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In-situ high temperature investigation of the phase transition of new manganese gallide ~Mn_2Ga_9

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New manganese gallides with the composition Mn_2Ga_9 were synthesized by reaction of "$MnGa_6$" precursor with an excess of Ga at different temperatures (160–360°C) with subsequent removing of the flux by high temperature centrifugation-aided filtration (HTCAF) and hydrochloric acid. Combining single crystal technique and *in-situ* high temperature diffraction performed at beamline ID31 of ESRF we have established that the compound Mn_2Ga_9 exists in three modifications. The crystal structure model of the *a* and *β* phases were determined with systematically twinned specimens: triclinic, $P\bar{1}$, a = 6.3020(5) Å, b = 9.9388(7) Å, c = 18.911(2) Å, α = 90.52(1)°, β = 90.79(1)°, γ = 90.43(1)° for the *a*-phase and monoclinic, $P2$, a = 6.2909(3) Å, b = 9.9685(5), c = 31.431(2), β = 90.79(1)° for the *β*-phase. The *γ*-modification of Mn_2Ga_9 is not accessible by simple quenching of the sample. It was detected in powder diffraction patterns collected at ID31: tetragonal, $P4/m$, a = 6.3464(1) Å, c = 10.0235(4) Å. The high temperature experiments clearly show that the *α–β* and *β–γ* phase transitions occur at ~145 °C and ~210 °C, respectively (Fig. 1). Whereas the temperature of the *β–γ* phase transition could be fixed by differential thermal analysis, the thermal effect for the *γ–β* transition was hardly to detect due to the displacive character of this transformation (Fig. 2). Finally, the compound Mn_2Ga_9 undergoes a peritectic decomposition at ~390°C: *α*-$Mn_2Ga_9 \rightarrow MnGa_4$ ($PtHg_4$ type) + *L*. The main building unit of the reported crystal structures are distorted tetragonal antiprisms [$MnGa_8$] which are condensed pairwise by their pseudo-tetragonal faces and interconnected via vertices into 3D network (Fig. 3). All modifications adopt similar structures, which differ only by small displacements and deformations of the building blocks. The crystal structures of the reported phases are related to that of $CuAl_2$, *α*- and *β*-$CoSn_3$, $PtSn_4$, Co_2Al_9, $PdGa_5$, Rh_4Ga_{21} and Rh_3Ga_{16} by the atomic environment of the transition metal atoms.

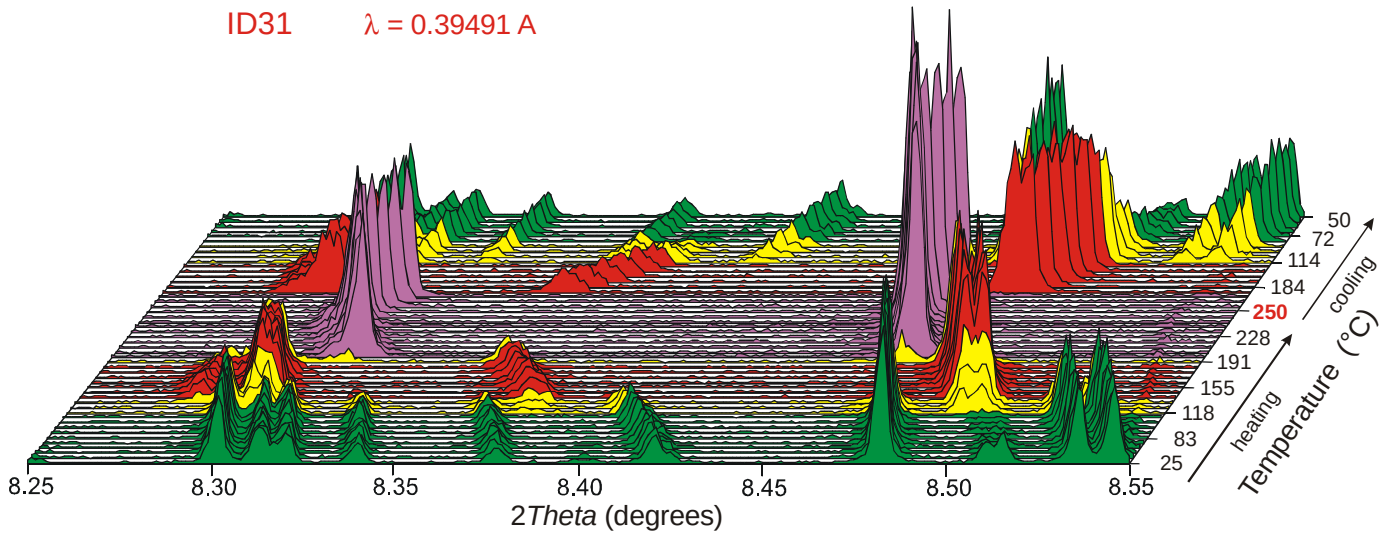

Fig. 1. Selected powder patterns collected between room temperature and 250 °C for the Mn_2Ga_9 phases. Green, red and violet patterns correspond to the α, β and γ modifications, respectively. Regions of α–β and β–γ transitions are indicated yellow.

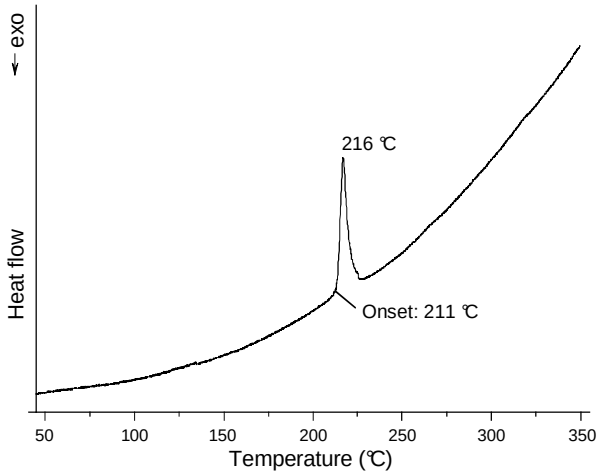

Fig. 2. Differential thermal analysis (DTA) measurement of Mn_2Ga_9. In contrast to the *in-situ* high temperature X-ray powder diffraction (Fig. 1) only the β–γ transition is clearly visible.

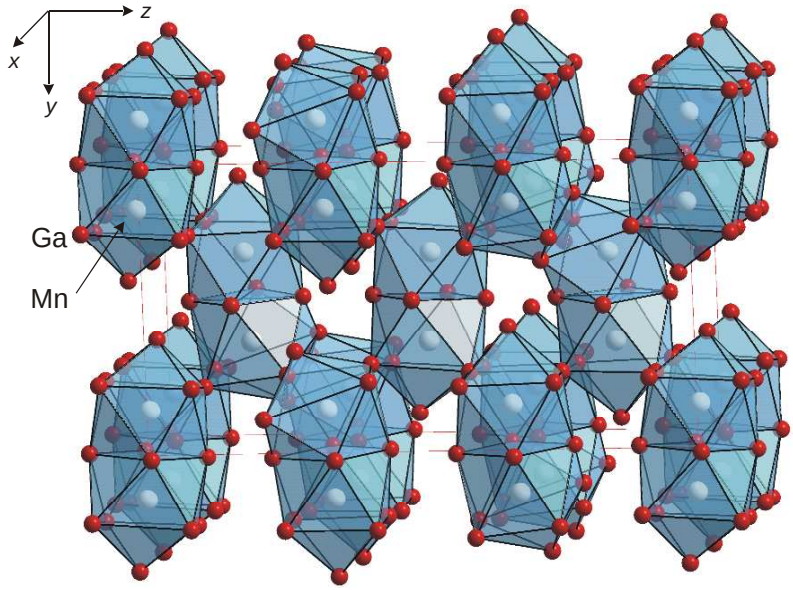

Fig. 3. The crystal structure of γ-Mn_2Ga_9 represented as an interconnection of mono-capped tetragonal antiprisms Ga_9 around Mn atoms.