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Critical assessment of heat capacity data in G.G. Gospodinov et al. articles

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Abstract

Heat capacity data for some mixed oxides obtained by DSC and published in *Thermochimica Acta* are critically revised.

Keywords: Heat capacity; Mixed oxides; DSC

1. Introduction

The goal of this publication is to inform colleagues about mistakes found in the articles of G.G. Gospodinov and co-authors, published in *Thermochimica Acta*.

2. G.G. Gospodinov, V.M. Marchev, The temperature relations of the thermodynamic properties of Ca, Sr, Ba and Pb zirconates, Thermochimica Acta 222 (1993) 137

An experimental study of the heat capacity of four zirconates was carried out with a Setaram DSC in the temperature range from 400 to 580 K for Ca and Sr zirconates, 680 K for $BaZrO_3$, and 480 K for $PbZrO_3$. Heat capacity data were smoothed and extrapolated by the Meyer–Kelly equation:

$$C_p = a + bT + cT^{-2}. \quad (1)$$

Smoothed heat capacity vs. temperature curves are shown in Fig. 1. In some cases the heat capacity curves have a very unusual shape. For calcium and lead salts, the calculated curves have a broad maximum. The curve for strontium zirconate has a broad minimum. In the high temperature region the heat capacity of most of the substances continuously increases if the substance has no phase transition. A maximum on the C_p–T curve can only exist in the case of a phase transition (broad or narrow maximum) or hindered rotation of structure fragments (broad maximum). No information about such phenomena was reported in the paper.

The most probable source of error is the author's use of an incorrect data treatment, i.e., the use of a well-known equation without evaluation of the results.

The heat capacity values for the alkaline earth zirconates differ in some cases by a factor often. The heat capacity depends on the substance, but the difference must be reasonable. A simple evaluation of the C_v limit leads to $\approx 125\ J\ K^{-1}\ mol^{-1}$ for alkaline earth zirconates. Thus, the heat capacity values for

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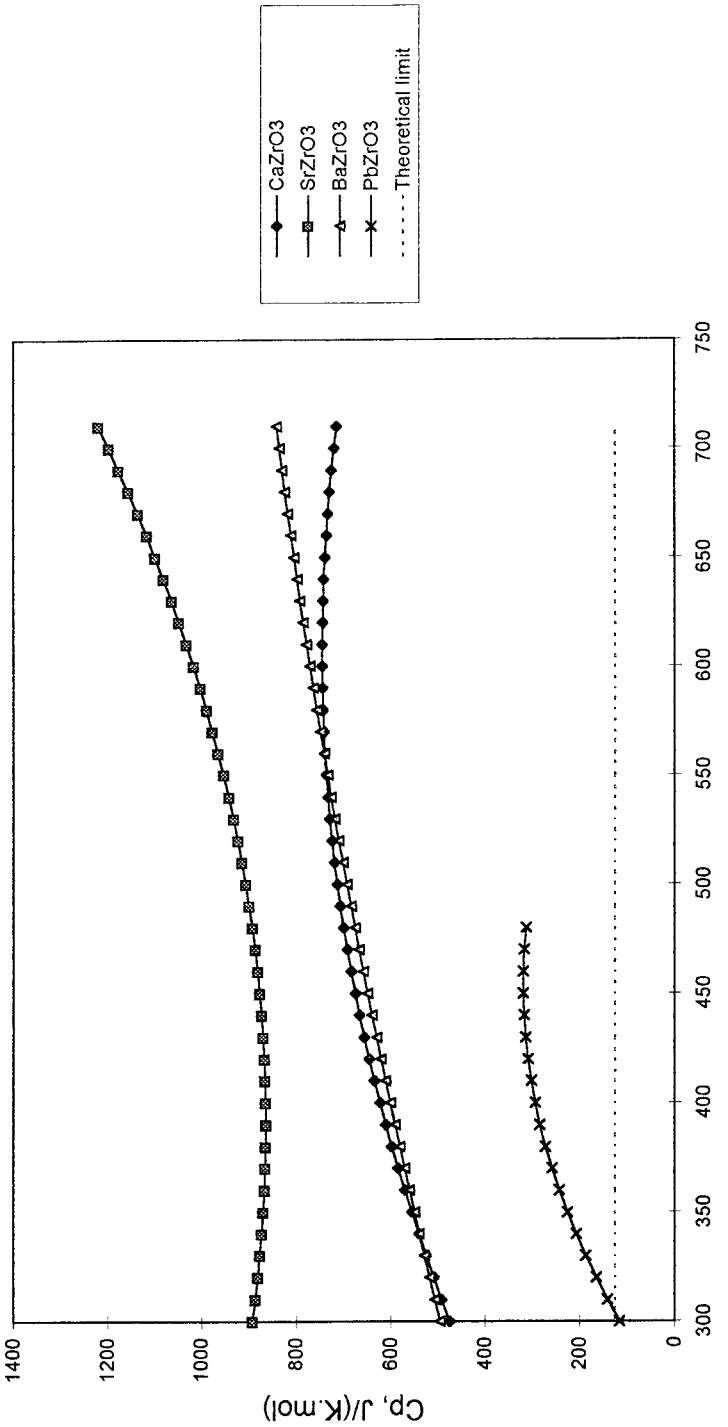

Fig. 1. Heat capacity of alkaline earth zirconates.

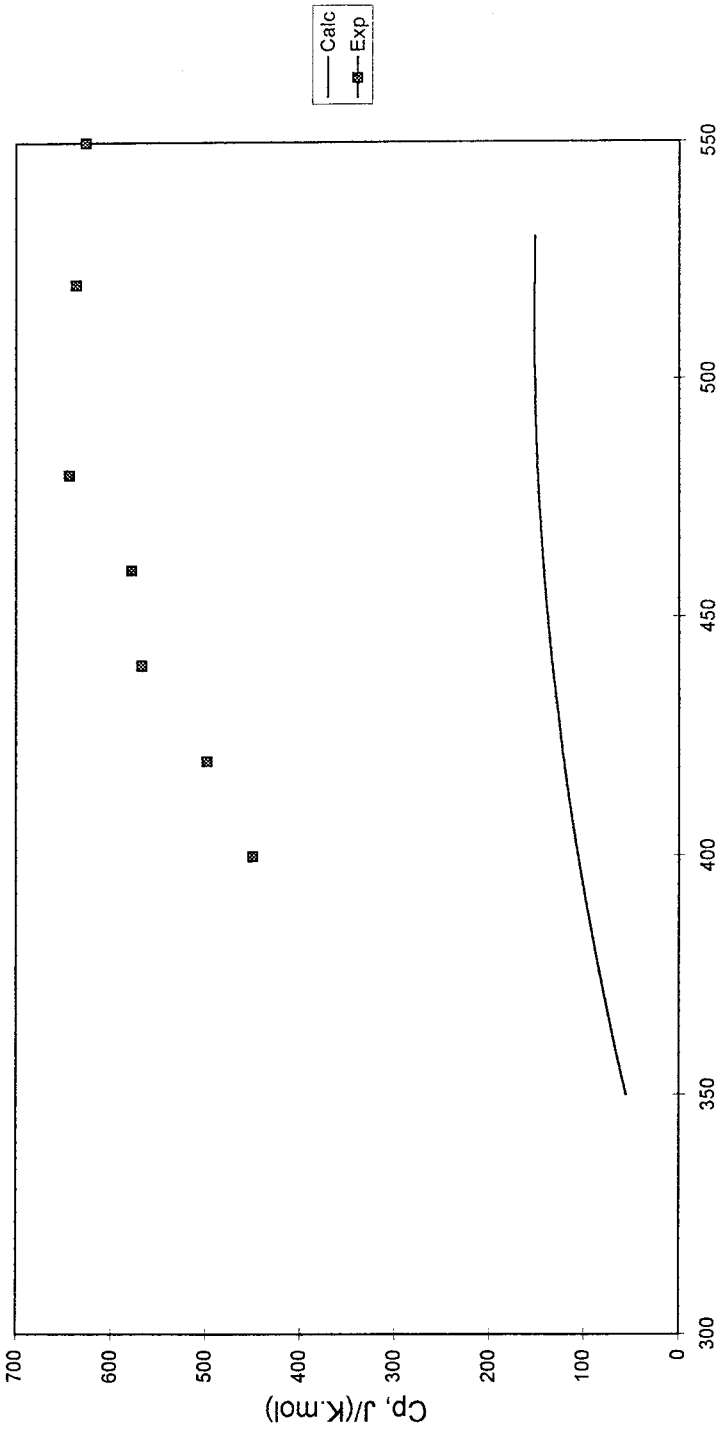

Fig. 2. Heat capacity of $Ba_3Y_2WO_9$.

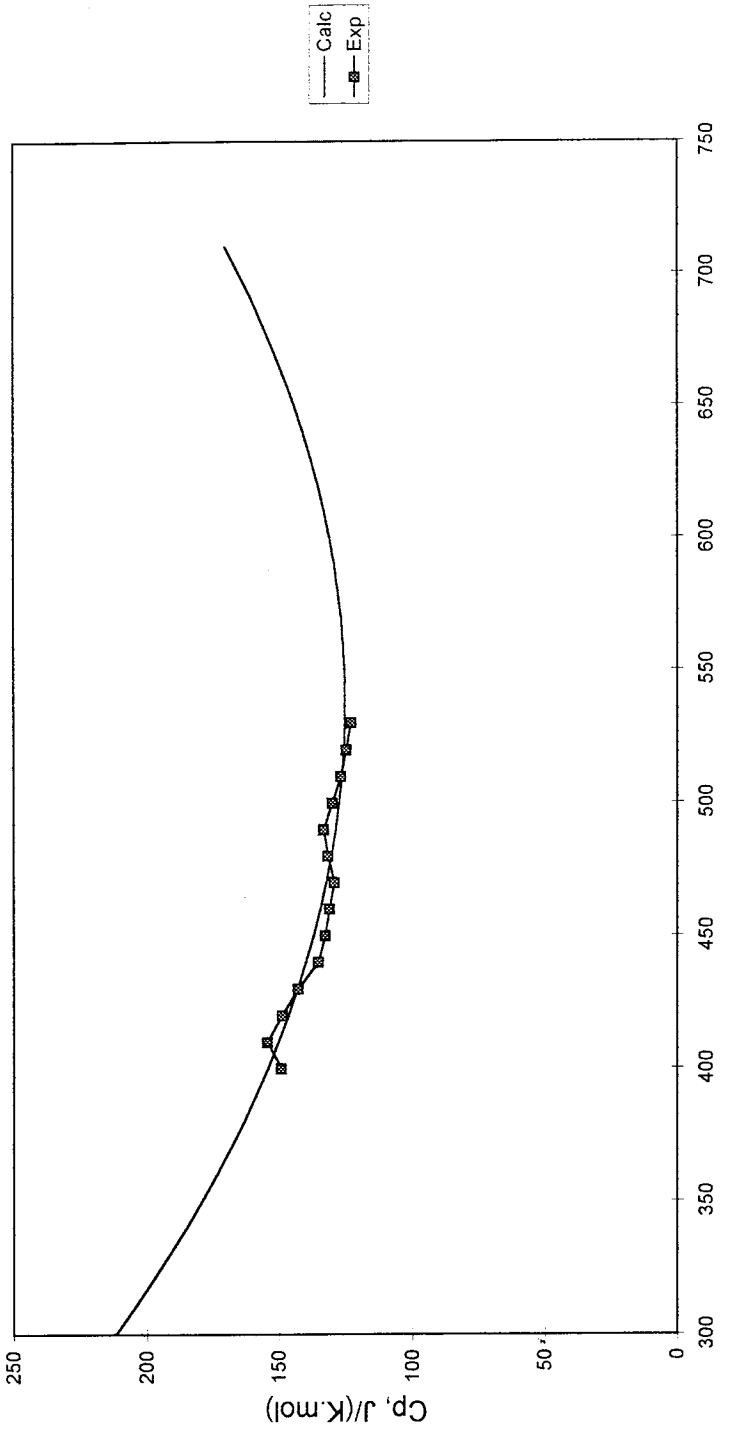

Fig. 3. Heat capacity of $ZnTeO_4$.

calcium, strontium and barium zirconates are too large. The data for lead zirconate must be evaluated further.

3. G.G. Gospodinov, V.M. Marchev, Thermodynamic data for some complex oxides used in electrolamp production, Thermochimica Acta 222 (1993) 143

This study of four compounds (Ba_2CaWO_6, $Ba_3Y_2WO_9$, $Ba_3Y_2MoO_9$, and $MgZrO_3$) was done with a Setaram DSC in the temperature range from 400 to 580 K (for Ba_2CaWO_6, $Ba_3Y_2MoO_9$, and $MgZrO_3$), and to 550 K for $Ba_3Y_2WO_9$. Heat capacity data were smoothed and extrapolated by the Meyer–Kelly equation. For $Ba_3Y_2WO_9$ the smoothed data differ crucially from the experimental data (Fig. 2), apparently a calculation error. For $Ba_3Y_2MoO_9$ the smoothed heat capacity curve has a maximum near 600 K. In our opinion the thermodynamic properties of $Ba_3Y_2WO_9$ are wrong as they were based on the incorrect heat capacity data. The data for $Ba_3Y_2MoO_9$ must be corrected.

4. G.G. Gospodinov, Some properties of zinc tellurates, Thermochimica Acta 233 (1994) 309

This work presents experimental and smoothed heat capacity data for zinc metatellurate $ZnTeO_4$. The experimental temperature range was 403–533 K and the extrapolation region from 298 to 710 K. Heat capacity data, measured with a Setaram DSC at a heating rate of 1 K min^{-1} are plotted in Fig. 3. The heat capacity appears to decrease as temperature rises which needs explanation. From the article, we know that zinc metatellurate is formed by a dehydration reaction. No information about the reverse reaction was given in the article. The apparent decrease in heat capacity could be caused by the substance decomposing, but the author assumed the stability of $ZnTeO_4$ up to 540°C (813 K).

Calculating thermodynamic properties with the formula

$$C_p = -1.0480 \times 10^2 + 2.7102 \times 10^{-1} T + 2.4216 \times 10^7 T^{-2} \quad (\mathrm{J\,K^{-1}\,mol^{-1}}), \quad (2)$$

gave results significantly different from those given in Table 2 of Gospodinov's paper.