Programme and Book of Abstracts

Fifth Meeting of the Italian (AIC) and Spanish Crystallographic (GE3C) Associations (MISCA V)

Napoli, 4-7 September 2019

MISCA2019

Summary

Committees

Steering Committee

G. Diego Gatta
AIC President
Univ. Milano

Fernando Lahoz
Past GE3C President
CSIC, Zaragoza

Organizing Committee

Luigi Vitagliano
IBB-CNR, Napoli, Chair

Michele Saviano
IC-CNR, Bari, Chair

Filomena Sica
Univ. Federico II, Napoli

Piergiulio Cappelletti
Univ. Federico II, Napoli

Consiglia Tedesco
Univ. Salerno

Luciana Esposito
IBB-CNR, Napoli

Rita Berisio
IBB-CNR, Napoli

Luca De Luca
IBB-CNR, Napoli

Alessia Ruggiero
IBB-CNR, Napoli

Nicole Balasco
IBB-CNR, Napoli

Annalisa Guerri
Univ. Firenze

Simona Galli
Univ. Insubria

Scientific Committee

Matteo Alvaro
Univ. Pavia

Giuseppe Falini
Univ. Bologna

Felipe Gándara
CSIC, Madrid

Pilar García Orduña
CSIC, Zaragoza

Andrea Ilari
IBPM-CNR, Roma

Sol López-Andres
Univ. Complutense, Madrid

Lucia Maini
Univ. Bologna

Alfonso Martínez de la Cruz
CICBioGUNE, Bilbao

Paolo Pio Mazzeo
Univ. Parma

Marta E.G. Mosquera
Univ. Alcalá de Henares

MS2 – P2: Compressibility of hibonite (CA6): a single crystal synchrotron radiation high-pressure study.

Fernando Cámara[a], Paolo Lotti[a], Davide Comboni[a], Marco Merlini[a]

[a]*Dipartimento di Scienze della Terra 'A. Desio', Università degli Studi di Milano, Via L. Mangiagalli 34, I-20133 Milano, Italy. fernando.camara@unimi.it*

The elasticity of hibonite (ideally $CaAl_{12}O_{19}$, space group $P6_3/mmc$) has been investigated by synchrotron radiation high-pressure single crystal X-ray diffraction, using a membrane-driven diamond anvil cell mounting Boehler-Almax design diamonds and methanol:ethanol:water (16:3:1) and helium as pressure-transmitting fluids, at the ID15B beamline of ESRF, Grenoble, (λ = 0.4111 Å) up to 19.5 GPa. We collected 26 pressure data points. On compressing, no displacive phase transition has been observed. We have fitted lattice volume data with a *BM*2 EoS, using EosFit7c [1], and obtain zero-pressure isothermal bulk modulus (K_{0T}) of 204(1) GPa and a unit-cell volume of 590.44(14) Å^3. Linearized EoS were fitted using cubed lattice parameters [1] and obtained zero-pressure isothermal bulk modulus (K_{0T}) of 256(3) GPa for *a* lattice parameter and of 141(1) GPa for *c* lattice parameter. Therefore, the structure is significantly stiff, and strain develops predominantly on the *c* direction. Hibonite structure is based on the periodic repetition along [0001] of ten layers of approximately closest-packed oxygen atoms. The sequence can be expressed as (*chhhcchhhc*), where *c* and *h* symbolize cubic and hexagonal closest-packed layers, respectively. The cubic close-packed layers constitute blocks that have the spinel structure ($S = [M_6O_8]^{2+}$) and are interlayered between blocks having the hexagonal close-packed character R (= $[AM_6O_{11}]^{2-}$), resulting in a staking with a $S'RSR'S'$ sequence, where R' and S' are rotated 180° around *c* relative to *R* and *S*. Hibonite has the structural formula $A^{[XII]}M1^{[VI]}M2^{[V]}M3_2^{[IV]}M4_2^{[VI]}M5_6^{[VI]}O_{19}$, where Ca is 12- fold coordinated at site *A* and Al^{3+} ions are distributed over three distinct octahedra [*M*1, *M*4 and *M*5], the *M*3 tetrahedron, and the unusual fivefold coordinated trigonal bipyramid *M*2. The hibonite sample comes from Sierra de Comechingones (Argentina) and has composition $(Ca_{1.01}Na_{0.01})_{1.02}(Al_{11.58}V_{0.33}Ti_{0.02}Mg_{0.06}Si_{0.01})_{1.00}O_{19}$. Structure refinements yields V ordered in $M2^{[V]}$ $M4_2^{[VI]}$ sites with composition $^{M2}(Al_{0.94}V_{0.06})$ and $^{M4}(Al_{1.73}V_{0.27})_2$ whereas Mg orders in $M3_2^{[IV]}$ (with composition $^{M3}(Al_{1.94}Mg_{0.06})_2$). Evolution of polyhedral volumes show that $M2^{[V]}$ $M4_2^{[VI]}$ and A show a decrease of ca. 10% whereas it is lesser for the rest of the sites. The $M2^{[V]}$ $M4_2^{[VI]}$ and A sites belong to the *R*-block, whereas $M1^{[VI]}M3_2^{[IV]}M5_6^{[VI]}$ constitute the *S*-block. Therefore, there is a heterogeneity of the strain along [0001], which alternates between the *S*-blocks and the more compliant *R*-block. Congruently, high-*T* studies [2] have observed that the *R*-block expands more than the *S*-block. It remains uncertain if this heterogeneity is due to compositional stain (V ordered at the *R*-block) or to intrinsic behavior of the hibonite structure.

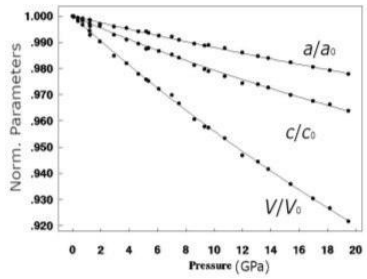

Figure 1. Normalized parameters versus pressure (in GPa).

[1] R.J. Angel, J. Gonzalez.Platas, M. Alvaro *Z. Kristallogr*. **2014**, *229*, 405.
[2] M. Nagashima, T. Armbruster, T. Hainschwang *Min. Mag.* **2010**, *74*, 871