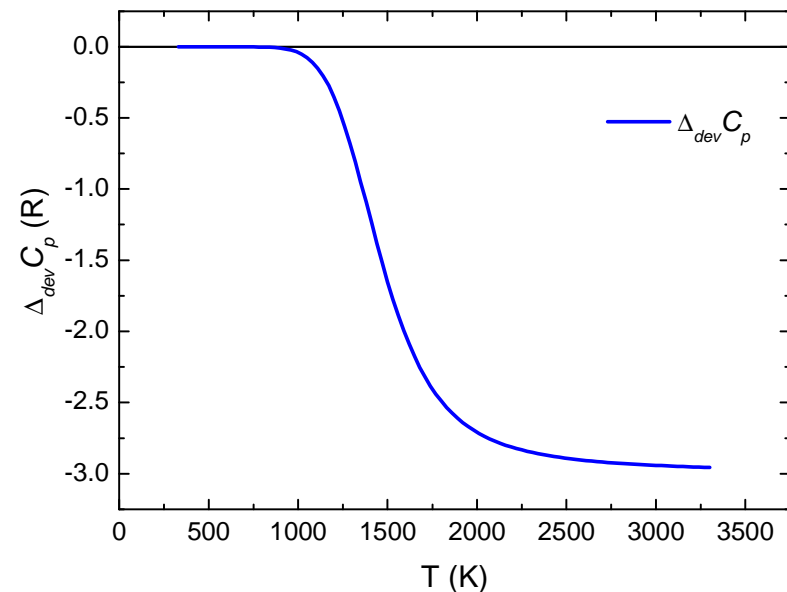
$$\Delta_{dev} C_p = (Y_f - Y_f^\circ) C_{p,f}^\circ + \underbrace{\int_{Y_f^\circ}^{Y_f} \left(\frac{\partial \Delta \bar{H}_f}{\partial T} \right) dY_f}_{\text{pro } A_1 X_y} = \delta C_{p,f}^\circ + \int_0^\delta \left(\frac{\partial \Delta \bar{H}_f}{\partial T} \right) d\delta$$

Nestechiometrický oxid $MO_{n-\delta}$

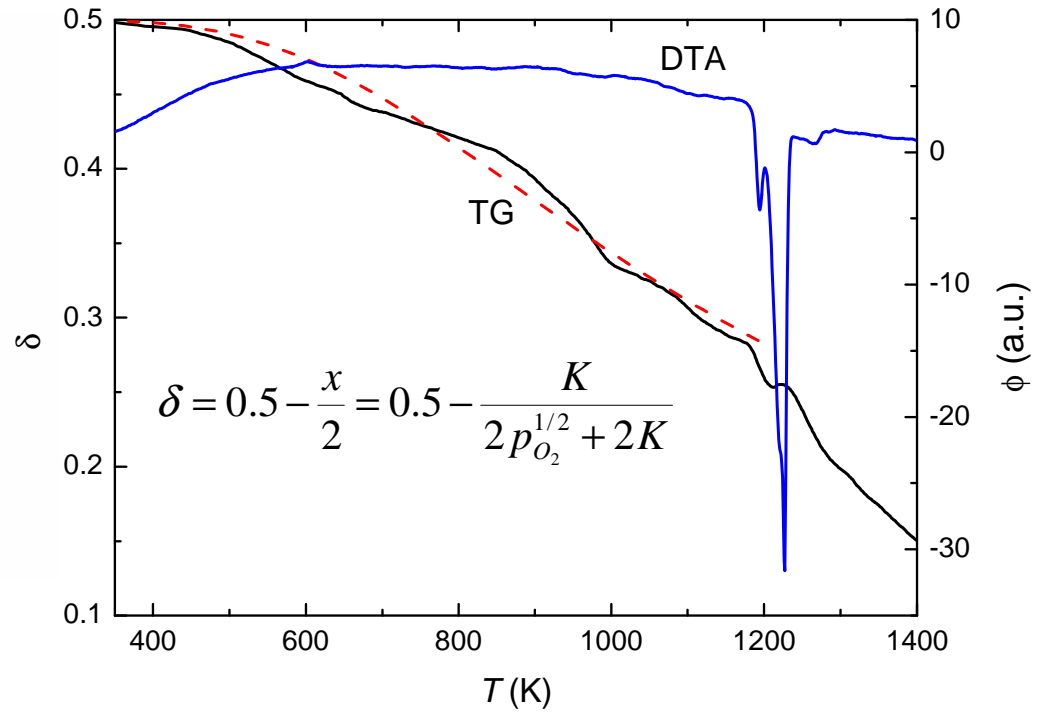
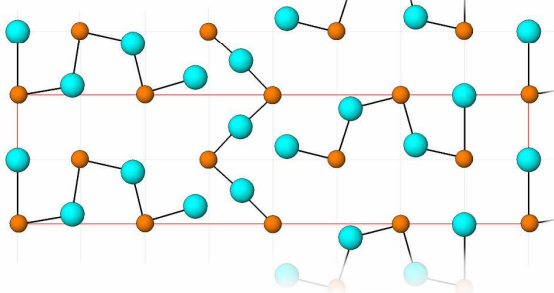
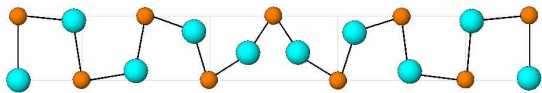
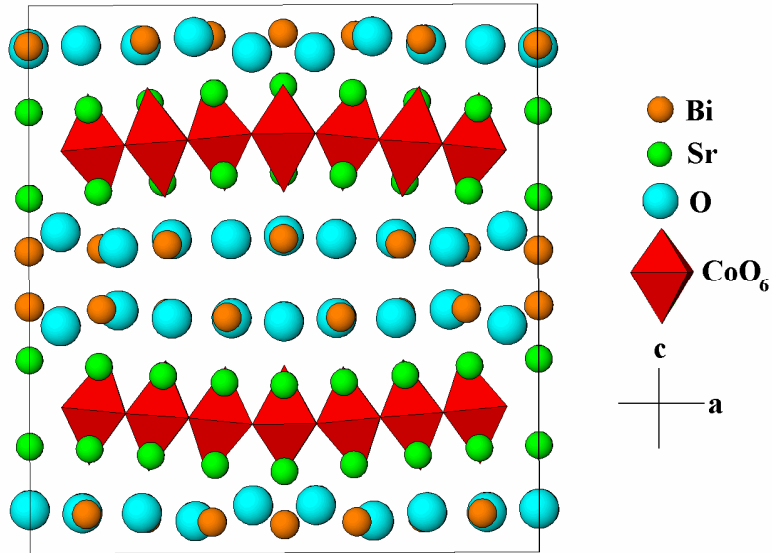
entalpie vibračních modů volné složky

$$h_{vO} = 3R\Theta_{E_o} \left[\frac{1}{\exp(\Theta_{E_o}/T) - 1} + \frac{1}{2} \right]$$

$$\Delta_{dev} C_p = - \int_0^\delta \left(\frac{\partial \bar{H}_o}{\partial T} \right) d\delta \cong - \left(\frac{\partial h_{vO}}{\partial T} \right) \frac{nK_o}{p_{O_2}^{1/2} + K_o}$$



Kyslíková nestechiometrie $\text{Bi}_2\text{Sr}_2\text{CoO}_{6+\delta}$

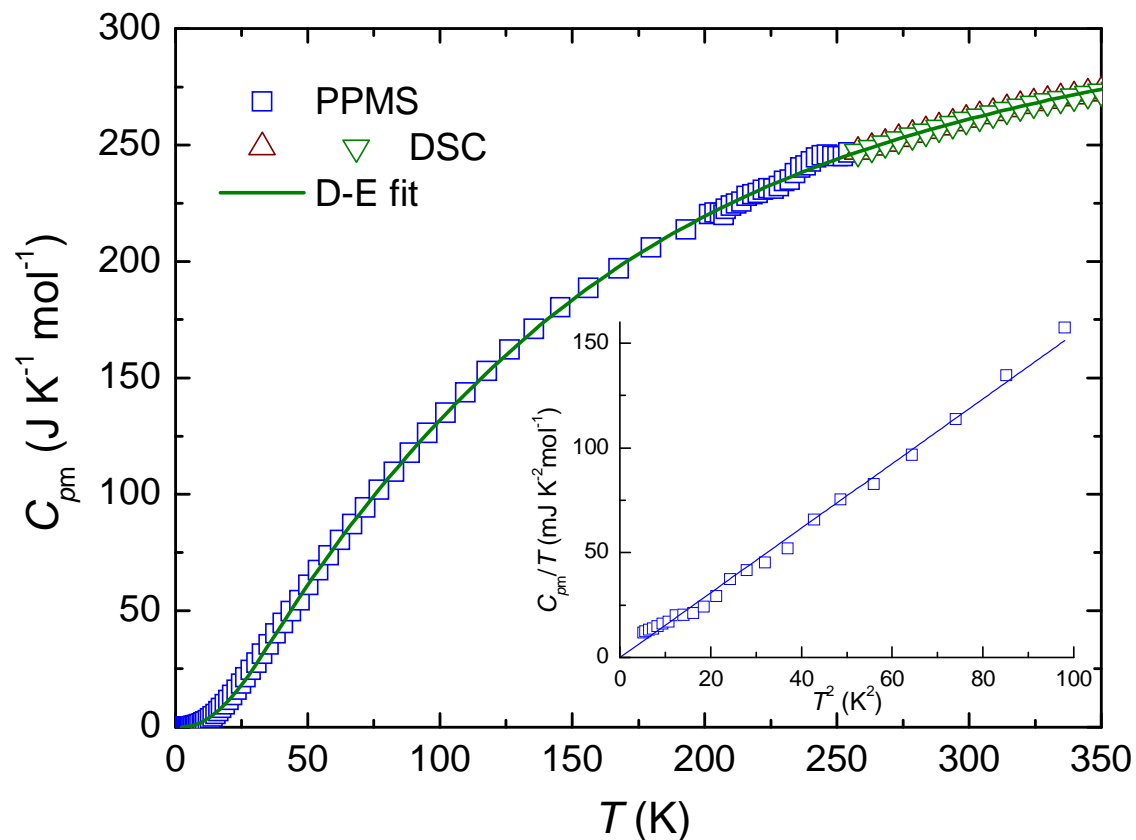


$$K = e^{\frac{\Delta\bar{H}_o}{RT} - \frac{\Delta\bar{S}_o}{R}} = \frac{xp_{\text{O}_2}^{1/2}}{1-x}$$

$$\Delta\bar{H}_o = -26.22 \pm 0.24 \text{ kJ mol}^{-1}$$

$$\Delta\bar{S}_o = -13.19 \pm 0.25 \text{ J mol}^{-1} \text{ K}^{-1}$$

Tepelná kapacita $\text{Bi}_2\text{Sr}_2\text{CoO}_{6+\delta}$



$$C_p = A + B \cdot T + C \cdot T^{-2}$$

$$\Delta H(T) = H(T) - H(T_0) = A \cdot (T - T_0) + \frac{1}{2} B \cdot (T^2 - T_0^2) - C \cdot \left(\frac{1}{T} - \frac{1}{T_0} \right)$$

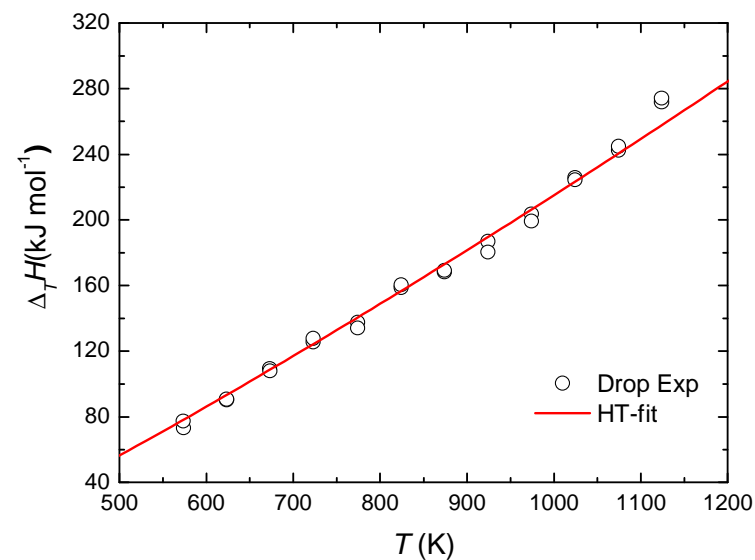
$$C_p = [(256.3 \pm 18.2) + (0.09708 \pm 0.02813) \cdot T - (2.2284 \pm 0.8903) \cdot 10^6 \cdot T^{-2}] \text{ J K}^{-1} \text{ mol}^{-1}$$

Debye – Einsteinův model

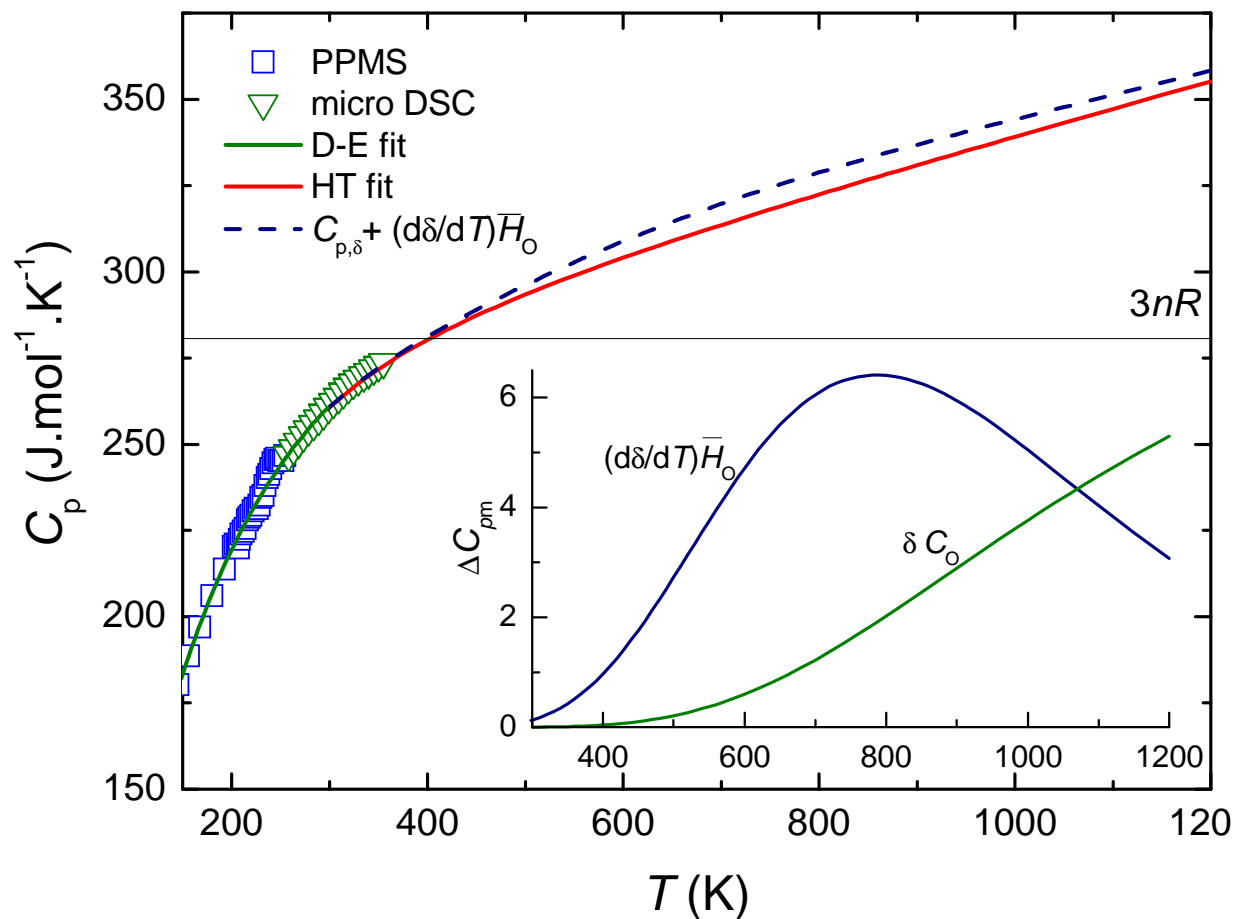
$$C_{\text{phD}} = 9R \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\frac{x_D}{T}} \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} dx$$

$$C_{\text{phEi}} = R \cdot \frac{w_i x_{Ei}^2 e^{x_{Ei}}}{(e^{x_{Ei}} - 1)^2}$$

$$C_p = C_{el} + C_{\text{phD}} + \sum_{i=1}^3 C_{\text{phEi}}$$



Tepelná kapacita $\text{Bi}_2\text{Sr}_2\text{CoO}_{6+\delta}$



$$\Delta_{sat} C_p = C_{p,p,O_2} - C_{p,\delta} = \bar{H}_O \left(\frac{\partial \delta}{\partial T} \right)_{p,p,O_2}$$

$$\bar{H}_O = 1/2 H_{O_2}^\circ + \Delta \bar{H}_O$$

$$C_{p,\delta=0.5} = C_{p,\delta} + \delta C_O$$

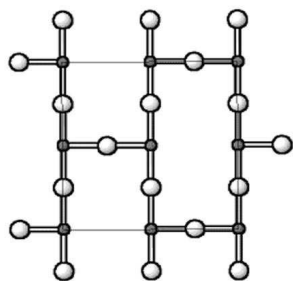
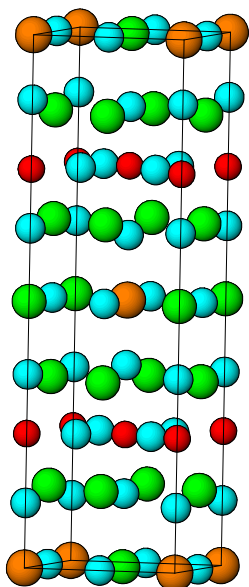
O. Jankovský, D. Sedmidubský, Z. Sofer, K. Rubešová, K. Růžička, P. Svoboda
 Oxygen non-stoichiometry and thermodynamic properties of $\text{Bi}_2\text{Sr}_2\text{CoO}_{6+\delta}$ ceramics
 Journal of the European Ceramic Society 34 (2014) 1219-1225

$$C_O = C_{\text{phEi}} = R \cdot \frac{w_i x_{Ei}^2 e^{x_{Ei}}}{(e^{x_{Ei}} - 1)^2}$$

$$w_i = 3$$

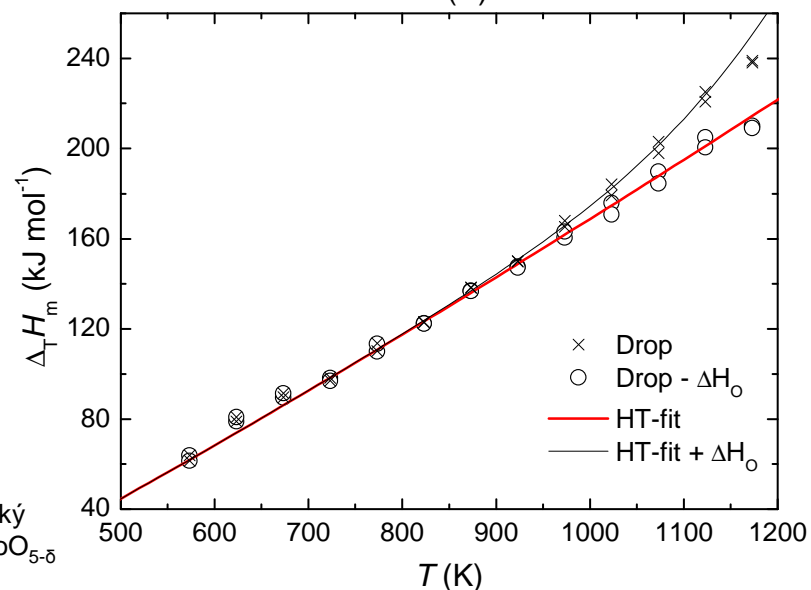
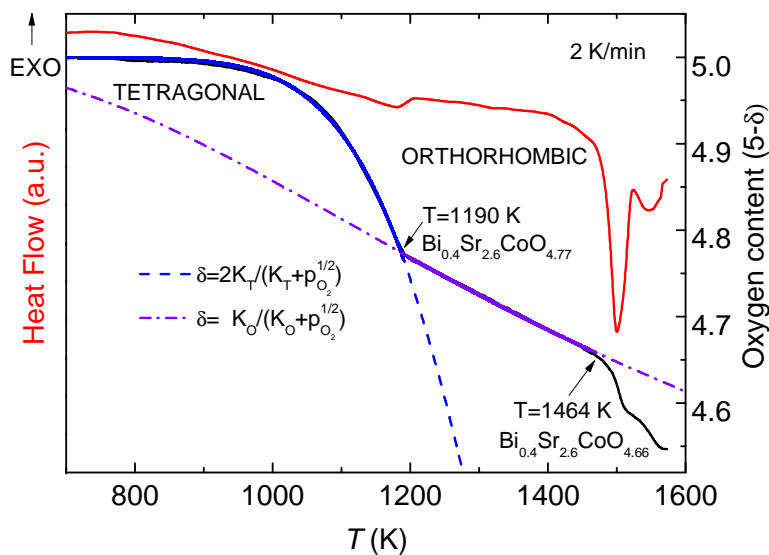
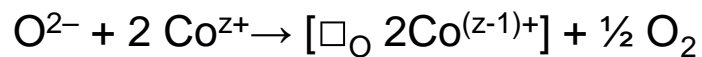
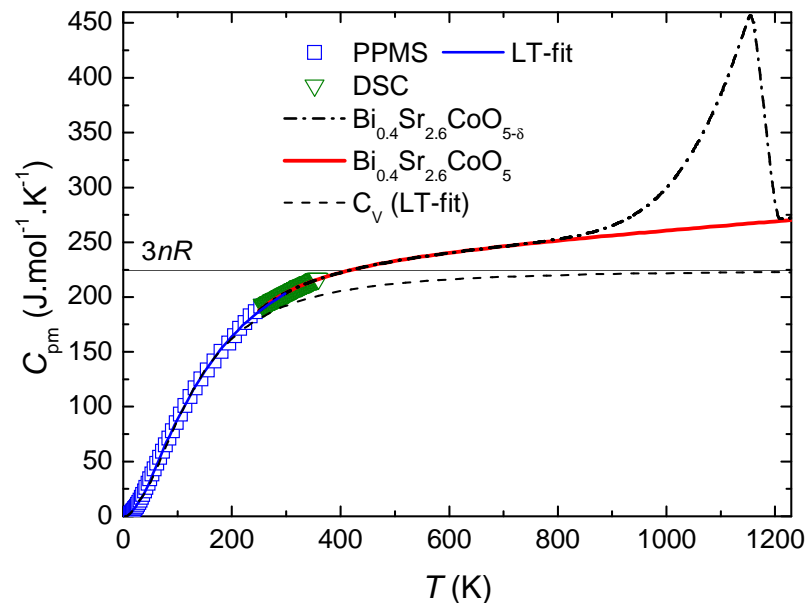
$$\theta_{E3} = 655 \text{ K}$$

Nestechiometrie a tepelná kapacita (Bi_{0.4}Sr_{0.6})Sr₂CoO_{5-δ}



$$K_T = \frac{(2-\delta)p_{O_2}^{1/2}}{\delta}$$

$$K_O = \frac{(1-\delta)p_{O_2}^{1/2}}{\delta}$$



O.Jankovský, Z.Sofer, J.Vítek, P.Šimek, K.Růžička, P.Svoboda, D.Sedmidubský
Structure, oxygen non-stoichiometry and thermal properties of (Bi_{0.4}Sr_{0.6})Sr₂CoO_{5-δ}
Thermochimica Acta, 600 (2015) 89-94

Vliv nestechiometrie na teplotní roztažnost a stlačitelnost

tlaková ftochabilita: $\kappa_{fp} = -\left(\frac{\partial Y_f}{\partial p}\right)_{a_f, T}$

teplotní roztažnost

$$\Delta_{sat} \alpha = \alpha_{a_f} - \alpha_{Y_f} = -\left(\frac{1}{V}\right) \bar{V}_f \kappa_{fT} = -\left(\frac{1}{V}\right) (V_f^\circ + \Delta \bar{V}_f) \kappa_{fT}$$

$$\Delta_{dev} \alpha = \delta \alpha_{p,f}^\circ + \int_0^\delta \left(\frac{\partial \Delta \bar{V}_f}{\partial T}\right)_p d\delta$$

izotermní stlačitelnost

$$\Delta_{sat} \beta = \beta_{T,a_f} - \beta_{T,Y_f} = -\left(\frac{1}{V}\right) \bar{V}_f \kappa_{fp} = -\left(\frac{1}{V}\right) (V_f^\circ + \Delta \bar{V}_f) \kappa_{fp}$$

$$\Delta_{dev} \beta = \delta \beta_{T,f}^\circ + \int_0^\delta \left(\frac{\partial \Delta \bar{V}_f}{\partial p}\right)_T d\delta$$

$$\Delta \bar{V}_f = RT \left(\frac{\partial \ln a_f}{\partial p}\right)_{T, Y_f} = RT \frac{\kappa_{fp}}{\kappa_{ff}}$$

$$\frac{\kappa_{fT}}{\kappa_{fp}} = \left(\frac{\partial T}{\partial p}\right)_{a_f, Y_f} = -\frac{\Delta \bar{H}_f}{T \Delta \bar{V}_f}$$

Příspěvek nestechiometrie k dilatačnímu členu tepelné kapacity

Dilatační člen C_p $\Delta_{dil} C = C_p - C_V = \frac{V\alpha^2}{\beta} T$

$$\Delta_{dil} C = \frac{(V_0 + \Delta_{dev} V)(\alpha_0 + \Delta_{dev} \alpha)^2}{(\beta_0 + \Delta_{dev} \beta)} T = \Delta_{dil} C_0 \cdot M_{dev}$$

$$\Delta_{dil} C_0 = \frac{V_0 \alpha_0^2}{\beta_0} T \quad M_{dev} = \frac{(1 + \Delta_{dev} V / V_0)(1 + \Delta_{dev} \alpha / \alpha_0)^2}{(1 + \Delta_{dev} \beta / \beta_0)}$$

$$\Delta_{dev} V = n_c \int_0^{\delta} \bar{V}_f d\delta = n_c \left(\delta V_f^\circ + \int_0^{\delta} \Delta \bar{V}_f d\delta \right)$$

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Fázové diagramy – experiment a modelování

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