

Comment on "Pressure-Induced Transformations of the Low-Cristobalite Phase of GaPO₄"

In a recent Letter Robeson, Winters, and Hammack [1] demonstrated that the low-cristobalite phase of GaPO₄ undergoes a pressure-induced transition at 15.9 GPa to a "novel phase" in space group *Cmcm*. They claim that this is in accord with the molecular dynamics predictions for SiO₂ low cristobalite by Tsuneyuki *et al.* [2]. In this Comment, we show that this phase is not a new one as it has been already documented in a number of closely related compounds (see Table I).

In literature, it is usually referred to as the "CrVO₄" structure in which cations have sixfold coordination and anions are four coordinated [3]. The atomic positions here are similar to the *Cmcm* phase predicted by Tsuneyuki *et al.* [2]. The total energy calculations of Chaplot and Sikka [4] suggest that for AlPO₄, the *Cmcm* phase is the more stable one at pressures above 10 GPa, even though, due to the reasons of kinetics, it fails to transform to this phase under pressure. But in GaAsO₄ and AlAsO₄ this phase is known [5] to result from the compression between 4–7 GPa. We should also point out that the observation of this phase in GaPO₄ in no way supports the prediction of this phase in SiO₂ cristobalite by Tsuneyuki *et al.* [2]. When this phase has not been observed in cristobalite itself, as noted by Robeson, Winters, and Hammack [1], its observation in *c*-GaPO₄ should be viewed as a mere coincidence.

The prediction of new phases by molecular dynamics calculation depends very much on the accuracy of atom-specific interactions and therefore, until explicitly shown, it may be mere conjecture to transfer the conclusions to other systems. In this context it should be enough to point out that even for cristobalite SiO₂, if one uses the potential parameters of van Beest, Kramer, and van Santen [8] (which give excellent predictions for the α -quartz phase [9]) this *Cmcm* phase is not seen in the simulation [10].

In view of these facts, it is appropriate to conclude that the observation of the *Cmcm* phase in *c*-GaPO₄ is not an unusual result. In fact its occurrence conforms to a general trend of phase transitions under high pressures,

TABLE I. Comparison of axial ratios for some *Cmcm* phase compounds.

Compound	$a : b : c$	Reference
GaPO ₄	0.700 : 1 : 0.810	[1]
SiO ₂	0.689 : 1 : 0.750	[2]
AlAsO ₄	0.671 : 1 : 0.731	[5]
GaAsO ₄	0.667 : 1 : 0.727	[5]
InPO ₄	0.675 : 1 : 0.862	[6]
TiPO ₄	0.674 : 1 : 0.880	[6]
CrPO ₄	0.662 : 1 : 0.786	[7]

i.e., the pressure homology rule which states that compression and chemical substitution by an element with a higher atomic number in the same column of periodic table generally result in the same structural trend.

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