



	<b>Experiment title: Exploring structural, magnetic and orbital orderings in <math>ZnV_2O_4</math></b>	<b>Experiment number:</b>
<b>Beamline:</b> ID22	<b>Date of experiment:</b> from: 15/07/21 to: 17/07/21	<b>Date of report:</b> 08/09/21
<b>Shifts:</b> 6	<b>Local contact(s):</b> Giorgia Confalonieri	<i>Received at ESRF:</i>
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**Report:** Geometric magnetic frustration arises when the magnetic moments in a crystalline material are unable to align in the most energetically favourable way leading to unconventional magnetic ground states [1]. In three dimensions, a model system in which to explore geometric frustration is the pyrochlore antiferromagnet, whose structure is comprised of a network of corner sharing tetrahedra. This network is realised within cubic spinels, such as  $ZnV_2O_4$ , where the antiferromagnetically coupled  $S = 1 V^{3+}$  ions form a pyrochlore sublattice [2]. However, the ground states in  $ZnV_2O_4$  are complex to comprehend, which is largely due to the interplay of (dis)order within the structural, magnetic and orbital states.

Previous characterisation shows that in polycrystalline samples there are commonly two phase transitions; structural (cubic to tetragonal distortion),  $T_S = 50$  K and ordered antiferromagnetic,  $T_N = 40$  K [3,4]. For single crystal samples, the reported structure remains cubic, and only a single transition is observed in magnetic susceptibility data at 11K, which is attributed to the formation of a frustrated spin glass phase [5]. Crushing these single crystals led to the two transitions returning, albeit at much lower temperatures than reported for powder samples. More recently, reports in the literature demonstrate that doping powder samples of  $ZnV_2O_4$  with non-magnetic ions, such as  $Ga^{3+}$  [4], and magnetic ions, such as  $Ni^{2+}$  [5], eventually suppresses the structural transition, leaving only a single glass transition, like in the single crystal. This has been explained due to the orbital disorder caused as a result of doping. We believe that this idea could be extended to explain the origin of the apparent sample dependence of  $ZnV_2O_4$ , with subtle variations in the structure, stemming from the preparation method, strongly affecting the magnetic ground state.

To explore this, we prepared two polycrystalline samples of  $ZnV_2O_4$ , one via a traditional sintering method and the other via a rapid microwave assisted route (MW) [6]. In this experiment we conducted a high-resolution diffraction experiment on ID22 to explore the average structures of our samples. Key findings from our data are summarised in Figure 1, where we focus on the (800) reflection at  $19.4^\circ$ . Here it can be seen that in the sintered sample there is a clear peak splitting from  $\sim 35$  K, which is indicative of a phase transition to the  $I4_1/amd$  structure and is in accordance with previous reports of powdered samples. Whereas in the MW sample, there is

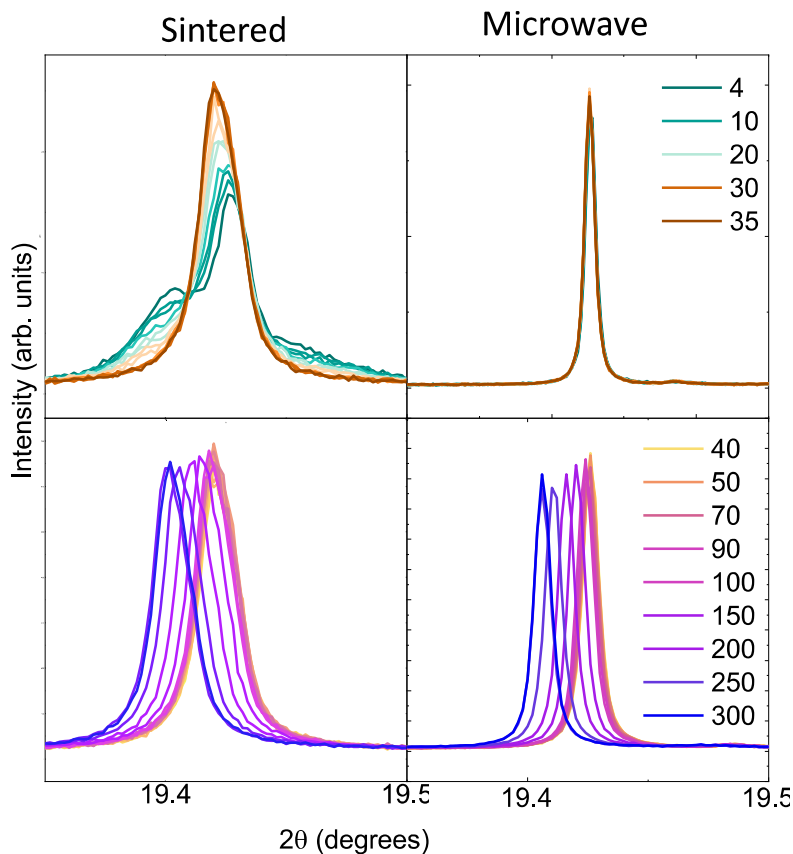


Figure 1: High-resolution ID22 data for the sintered (right) and MW (left) samples as a function of temperature. Top: Low temperature data ( $< 35\text{ K}$ ), where a clear peak splitting appears in the sintered sample, indicating a phase transition, whereas the MW sample remains completely cubic down to 4 K. Bottom: High temperature data ( $>90\text{ K}$ ), show very similar behaviour between the two samples implying the average structures are similar in this temperature range.

no change in the peak height, width, or lattice parameters over the same temperature range which therefore shows that this sample stays within the cubic  $Fd\bar{3}m$  spinel phase, like what was reported for the single crystal. Curiously, at high temperatures, the data are remarkably similar between the two samples, showing a standard lattice expansion between 90 K and 300 K. This may mean that the average structures are similar between our two samples, but they have completely different local structures which ultimately leads one to transition and the other to not. Additionally, the peaks in our sintered sample are inherently broad, at least 2x broader than the MW sample, which is another indicator of potential local disorder.

We have begun by analysing our high-temperature data by Rietveld refinement. We are exploring the effect of different types of strain analysis on our samples, and looking closely at the effect of refining occupancies and atomic co-ordinates. We hope this will shed new light on the interesting behaviour that is seen in not only our samples but also from ones previously reported.

**References:** [1] L. Balents *Nature* **464**, 199 (2010), [2] P. G. Radaelli *New J. Phys.* **7**, 54 (2005), [3] Y. Yamashita and K. Ueda, *Phys. Rev. Lett.* **85**, 4960 (2000), [4] A. J. Browne and J. P. Attfield *Phys. Rev. B* **101**, 024112 (2020), [5] M. Singha et al. *Physica B. Condens. Matter* **563**, 101 (2019), [6] E. E Levin *et al.* *Chem Mater.* **31** 18, 7151 – 7159 (2019).