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CHROMIUM–MANGANESE-SPINELS WITH JAHN-TELLER PHASE TRANSITIONS AS POTENTIAL HIGH TEMPERATURE DTA-STANDARDS*

H. R. OSWALD, J. P. MATTHIEU AND M. WIRZ
Institute for Inorganic Chemistry, University of Zürich, Zürich (Switzerland)

EXTENDED ABSTRACT

DTA and DSC methods are not only excellent means for investigations into the details of chemical reactions, but they are also well suited to characterize transitions between structurally related phases of very similar energies.

A well-known strong tetragonal distortion of coordination octahedra formed by six equal ligands around Cu^{2+} or Mn^{3+} ions is commonly interpreted as a consequence of the Jahn-Teller theorem. In solids this distortion normally causes a lowering of the macroscopical symmetry, e.g., from cubic to tetragonal or orthorhombic: "static Jahn-Teller effect". Nevertheless, there exist examples of highly symmetrical solid Cu^{2+}- or Mn^{3+}-compounds, where X-ray and neutron-diffraction as well as EPR data point to a non-distorted octahedral coordination around the metal ions, but ligand field spectra on the other hand, with their very short time of measurement in the order of 10^{-14} sec, still speak for the presence of distorted octahedra. In such cases an oscillation within three equivalent possible directions of tetragonal distortion of the octahedra is adopted, leading to an undistorted coordination in time-average: "dynamic Jahn-Teller effect". Upon lowering of temperature, cooperative elastic interactions between the coordination polyhedra may become dominating, causing the dynamic effect to "freeze" into a static one. The thermal analytical characterization of such reversible, in the heating mode endothermic "Jahn-Teller phase transitions" has been reported by Dubler et al.[1] with special emphasis on the system $M_2[PbCu(NO_2)_6]$, where M = K, Rb, Cs. First order transition temperatures T_u between 0 and 130°C and ΔH values in the order of 0.2 cal g^{-1} were found.

Similar phenomena can be observed, although at much higher temperatures, if oxide systems are studied. T_u may occur at such high values that the dynamization of a static Jahn-Teller effect cannot be observed at all before decomposition takes place. If, however, the Cu^{2+} or Mn^{3+} are isomorphically replaced by other, non "Jahn-Teller active" ions, this leads to a continuous decrease of T_u—due to a decrease of cooperative interactions—with increasing degree of isomorphous dilution. At very

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low Cu^{2+} or Mn^{3+} content, the Jahn-Teller effect is usually dynamic even at very low temperatures.

Such a system seems to be present in the spinel mixed crystal series $MnCr_2O_4$-Mn_3O_4 resp. $Mn_xCr_{3-x}O_4$ as reported by Holba et al.[2]. The compounds are normal spinels with Mn^{2+} ions at tetrahedral and Mn^{3+} resp. Cr^{3+} ions at octahedral sites. At room temperature the lattice is tetragonal, i.e. statically distorted, with c/a = 1.16 to 1.05 for x = 3.0 to 2.0. T_u for the transition tetragonal → cubic is 1178°C (or 1172°C according to ref. 2) for x = 3.0, corresponding to pure Mn_3O_4, and decreases continuously to about 300°C for x = 2.0. As there exist at present no certified ICTA temperature standards[3] for DTA in the region above 930°C, the question arises whether such spinels with small, well-defined Cr^{3+}-contents might become useful for temperature standardization purposes. We have in this context executed a series of repeated measurements on a few samples from the above-mentioned $Mn_xCr_{3-x}O_4$ system which were sent to the ICTA Committee on Standardization by Dr. J. Šesták from Prague. These experiments resulted in a sufficient stability of the samples and constancy of the phase transition temperature in air as well as under streaming purified argon. From isothermal TG runs it can be concluded that in argon the decomposition of pure Mn_3O_4 starts very slowly near 1230°C, i.e., at about 50°C above the phase transition temperature. Trivalent chromium has a stabilizing effect on the lattice, leading to an even higher decomposition temperature in the region of 1300°C.

If larger sample quantities are needed, their homogeneity becomes an important factor. Holba et al.[2] have prepared their phases in the usual manner by repeated sintering of mixtures from Cr_2O_3 and $MnCO_3$ at temperatures up to 1350°C in air, followed by rapid quenching. We have, in contrast, sought for a possible precursor of the desired spinel phases which already contains the cations involved in a statistical and homogeneous distribution, in order to avoid the necessity for long diffusion paths (we call this the principle of "atomar mixture"). Such a precursor system could be found and characterized by high resolution X-ray powder diffractometry in the form of a true mixed crystal series between the isomorphous Mn(III)- and Cr(III)-acetylacetonate complexes[4], $(Mn, Cr)(acac)_3$. These mixed crystals leave upon thermal decomposition and annealing at 1100°C pure homogeneous spinel phases $Mn_xCr_{3-x}O_4$. As in the course of the experiments the suspicion arose that in spite of the relatively low preparation temperature minor losses of Cr(III) by volatilization might have occurred, further evaluations were based upon the true analytical composition of the spinel samples, as determined by potentiostatic coulometry to an absolute accuracy of ± 0.3% or about ± 0.01 in x. The tetragonal c/a-values determined from X-ray powder diffractometry as a measure for the tetragonal lattice distortion due to the static Jahn-Teller effect below the transition temperature, as well as the extrapolated onset of the phase transitions correlate well with the analytically determined x.

DTA heating and cooling curves of pure Mn_3O_4 and three $Mn_xCr_{3-x}O_4$ samples with x-values of 2.89, 2.83 and 2.77 are reproduced in Fig. 1. The dependence

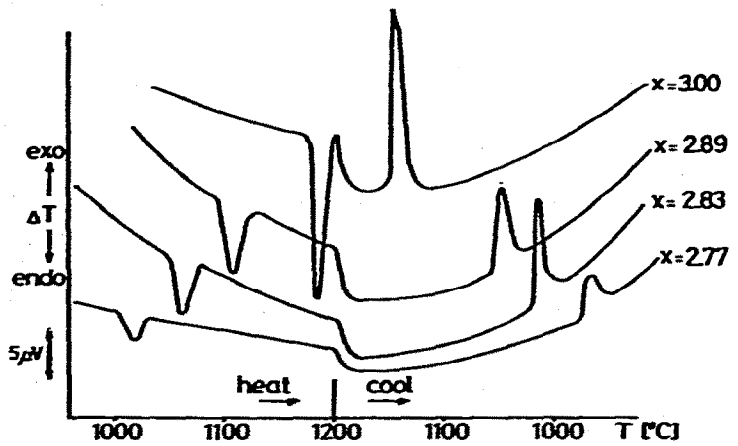

Fig. 1. DTA heating and cooling curves for pure Mn_3O_4 and three $Mn_xCr_{3-x}O_4$ samples prepared from (Mn, Cr)(acac)$_3$ mixed crystals (Mettler TA-1, sample weights ca. 35 mg, 10°C min^{-1}, flowing argon, x-values by chemical analysis).

of the extrapolated onset temperatures in the heating curves (1178, 1087, 1048, 998°C, calibrated with Ag and Au) on the x-values is, however, very strong. An analytical error of $\pm$ 0.01 in x corresponds to about $\pm$ 8°C in the extrapolated onset temperature, whereas the reproducibility of the phase transition temperature measurement for different DTA-runs on one and the same sample is as low as $\pm$ 1 to 2°C.

This means that DTA is able to react with an extreme sensitivity on the chemical composition of the samples. Should these ever be used in practice for DTA temperature standardization purposes, it must be possible to prepare them in 100 g quantities in a reproducible and completely homogeneous form, and their characterization has to occur by DTA rather than by chemical analysis. The spinels under consideration appear fascinating as they allow to control the phase transition temperature by means of the chemical composition within very broad limits, but on the other hand, the general question arises whether non-stoichiometric systems should or should not be chosen for standardization purposes. Regardless of this problem, it is already certain that Mn_3O_4, synthetic hausmannite, which can easily be prepared in sufficient purity and quantity, is a well suited temperature standard material for DTA at 1178°C. Moreover, it might also become useful as an enthalpy standard in the same temperature region.

This preliminary report is taken from work which is in part still under progress and will be published in full detail later.

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