

MS20-P20 Irreversible pressure induced phase transformation in blossite, α -Cu₂V₂O₇, mineral

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Anhydrous copper vanadates are characteristic minerals of high-temperature volcanic fumaroles [1]. Among the list of fumarolic mineral species containing Cu and V, Cu₂V₂O₇ appears in the form of either blossite, α -Cu₂V₂O₇ [2], or ziesite, β -Cu₂V₂O₇ [3]. An additional polymorph modification as a γ form has been also reported which is related to the β -A₂P₂O₇ structure-type [4]. These 3 polymorphs, which are similar in structure but differ markedly in the kinetics of their formation and reversibility of their transformations [5]. Cu₂V₂O₇ material has been attracted a lot of attention, not only in mineralogy but also due to its importance as cathode material for rechargeable lithium batteries [6]. Recently, this material received further attention from the physics community. Cu₂V₂O₇ exhibits low dimensional magnetic properties [7] and due to the polar structure of blossite (α -Cu₂V₂O₇ phase, space group Fdd2), it has been shown to be a promising new multiferroic material [8]. Despite all these investigations, yet very little is known about the pressure dependence of this material. In order to gain further understanding of Cu₂V₂O₇, we have investigated the effect of pressure at room temperature on the crystal structure of blossite up to 6 GPa. We report on a new δ -Cu₂V₂O₇ polymorph arising from an irreversible phase induced transition at room temperature. Using high resolution x-ray powder diffraction, we were able to solve the structure of this new polymorph. It exhibits symmetry P21/c with cell parameters $a = 9.4547(3)$ Å, $b = 11.4168(3)$ Å, $c = 5.0652(1)$ Å, and $\beta = 97.12^\circ$. We discuss this new phase in relation to the previously reported polymorphs. [1] J. M. Hughes, R. E. Stoiber, *J. Volcanol. Geotherm. Res.* 24, 283-291., (1985) [2] P. D. Robinson, et al., *Am. Mineral.* 72, 397-400 (1987). [3] J. M. Hughes, et al., *Am. Mineral.* 65, 1146-1149 (1980). [4] S. V. Krivovichev, et al., *Can Mineral* 43, 671-677 (2005) [5] B. V. Slobodin et al., *Inorganic Materials*, 2010, Vol. 46, pp. 196-200 [6] Tranchant, et al., *J. Electroanal. Chem.*, 1988, vol. 242, pp. 181-190. [7] O. Janson et al., *Phys. Rev. B* 83, 094435 (2011), A. A. Tsirlin et al., *Phys. Rev. B*, 82, 144416 (2010) [8] J. Sannigrahi, et al., arXiv:1501.00809

Keywords: phase transformation, high pressure, blossite

MS21. Advances in high-pressure methods

Chairs: Leonid Dubrovinsky, Ronald Miletich

MS21-P1 Kinetic control on high-pressures solid-state phase transitions

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Applying high pressure is a powerful method to induce transformations in the solid state. As a matter of fact, compression alters the thermodynamic state of a solid and can induce lattice strain, phase transitions or even chemical reactions. However, as in every physico-chemical transformation, an important role is played by the kinetic aspect of the process. Despite the increasing popularity of high-pressure investigations of solid state materials, kinetic effects are seldomly taken into account during experiments and data interpretation. We found that the compression rate adds a new perspective to phase diagrams of solids, which can even provide the key to explain complex polymorphic systems. Not only can the onset pressure of each transition and the ranges of coexistence of polymorphs be modified by controlling the compression rate, but also a particular pressure increase rate may trigger unexpected solid state transformations, producing otherwise inaccessible phases. These phenomena were initially observed and investigated for the system [CuF₂(H₂O)₂(pyz)]_n (pyz=pyrazine) which showed coexistence of two phases above ca. 3 GPa.¹ A new, even richer example is L-serine, characterized by a complex high pressure behavior with three known polymorphs, for which the critical pressure of each transition and the ranges of coexistence of the phases have been controversially reported.² In addition to this, the existence of an elusive fourth phase² has so far remained an open question. The puzzle could be solved by high pressure synchrotron powder X-ray diffraction, under controlled pressure increase rates.²

REFERENCES:

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(2) Fisch, M.; Lanza, A.; Boldyreva, E.; Macchi, P.; Casati, N. J. Phys. Chem. C 2015, [Online early access], DOI: 10.1021/acs.jpcc.5b05838; and references therein.

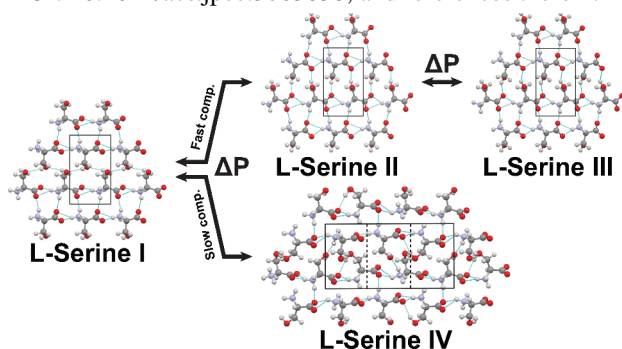


Figure 1. Two parallel pathways were found for L-serine in response to high pressure, evidencing that the compression rate can significantly affect the high pressure behaviour of solid state materials.

Keywords: Polymorphism, high-pressure crystallography, amino acids, synchrotron X-ray powder diffraction, solid-state kinetics, kinetic control

MS22. High response systems in practical and extreme conditions

Chairs: Yaroslav Filinchuk, Dmitry Chernyshov

MS22-P1 Engineering second and third generation MOFs and elucidating their structure property relationships

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A cursory glance of the literature reveals many reviews illustrating the enormity of the field of crystal engineering.^{1,2,3,4,5,6} The practically infinite number of combinations of organic bridging ligands with metals possessing different coordination geometries for the construction of functional MOF materials ensure that this field will continue to evolve and prosper for many years to come. Using a selection of carefully chosen components (two symmetrical N donor ligands, a flexible acid and either zinc or cadmium) under solvothermal conditions, several interesting materials have been obtained. These materials are all porous, possess varying degrees of interpenetration and show interesting SC SC transformations, guest sequestration and guest storage capabilities.

Although crystal engineering has not yet reached the point where one can reliably predict the outcome of a set of crystallisation components, work such as this, is intended to widen the general knowledge such that guidelines may eventually be established that will enable target directed MOF design.

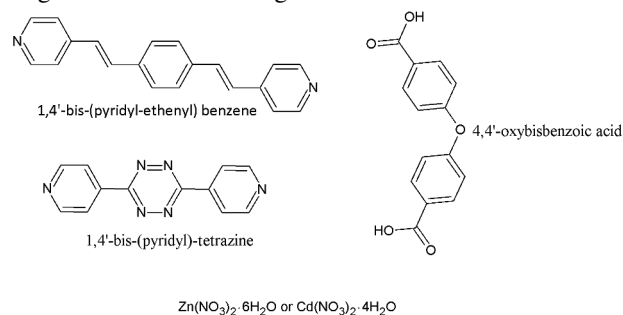


Figure 1. Synthetic components required for the formation of several interesting second and third generation MOFs.

Keywords: MOFs, Third generation, transformations, Single Crystal-Single Crystal