

The substituted basic Cu(II) chloride phase transformations

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The known polymorphs of composition $\text{Cu}_2\text{Cl}(\text{OH})_3$ are botallackite ($P2_1/m$), atacamite ($Pnma$), clinoatacamite ($P2_1/n$), anatacamite ($P\bar{1}$) and paratacamite ($R\bar{3}$). Paratacamite was originally described by Smith (1906) as having the composition $\text{Cu}_2\text{Cl}(\text{OH})_3$, but it is now accepted that the rhombohedral structure is stabilised by the presence of some essential Zn or Ni (Jambor *et al.*, 1996). The structure of paratacamite was determined by Fleet (1975) assuming the nominal formula $\text{Cu}_2\text{Cl}(\text{OH})_3$ and exhibits a pronounced sub-cell with $a' = 1/2a$, $c' = c$, space group $R\bar{3}m$. It is now known that this $R\bar{3}m$ structure is that of herbertsmithite and gillardite, $\text{Cu}_3M\text{Cl}_2(\text{OH})_6$, $M = \text{Zn}, \text{Ni}$, respectively (Braithwaite *et al.*, 2004; Clissold *et al.*, 2007). A series of compositionally related phase transformations are known to occur in this group as Cu is replaced by Zn or Ni. It is suggested that the order of phase transformations follow the series, $P\bar{1} \rightarrow P2_1/n \rightarrow R\bar{3} \rightarrow R\bar{3}m$ (Malcherek and Schlüter, 1999).

This series of potential transformations was explored by Raman spectroscopy for materials of composition $\text{Cu}_{4-x}M_x\text{Cl}_2(\text{OH})_6$ where $M = \text{Zn}$ or Ni , between $\text{Cu}_{3.90}M_{0.10}\text{Cl}_2(\text{OH})_6$ to $\text{Cu}_{3.08}M_{0.92}\text{Cl}_2(\text{OH})_6$. Additional measurements using powder and single-crystal X-ray methods were also made on natural and synthetic material in support of the analyses. The only observed compositionally related structural transformation observed at ambient temperatures is that of clinoatacamite ($P2_1/n$) \rightarrow herbertsmithite or gillardite ($R\bar{3}m$) with increasing substitution of Zn or Ni. The transformation occurs over the compositional range $\text{Cu}_{3.81}\text{Zn}_{0.19}$ – $\text{Cu}_{3.67}\text{Zn}_{0.33}$ and $\text{Cu}_{3.75}\text{Ni}_{0.25}$ – $\text{Cu}_{3.67}\text{Ni}_{0.33}$ and agrees with the work of Jambor *et al.* (1996). The Raman spectra of intermediate compositions of both Zn and Ni show localised $P2_1/n$ distortions in the $R\bar{3}m$ structure which decrease with increasing substitution.

This study prompted an assessment into the nature of the $R\bar{3}$ structure and consequently all data in the literature citing reference to it. It seems that the $R\bar{3}$ structure of paratacamite is incorrect. All previous Raman data on paratacamite was made on samples of herbertsmithite or gillardite with substantial Zn or Ni in its structure.

While this simplifies the series of transformations, the mineral paratacamite cannot be discredited. Its name has historical precedence and it was originally accepted as a new polymorph of $\text{Cu}_2\text{Cl}(\text{OH})_3$. Its true structure must be considered as unknown. To complicate matters, the crystal used by Fleet (1975) for structure determination is lost and it is now known that the type specimen contains a mixture of Zn-substituted clinoatacamite and herbertsmithite crystals (Braithwaite *et al.*, 2004). It is possible that the structure of paratacamite is that of herbertsmithite, but the origin of the reported weak super-cell reflections that denote $R\bar{3}$ symmetry remains unknown.

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