Thermochimica Acta, 22 (1978) 187–189

Note

Mn_2CrO_4–Mn_3O_4 solid solutions as materials for thermoanalytical calibration

M. NEVŘIVA
Institute of Solid State Physics, Czechoslovac Academy of Sciences, Prague 6, Cukrovarnická 10 (Czechoslovakia)
(Received 28 December 1976)

If an exact or quantitative evaluation is needed for thermoanalytical measurements, calibration of the measured data becomes necessary. The ICTA Standardization Committee tested a set of preselected materials[1], whose transition temperatures lie in the region from 128 to 925°C. These materials are commercially supplied and usually used as the second class standards in DTA. The non-uniformity of physical and chemical properties (colour, density, reactivity, etc.) of these compounds is, however, the main disadvantage for their application.

On the other hand, solid solutions, which have uniform physical and chemical properties, often prove to be more suitable materials for standardization work. The problem is to find such solid solutions, which show a definite phase transition, the temperature of which is strongly dependent on the change of composition.

For the first time, Smith et al.[2] pointed out the use of solid solutions as standard materials. They observed for the solid solution Na_2CO_3–$CaCO_3$ (molar ratio = 1 : 1) four transitions at 354, 397, 432 and 443°C and proposed its use for the calibration of temperature. The idea of employment solid solutions as standard materials for the calibration of temperature was developed by Judd and Poppe[3]. They investigated the system of $BaCO_3$–$SrCO_3$ solid solutions and found that between the transition temperatures of pure compounds ($BaCO_3$ at 810°C and $SrCO_3$ at 925°C) the dependence of transition temperatures on composition has a parabolic character with the minimum temperature of 776°C for the composition $Ba_{0.6}Sr_{0.4}CO_3$. Nevertheless, the application of both solid solutions is only limited to a part of the temperature region given by existing ICTA standards.

Solid solutions of Mn_2CrO_4–Mn_3O_4 spinels, prepared as materials for the study of the macroscopic Jahn–Teller effect[4–6], exhibit more suitable properties as materials for the calibration. The temperature of tetragonal–cubic transitions linearly increases in the region from 200°C up to 1172°C, as a consequence of the increasing manganese content (see Fig. 1). The transition is accompanied by the enthalpy change whose compositional dependence has a parabolic character (see Fig. 2). The first

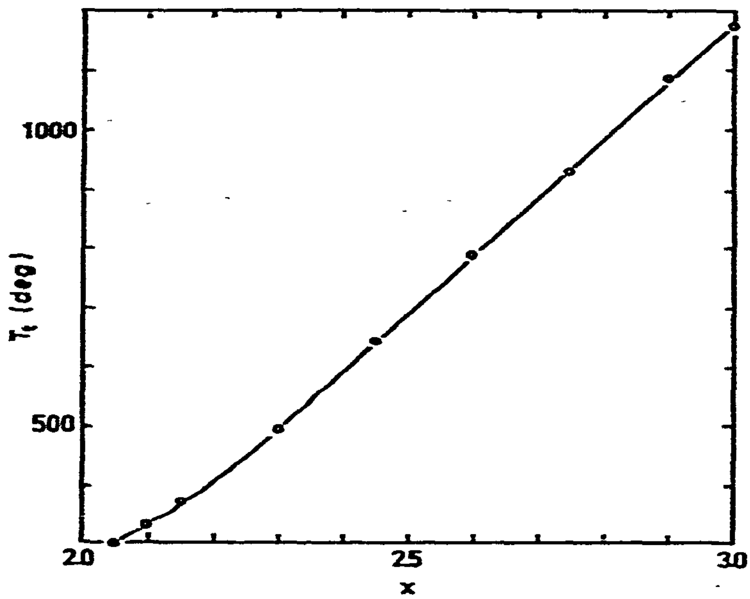

Fig. 1. Transition temperature dependence of $Mn_xCr_{3-x}O_4$ spinels versus composition x.

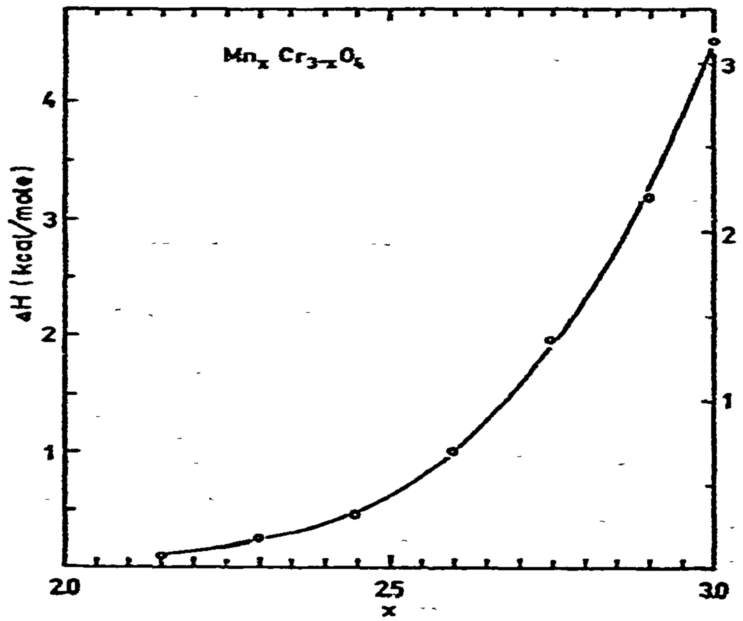

Fig. 2. Enthalpy change dependence of $Mn_xCr_{3-x}O_4$ spinels versus composition x.

advantage of such a set of solid solutions consists in extending the calibration region of temperatures by about 250 K to higher temperatures. Secondly, it is possible to prepare an arbitrary composition, so that the corresponding transition temperatures yield accurate and dense calibration points.

On the other hand, it is also possible that the temperatures of the transition fall into a two-phase region[7], where a phase separation can theoretically be assumed.

It was established, however, that the rate for this separation is negligible. For the composition 3 > x > 2.6 the phase separation was observed only if 1000 h firing treatment at 1000°C was applied. With the samples having Mn content lower than 2.6 phase separation was not indicated at all. Secondly, due to thermodynamic instability below about 900°C, the system may tend to oxidize to sesquioxides. This also need not be taken into account, because no oxidation of samples was observed during normal DTA measurement.

In conclusion, Mn_2CrO_4-Mn_3O_4 solid solutions appear useful as materials for the calibration of both temperatures and apparatus constants at DTA measurement for the temperature region from 200°C up to 1172°C. This material is also applicable for the calibration of temperatures in dilatometry.

ACKNOWLEDGEMENTS

The author appreciates the advice and assistance of Dr. J. Šesták (Institute of Solid State Physics, Prague) and Dr. P. Holba (Institute of Inorganic Chemistry, Řež) at the evaluation of the above results.

REFERENCES

1 H. G. McAdie, in H. G. Wiedemann (Ed.), *Thermal Analysis*, Vol. 1, *Proc. 3rd ICTA, Davos 1971*, Birkhäuser Verlag, Basel, 1972.
2 J. W. Smith, D. R. Johnson and W. A. Robb, *Thermochim. Acta*, 5 (1973) 365.
3 M. D. Judd and M. I. Poppe, *Thermochim. Acta*, 7 (1973) 247.
4 E. Pollert, P. Holba and M. Nevřiva, *TERMANAL '73*, S-75 (1973), *Proc. 6th Czechosl. Conf. Therm. Anal. SVŠT Bratislava, 1973.*
5 P. Holba, M. Nevřiva and J. Šesták, *Neorg. Mater.*, 10 (1974) 11.
6 P. Holba, M. Nevřiva and E. Pollert, *Mater. Res. Bull.*, 10 (1975) 853.
7 E. Pollert, P. Holba, M. Nevřiva and J. Novák, Preprints *8th Int. Symp. on the Reactivity of Solids, Gothenburg, 1976*, p. 287.