Interactive experimentation and thermodynamic modeling

Weiping Gong[a], Marcelle Gaune-Escard[b], Zhanpeng Jin[a]

[a]State Key Lab of Powder Metallurgy, Central South University, Changsha, Hunan, P. R. China
[b]Ecole polytechnique, Mecanique Energetique, Technopole de Chateau-Gombert, Marseille, France.

The CODATA conference,
Beijing, China, 2006

Outline

1. Introduction
2. Structural behavior and thermodynamic properties of $SrZrO_3$
3. Thermodynamic modeling and experimentation of KBr-$TbBr_3$ system
4. Summaries

Introduction

- **Phase diagram's functions: blueprints or roadmap for materials design, development, processing and basic understanding**
  - visual representations of the state of a material: T, P, C

- **The correlation between thermodynamics and phase equilibrium**
  - J. W. Gibbs
  - Modern development: modeling and computer technology

    → phase equilibrium computer calculation possibility
  - Crucial thermodynamic modeling in binary system
  - can be extrapolated to multi-component systems
  - Question: Can we believe the results of modeling?

- **Two method to check the results of modeling**
  - Comparison between the calculated and measured data in literature is the most usually employed test (example one on $SrZrO_3$)
  - the best way is to couple interactive experimentation and modeling (example two on KBr-$TbBr_3$)

- **Two example were used to illustrate theses two methods**
  - Structure behavior and thermodynamic properties of $SrZrO_3$
  - KBr-$TbBr_3$ Phase diagram and the decomposition of K_3TbBr_6

Example 1: structural behavior and thermodynamic properties of $SrZrO_3$

- **Two different reviews about the structure behavior of $SrZrO_3$ existed in literature**
  - One review: the room temperature structure of $SrZrO_3$ was pseudo-cubic, and this pseudo-cubic structure did not undergo any phase transformation upon heating
  - Second review: the room temperature structure of $SrZrO_3$ was orthorhombic, and the orthorhombic perovskite $SrZrO_3$ will transform through higher symmetries during heating, eventually to ideal cubic
- **A series of thermodynamic data available in literature but great difference existed**
  - Different structure?
  - Effect of impurities, minor departures from nominal stoichiometry, or changes in synthesis temperatures?

- **How to identify and resolve the inconsistency between various kinds of experimental data?**
  - Basic tool: thermodynamic modeling
  - complementary experimentation

Thermodynamic modeling on $SrZrO_3$

- **Experimental data evaluation and thermodynamic modeling**
  - Thermodynamic data and structural information evaluation, thus two optimization procedure were adopted
    - One optimization procedure: don't consider structure transformation

      Thermodynamic modeling of $SrZrO_3$:

      $$G_{SrZrO3} = a_1 + b_1 \cdot T + c_1 \cdot T \cdot \ln T + d_1 \cdot T^2 + e_1 \cdot T^{-1} \quad (1)$$

    - Second optimization procedure: consider structure transformation,

      Thermodynamic modeling of $SrZrO_3$:

      similar equation as (1) to describe orthorhombic $SrZrO_3$

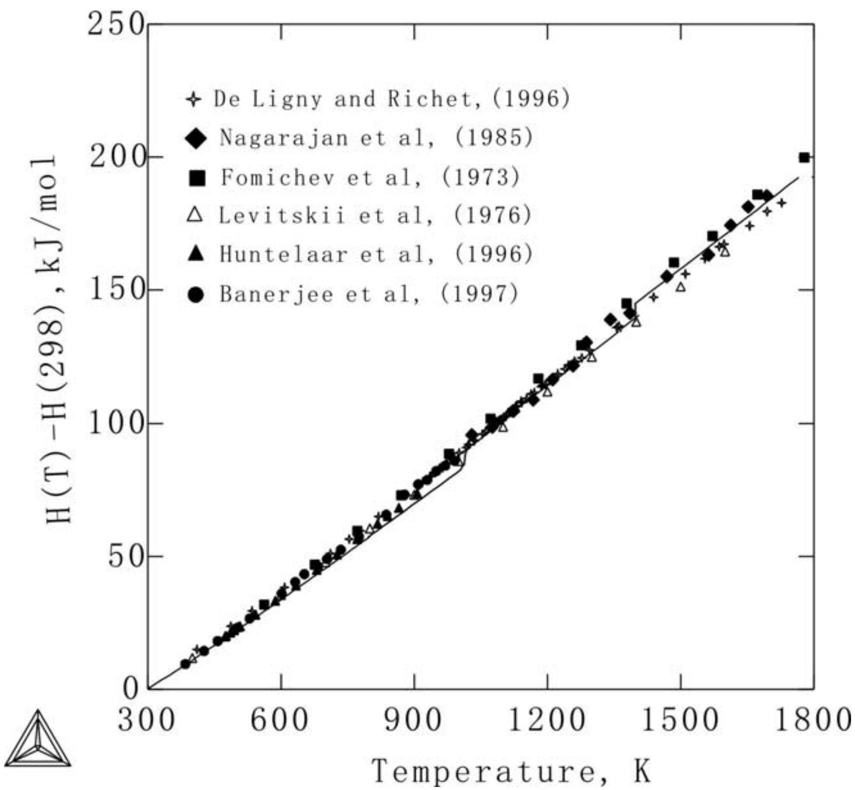
      $${}^{p}G_{SrZrO3} = {}^{o}G_{SrZrO3} + \Delta H_1 - T \cdot \Delta S_1 \quad (2)$$

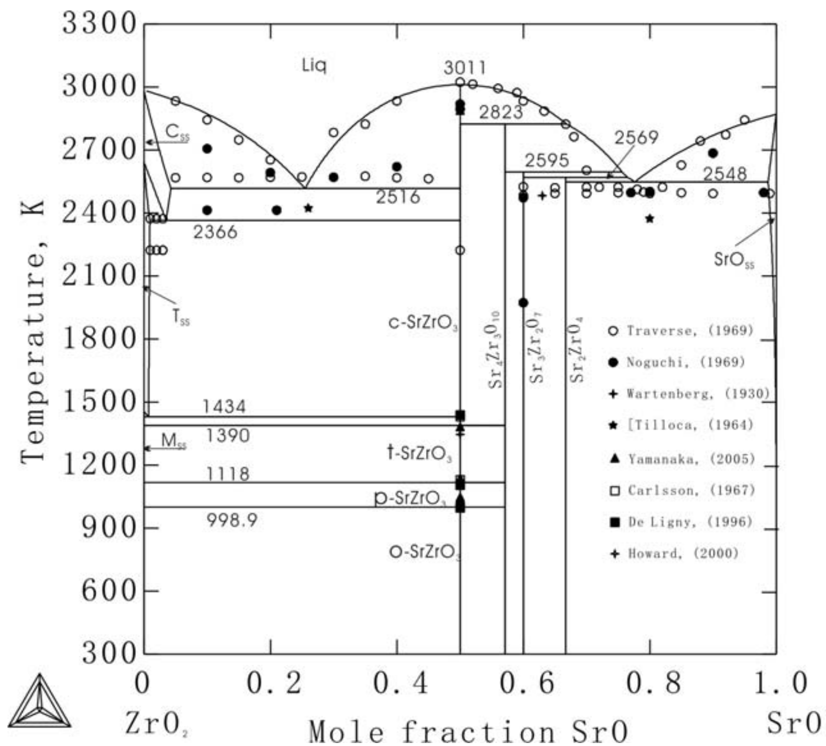
      $${}^{t}G_{SrZrO3} = {}^{p}G_{SrZrO3} + \Delta H_2 - T \cdot \Delta S_2 \quad (3)$$

      $${}^{c}G_{SrZrO3} = {}^{t}G_{SrZrO3} + \Delta H_3 - T \cdot \Delta S_3 \quad (4)$$

      ΔH_1, ΔS_1, ΔH_2, ΔS_2, ΔH_3, ΔS_3 are the corresponding enthalpies and entropies of the transformations

- **Comparison between Experimental data and Thermodynamic calculation**





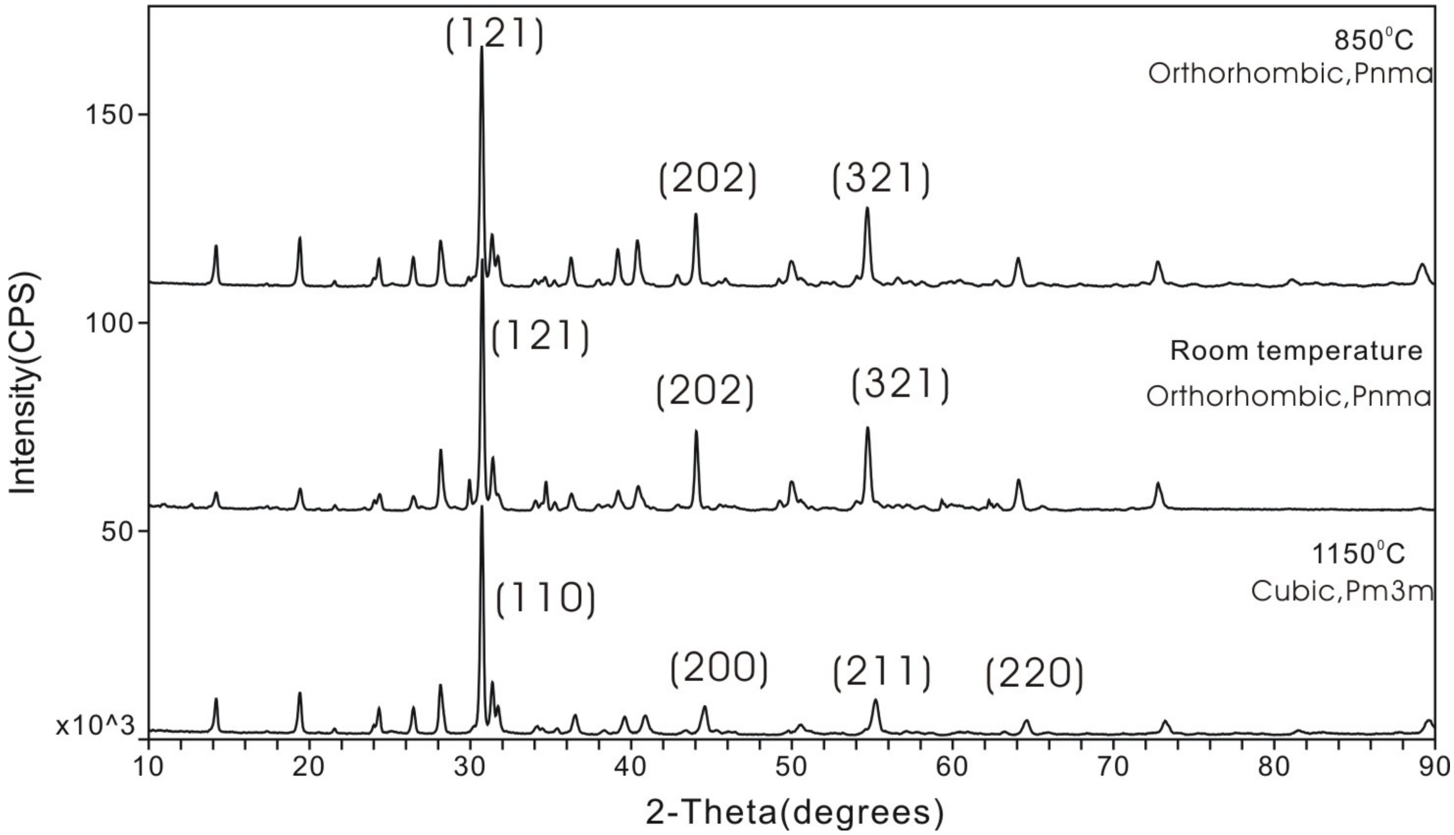
Structure transformation and the corresponding enthalpy were detected by thermodynamic modeling

Experimentation on $SrZrO_3$

- **Prepare the samples**
  - Solid reaction to prepare $SrZrO_3$: $SrCO_3 + ZrO_2$
  - Heat-treated at 1150, 1000, 850 ^{0}C
  - Air quenched or furnace-cooled

- **XRD determination**

- **XRD curve:** sample quenched from 1150 ^{0}C and furnace-cooled to room temperature show the cubic and orthorhombic structure, respectively.



he observed patterns from $SrZrO_3$, showing the fundamental perovskite reflections. The

- **XRD curve results illustrate:**

  negative the pseudo-cubic $SrZrO_3$ in room temperature,

  confirm the structure transformation

  it's quite difficult to obtain the tetragonal $SrZrO_3$ due to

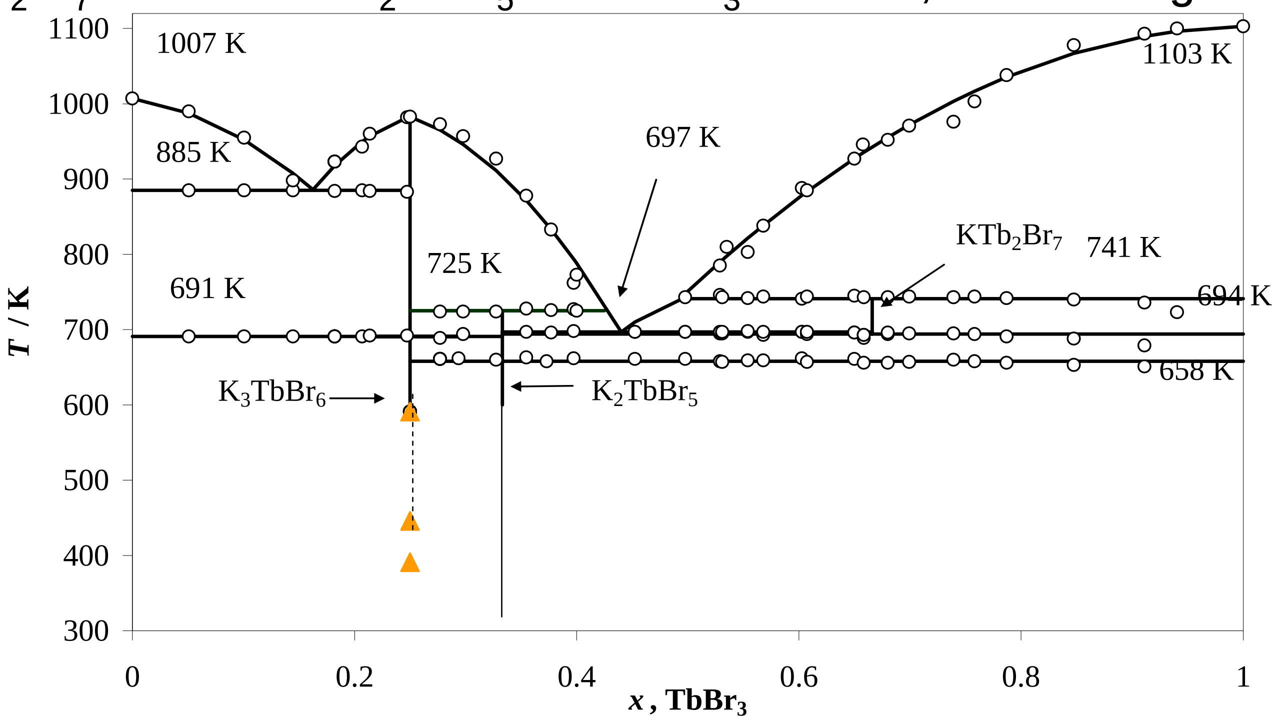
  the impurity, minor departures from nominal stoichiometry

Conclusions

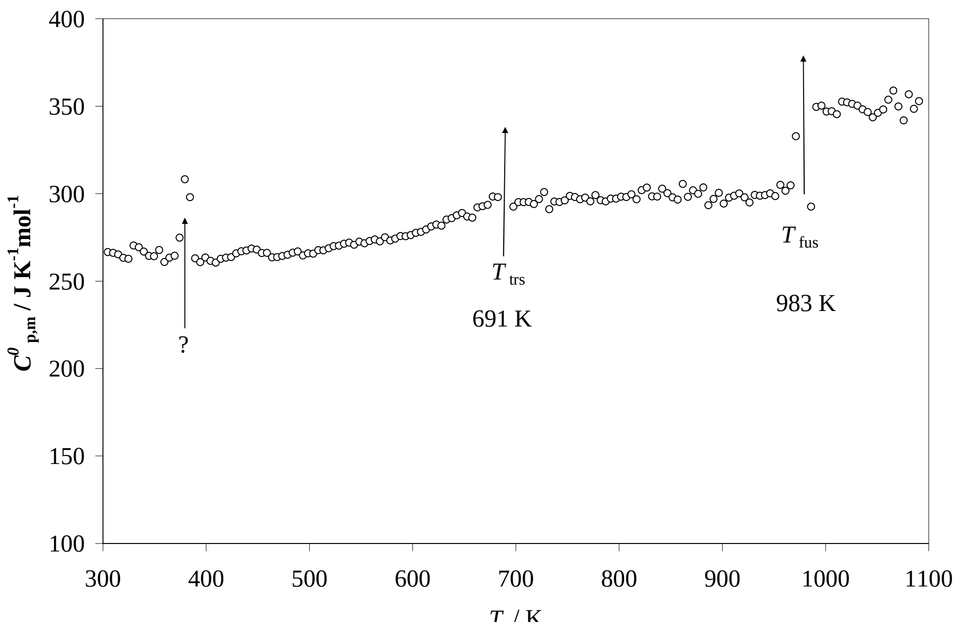
- **Thermodynamic modeling and experimentation benefit the structure behavior and thermodynamic properties investigation**
- **Thermodynamic modeling is based on the experimental information and can be used to identify and resolve the inconsistency between various kinds of experimental**

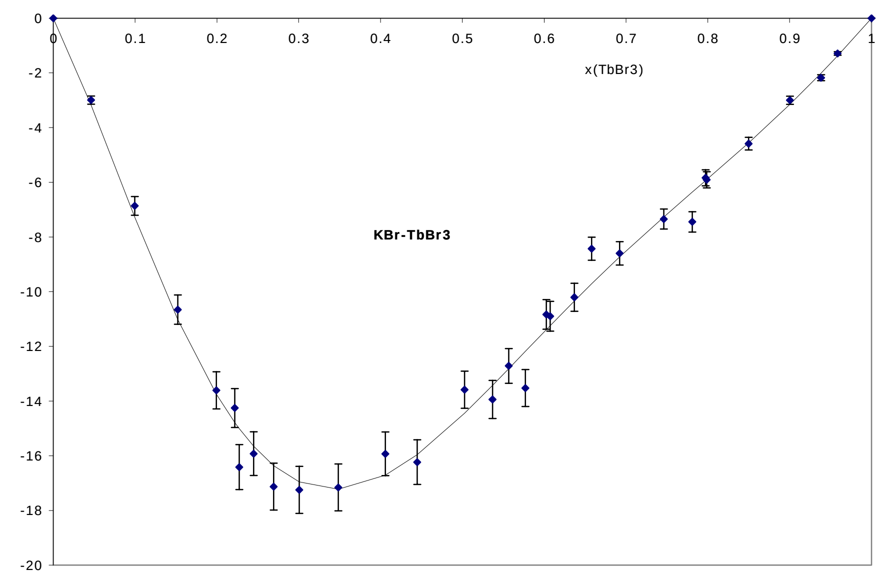
Example 2: KBr-$TbBr_3$ system

- **Measured KBr-$TbBr_3$ phase diagram by L. Rycerz *et al***
  - Two eutectic reactions
  - Three compounds
    - K_3TbBr_3: a solid phase transition at 691 K, melt congruently at 983 K
    - K_2TbBr_5: a solid phase transition at 658 K, melt incongruently at 725 K
    - KTb_2Br_7: form from K_2TbBr_5 and $TbBr_3$ at 694K, melt incongruently at 741 K



- **Measured thermodynamic data by L. Rycerz and M. Gaune-Escard**
  - Heat capacity of K_3TbBr_6:thermal effect at about 691 and 983K
  - Enthalpy of mixing of liquid at 1113 K: the minimum located at about 0.3 KBr suggested the existence of $TbBr_6^{-3}$





Thermodynamic modeling of $KBr-TbBr_3$ system

- **thermodynamic modeling of each phase**
  - Phase without composition range: G(*T*) function
    - Compounds without thermodynamic data: Neumann-Kopp rule

      K_2TbBr_5: $A_1+B_1\cdot T+2/3\cdot G_{KBr}(s)+1/3\cdot G_{TbBr3}(s)$

      KTb_2Br_7 : $A_2+B_2\cdot T+1/3\cdot G_{KBr}(s)+2/3\cdot G_{TbBr3}(s)$
    - K_3TbBr_6 with thermodynamic data and structural information

      two equations were used to describe two forms of K_3TbBr_6

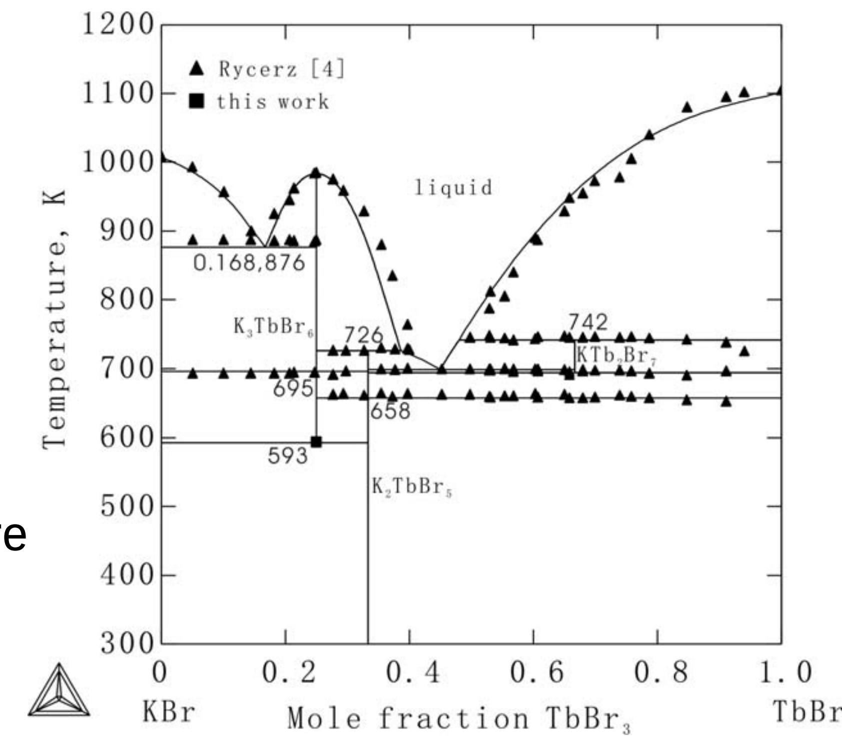
      ${}^{l}G_{K3TbBr6}= a_1+b_1\cdot T+c_1\cdot T\cdot \ln T+d_1\cdot T^2+e_1\cdot T^{-1}$

      ${}^{h}G_{K3TbBr6}= a_2+b_2\cdot T+c_2\cdot T\cdot \ln T+d_2\cdot T^2+e_2\cdot T^{-1}$
  - Thermodynamic description of liquid phase:
    - associated solution $(K^+)_P$ (Br-, $TbBr_6^{-3}$, $TbBr_3)_Q$ was introduced to describe short-range order around K_3TbBr_6 composition

Thermodynamic calculation and comparison (Thermo-Calc software)

- Calculated phase diagram
  - Good agreement
  - Exception:

    decomposition of K_3TbBr_6 at 593 K
- The detected thermo effect in the heat capacity curve of K_3TbBr_6 at low temperature
  - Assessed to be structure change
  - Key experiments were conducted to check the existence temperature range of K_3TbBr_6



Key experiments to check the existence temperature of K_3TbBr_6

- **Prepare the samples**
- **DSC measurements between room temperature and 650 K with a rate of 1 K/min**
  - DSC heating and cooling curve:

    thermal effect at about 593K
  - Results:

    $K_3TbBr_6 \leftrightarrow KBr + K_2TbBr_5$

    at 593 K

DSC heating and cooling traces on K_3TbBr_6 compound

Conclusions

- **Based on the measured data, each phase in KBr-$TbBr_3$ system was thermodynamically modeling, KBr-$TbBr_3$ phase diagram and thermodynamic properties were preliminarily calculated.**
- **Guided by the calculated phase diagram and thermodynamic properties, key experiments were carried out, then model of the relate phases were modified to explain the literature and the present measured experimental data.**
- **The finally obtained thermodynamic properties and phase diagram were more reasonable**

Summaries

- **Two examples, i.e. structure behavior of $SrZrO_3$ and the phase diagram of KBr-$TbBr_3$ system were provided to illustrate the interactive experimentation and thermodynamic modeling**
- **Thermodynamic calculation is based on the experimental data and can provide important information for materials experiments, thus guide materials design, development, processing and materials understanding.**


Thank You !
Welcome to China