INTERACTIVE EXPERIMENTATION AND MODELING FOR PHASE EQUILIBRIUM

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ABSTRACT

The thermodynamic descriptions of the perovskite phase $SrZrO_3$ and the $TbBr_3$-KBr molten salt system were carried out using the available experimental information. Special attention was paid to the structural behavior of $SrZrO_3$ and the decomposition of K_3TbBr_6 at low temperature, respectively, to illustrate how to select an appropriate thermodynamic model based on crystal structure and chemistry information, how to identify and resolve the inconsistency between various kinds of experimental data, and how to use thermodynamic modeling as a basic tool in the development and optimization of materials and process. In the present work, different structures of $SrZrO_3$ were explained by thermodynamic calculation and confirmed with experimental technologies. The decomposition of the compound K_3TbBr_6 at about 593 K was detected by the present thermodynamic calculation and the new complementary experimental measurements. Comparison between the calculated and measured phase diagrams as well as thermodynamic quantities provided the final test of the overall consistency between the reliable experimental information and the present modeling and thermodynamic computation.

Keywords: Experimentation, Thermodynamics modeling, Interaction, $SrZrO_3$, K_3TbBr_6

1 INTRODUCTION

Phase diagrams are visual representations of the state of a material as a function of temperature, pressure, and concentrations of the constituent components and therefore are frequently described as basic blueprints or roadmaps for materials design, development, processing, and basic understanding. While the correlation between thermodynamics and phase equilibrium was established more than a century ago by J.W. Gibbs, it is only modern developments in modeling and computational technology that have made computer calculations of complex phase equilibrium a realistic possibility. Modeling is crucial in that it allows consistent description of binary systems that can be safely used for further computation of complex multi-component phase equilibrium.

Often the question arises; can we believe the results of modeling? Comparison of calculated results with experimental data available in literature is the test method most usually employed, but sometimes, the best way to get the answer is to couple experimentation and modeling interactively.

Two examples, namely the perovskite phase $SrZrO_3$ and the $TbBr_3$-KBr systems are given in this paper to illustrate the how the interaction between modeling and experiment proceeds.

2 INTERACTIVE EXPERIMENTATION AND MODELING FOR STRUCTURAL BEHAVIOR OF $SrZrO_3$

The structural behavior of the perovskite phase $SrZrO_3$ has been the subject of many investigations associated with its technological application. However, because of slight distortion in its structure, it has been argued that impurities, minor departures from nominal stoichiometry, or changes in synthesis temperatures could result in different crystal symmetries and phase transformations of $SrZrO_3$. Two different views of the crystallographic structure of $SrZrO_3$ exist in the literature. One is that the room temperature structure of $SrZrO_3$ is pseudo-cubic (p- $SrZrO_3$) [1-6] and that this pseudo-cubic structure does not undergo any phase transformation upon heating [4, 5]. The second view is that the room temperature structure of $SrZrO_3$ is orthorhombic [7-15] and that the orthorhombic perovskite $SrZrO_3$ (o-$SrZrO_3$) will transform through higher symmetries during heating, eventually leading to ideal cubic (c-$SrZrO_3$) [11-15].

Several groups of authors [14-26] have investigated the thermodynamic properties of $SrZrO_3$, but the data do not agree very well. Because the structure of the samples used by most of investigators was not described clearly, the present work analyzed all of the experimental thermodynamic data critically to optimize the Gibbs energies of $SrZrO_3$ by using the following equation:

$$^{0}G_{SrZrO_3} = a_1 + b_1 \cdot T + c_1 \cdot T \cdot \ln T + d_1 \cdot T^2 + e_1 \cdot T^{-1} \qquad (1)$$

The coefficients c_1, d_1 and e_1 can be evaluated based on the experimental thermodynamic data.

It was rather difficult to reproduce the selected experimental data by the above equation. Further, the reported enthalpies and entropies attached to the phase transformations, although very small, were determined by de Ligny and Richet [14] and Jocab and Waseda [15]. Therefore, a structural transformation was considered in a second optimization procedure. The Gibbs energies of room temperature o-$SrZrO_3$ were evaluated by using an equation similar to equation 1, and the other structures of $SrZrO_3$ were evaluated based on that of room temperature $SrZrO_3$, neglecting any difference of heat capacity between these forms. Thus the following equations were adopted:

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

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

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

ΔH_i and ΔS_i (i=1, 2, 3) are the enthalpies and entropies of the transformations, which were evaluated in next section by using the corresponding thermodynamic data [14, 15]. The superscripts p, c, o, and t refer to pseudo-cubic (p), cubic (c), orthorhombic (o), and tetragonal (t) respectively.

The coefficients obtained in this way can explain most of the experimental thermodynamic data well. Figure 1 shows the present calculated enthalpy increments in the temperature range from 300 K to 1800 K, with the corresponding measured data. Good agreement is obtained.

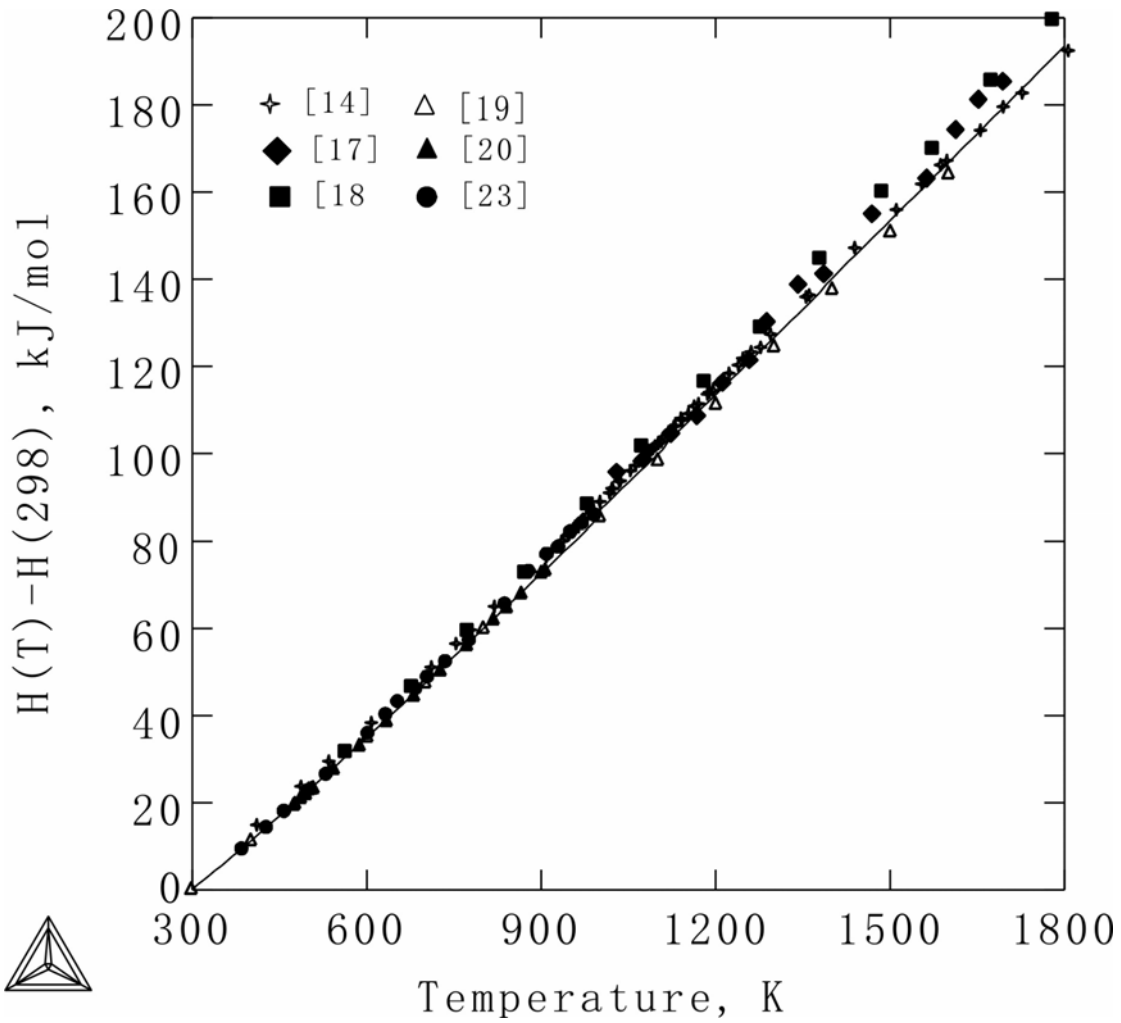


Figure 1. Calculated *H*(*T*)-*H*(298) (solid line) with the corresponding measured data.

In the present work, we prepared the compound $SrZrO_3$ by solid reaction with the suitable rate of $SrCO_3$ and ZrO_2 at 1150℃. The obtained $SrZrO_3$ was heat-treated at 1150, 850 and 700°C for 8 hours, respectively, followed by air quenching or furnace-cooling. The samples so prepared were analysed with X-ray diffraction (XRD) to identify the phase structure. As shown in Figure 2, the furnace-cooled samples have orthorhombic structure, while those quenched from 1150°C have cubic structure, which is consistent with the second view and demonstrates the structure transformation of $SrZrO_3$. Additionally, this experimental measurement failed to detect the previously reported pseudo-tetragonal and tetragonal structures in the moderate temperature range (734~1121℃). Combining the present thermodynamic modeling and experiments, the sequence of structure transformations of $SrZrO_3$ at 1007 K, 1121 K and 1389 K, respectively, has finally been rationalized.

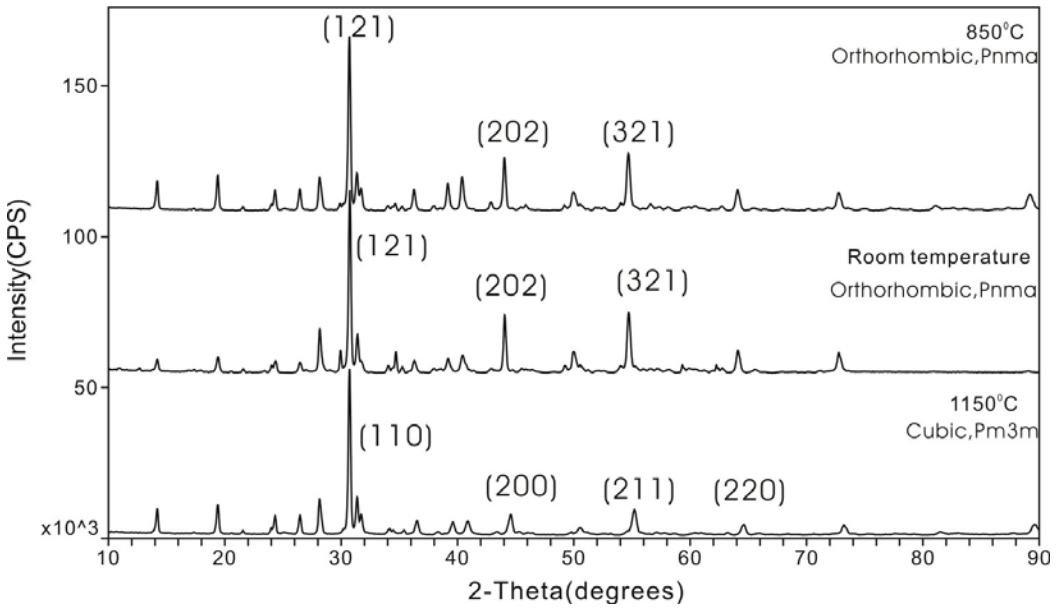


Figure 2. A segment from the observed patterns from $SrZrO_3$, showing the fundamental perovskite reflections. The patterns were recorded at room temperature, 850°C, and 1150℃, respectively.

3 INTERACTIVE EXPERIMENTATION AND MODELING ON THE KBr-$TbBr_3$ SYSTEM

Lanthanide halide-alkali metal halide systems are very challenging from both a scientific and technological point of view. Thus a wide and systematic research program was performed on an international level on a series of binary molten salt systems. Here we present work on the KBr-$TbBr_3$ system as an example to illustrate how the experimentation and thermodynamic modeling interact with each other, thus making the phase diagram and thermodynamic properties more accurate.

KBr-$TbBr_3$ phase diagram in the whole composition range has been measured by M. Gaune-Escard and her group, producing quite accurate measurements that were used to optimize the thermodynamic functions of all phases included in the systems and to calculate the phase diagram of KBr-TbBr3. In the work of Rycerz et al. [27], the phase diagram of the KBr-TbBr3 system includes two eutectics located at about χ_{TbBr3} = 0.163 mol, T = 885 K, and χ_{TbBr3} = 0.433 mol, T = 697 K and three intermediate compounds K_3TbBr_6, K_2TbBr_5, and KTb_2Br_7. K_2TbBr_5 shows a solid phase transition at 658 K and melted incongruently at 725 K. KTb_2Br_7 formed from K_2TbBr_5 and $TbBr_3$ at 694 K and melted incongruently at 741 K. K_3TbBr_6 was found to undergo a solid phase transition at 691 K and to melt congruently at 983 K with the corresponding enthalpies 8.0 and 48.0 kJ/mol.

Rycerz *et al.* [28, 29] measured the heat capacity of K_3TbBr_6 and enthalpy of mixing of liquid at 1113 K, respectively. The thermal effects in the heat capacity curve were consistent with the reported solid phase transformation and the melting of K_3TbBr_6 [27]. The minimum values of enthalpy of mixing located at about 0.3 KBr [29] illustrate the existence of cluster $TbBr_6^{-3}$.

With the experimental phase diagram and thermodynamic data available, each phase was modeled separately.

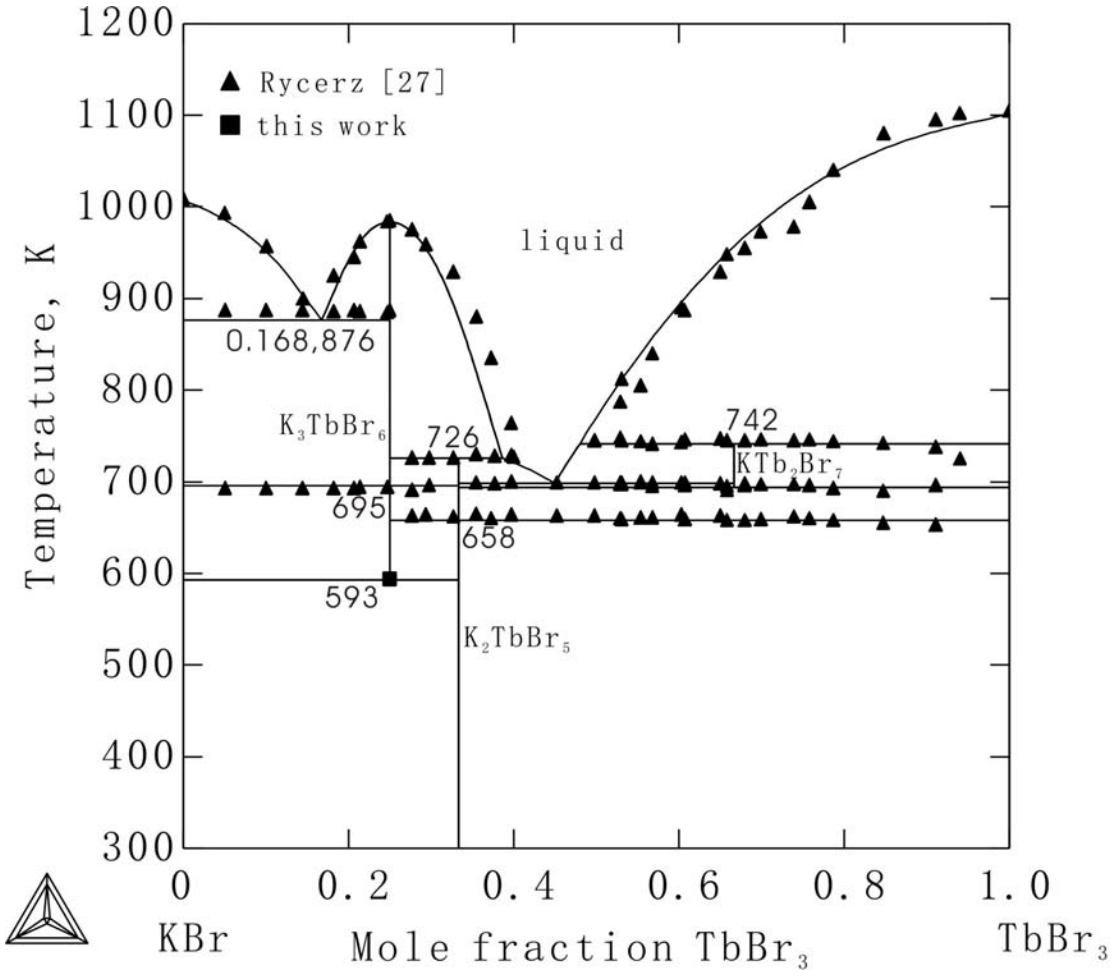
Because there were not thermodynamic data, K_2TbBr_5 and KTb_2Br_7 were modeled by Neumann-Kopp rule. The following equation was used to describe the measured enthalpy and heat capacity of K_3TbBr_6:

$$^{o}G^{S}_{K_3TbBr_6} = a + b \cdot T + c \cdot T \cdot \ln T + d \cdot T^{2} + e \cdot T^{-1} \qquad (7)$$

For the liquid phase, the associated solution model $(K^{+})_P$ $(Br^{-}, TbBr_6^{-3}, TbBr_3)_Q$ was introduced to describe short-range order around K_3TbBr_6 composition, and from the thermodynamic models, the KBr-$TbBr_3$ phase diagram and thermodynamic properties such as heat of transformation, chemical potential, heat capacities, etc, were calculated. Figures 3 and 4 show the present calculated KBr-$TbBr_3$ phase diagram and heat capacity of K_3TbBr_6, respectively. Excellent agreement is obtained except for the decomposition of K_3TbBr_6 at 593 K according to the reaction,

$$K_3TbBr_6 \xleftrightarrow{eutectoid} KBr + K_2TbBr_5.$$

Although this reaction was not reported in the previous phase diagram measurements, an endothermic effect in K_3TbBr_6 compound at a lower temperature [28] was observed. In the absence of additional information, this thermal effect was assessed to be a possible structural change.



Figures 3. The present calculated KBr-$TbBr_3$ phase diagram.

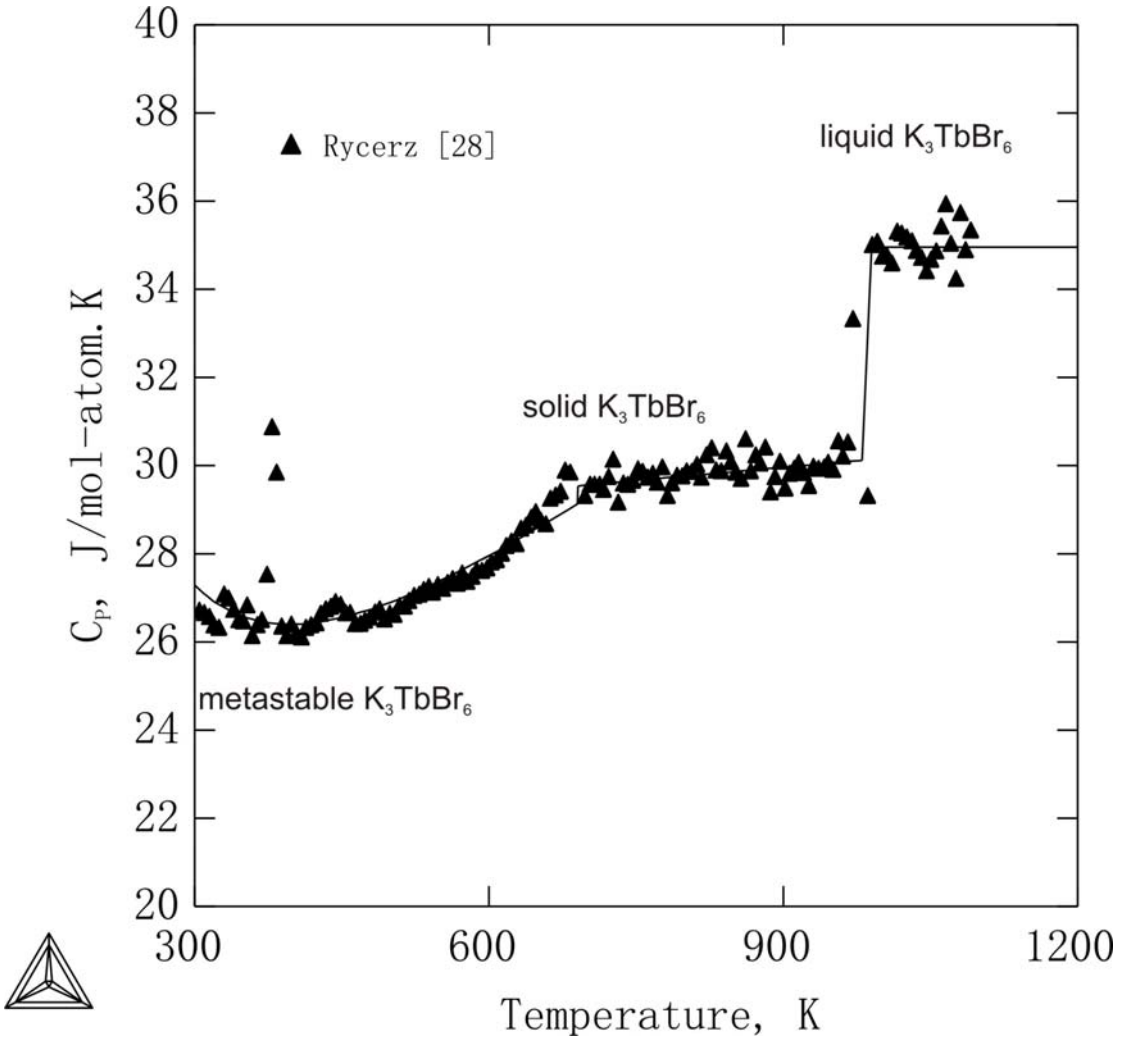


Figure 4. Calculated heat capacity of K_3TbBr_6.

Combined with the present calculated phase diagram and the previous detected thermal effect in the heat capacity curve by Rycerz *et al.*[28], key experiments were conducted in this work with the aim of checking the existence of the possible effect of K_3TbBr_6. Differential Scanning Calorimetry (Setaram DSC 121) measurements were performed on powdered samples consisting of mechanical mixtures of appropriate amounts of pure KBr and $TbBr_3$. Heating and cooling runs were conducted between room temperature and 650°K with a heating and cooling rate of 1 K/min. The corresponding eutectoid temperature 593 ± 2 K derived from the DSC during the heating procedure was detected. However, no thermal effect was observed in this temperature range during the cooling procedure, even at different cooling rates, which once again demonstrated the strong tendency of the K_3TbBr_6 compound to exist in metastable state at low temperature. Figure 5 is the new DSC heating and cooling traces on the K_3TbBr_6 compound.

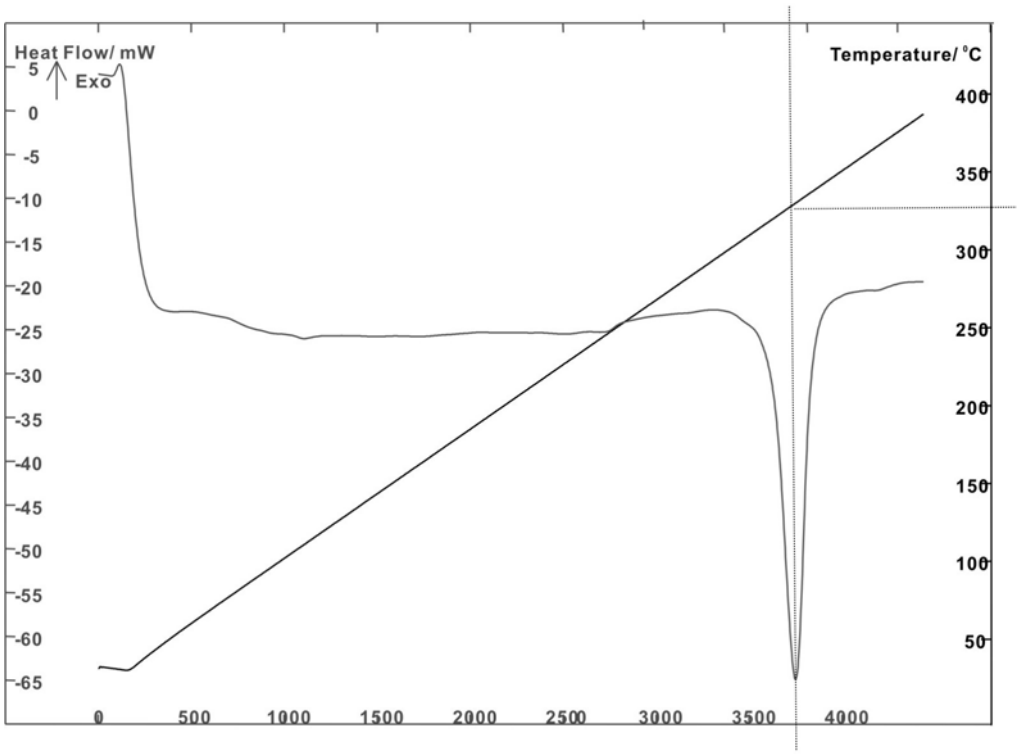


Figure 5. DSC heating and cooling traces on K_3TbBr_6 compound.

The present calculation and the new complementary experimental determination show clearly that the compound K_3TbBr_6 forms from the compounds KBr and K_2TbBr_5 at 593°K. This work provided a good demonstration of the power of interaction between experimentation and thermodynamic modeling.

4 CONCLUSIONS

Two examples, i.e. the structure behavior of SrZrO3 and the phase diagram of KBr-TbBr3 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 guiding materials design, development, processing, and understanding.

5 ACKNOWLEDGEMENT

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6 REFERENCES

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