Equation of state of $Ca_3Ga_2Ge_3O_{12}$ garnet: A combined experimental and theoretical study

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Abstract

Synthetic garnets exhibit physical properties leading to opportunities of application for example as components of solid-state lasers [1], as optical high-pressure sensors [2, 3], and as substrates for epitaxial superconducting films [4]. Mechanical and elastic properties of garnets are of interest for Earth science, as minerals of garnet structure are components of the deep interior of the Earth [5]. Multicomponent garnets $X_3Y_2Z_3O_{12}$, with divalent X, trivalent Y, and tetravalent Z cations exhibit properties such as high resistance for plastic flow even at high temperatures, and low thermal conductivity [6], and large Mohs hardness.

Sample preparation and measurements

The single crystal sample of cubic (S.G. *Ia*-3*d*) $Ca_3GaGe_3O_{12}$ was grown using a conventional slow-cooling flux method using PbO-PbF_2-GaO_2 as a solvent. The crystal was powdered in agate mortar up to fine size. The diffraction measurements were carried out at a modern laboratory Bragg-Brentano diffractometer (Philips X´Pert Pro Alpha1 MPD, Panalytical). The in-situ X-ray diffraction experiments were carried out at quasihydrostatic conditions using the energy-dispersive method at a synchrotron beamline equipped with a large-anvil diffraction press.

X-Ray powder diffraction data analysis

Analysis of the data collected for measured garnets, $Ca_3Ga_3Ge_3O_{12}$ shows that the garnet structure is conserved in the studied pressure range. The lattice parameters of garnets were determined using the Le Bail method performed employing the Fullprof2k program. The Rietveld-refinement program, Fullprof.2k (version 2.70), was used for the structural analysis. Pseudo-Voigt profile-shape function was assumed. The following parameters were refined: scale factor, lattice parameters, atomic positions isotropic atomic displacement parameters, peak shape parameters, systematic line-shifts parameters. Background was set manually.

Based on obtained V(p) dependence, experimental Birch-Murnaghan equation of state was determined.

Figure 1. Structure of garnet-type $Ca_3GaGe_3O_{12}$ crystals (space group Ia-3d).

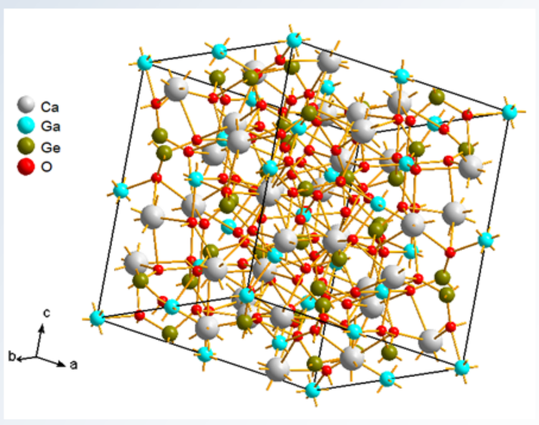
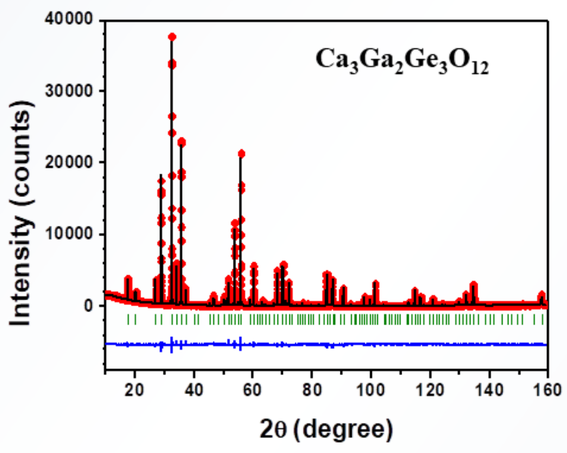


Figure 2. Graphical results of Rietveld refinement for investigated sample.



Atom type	Atomic position			Site
	x	*y*	*z*	
Ca	0.125	0	0.25	24 c
M	0	0	0	16 a
Ge	0.374	0	0.25	24 d
O	~ 0.1	~ 0.2	~ 0.3	96 h

Table 1. Atomic positions of cubic garnet type structure.

Table 2. Refinement and calculation results for $Ca_3Ga_3Ge_3O_{12}$ crustal at ambient conditions. The errors indicated are the standard deviations given in the program output.

Sample name	Lattice parameter, Å	Oxygen atomic position			Method, source
		x	*y*	*z*	
$Ca_3Ga_2Ge_3O_{12}$	12.26079(6)	0.09891(18)	0.19843(17)	0.28408(17)	X-ray, this work
$Ca_3Ga_2Ge_3O_{12}$	12.25385	0.09915	0.19888	0.28274	DFT, this work
$Ca_3Ga_2Ge_3O_{12}$	12.2562(1)	0.09993	0.19966	0.28376	X-ray, [10]

Acknowledgment: We thank mgr. Eva Werner-Malento for assisting in high pressure measurements.

Ab initio total-energy simulations

Ab initio total-energy simulations were carried out within the framework of density functional theory (DFT) and The Vienna Ab-initio Simulation Package (VASP) [8] was used to perform calculations with the pseudopotential method and the projector augmented waves (PAW) scheme The set of plane waves was extended up to a kinetic energy cutoff of 520 eV, providing highly converged results. The exchange-correlation energy was obtained in the generalized gradient approximation (GGA) with the PBEsol prescription [9]. A dense Monkhorst−Pack grid o 4x4x4 of k-special points was used to perform Brillouin zone (BZ) integrations to ensure high convergence of 1-2 meV per atom in the total energy. Through the calculation of the forces on atoms and the stress tensor, the atomic positions and the unit cell parameters were fully optimized to obtain the relaxed structures at selected volumes. In the relaxed optimized configurations, the resulting forces on the atoms are less than 0.006 eV/Å, with deviations of the stress tensor from hydrostatic conditions (diagonal tensor) lower than 0.1 GPa.

High Pressure Results

The study provided the information on structure variation of Ca3GaZGe3O12 under high pressure and on its elastic properties. Experimental and theoretical variation of unit cell volume with pressure is illustrated in Fig. 3 The fitted value of bulk modulus is 159(5) GPa (experimental) and 140.9(7) GPa (theoretical). Its derivative is found to be 4 (experimental) and 4.56(3) (theoretical). The oxygen position, determined theoretically, marginally depends on pressure (see Fig. 4).

Figure 3. Relative unit-cell volume as a function of pressure for $Ca_3M_2Ge_3O_{12}$ crystal . The solid lines correspond to the second order Birch-Murnaghan EOS fit.

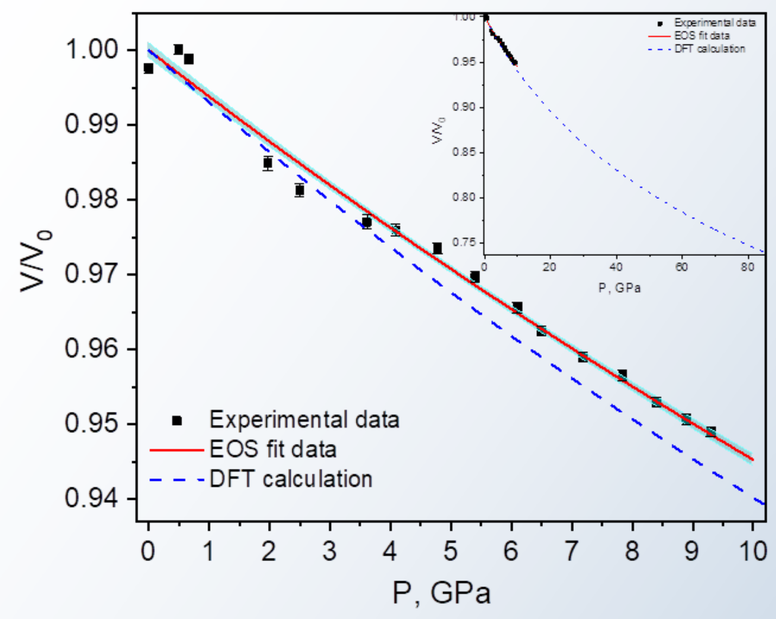


Figure 4. Oxygen atomic positons as a function of pressure for $Ca_3M_2Ge_3O_{12}$ crystal .

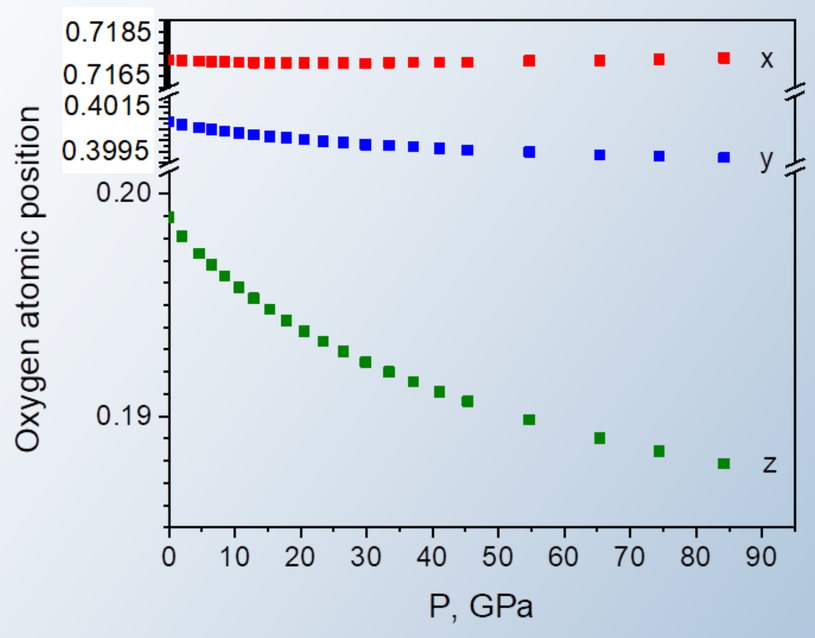


Table 3. Experimental and calculated EOS data

V_0, Å^3	B_0, GPa	B′	Method, source
1818.8(18)	159(5)	4 (fixed)	X-ray, this work
1836.0(6)	140.9(7)	4.56(3)	DFT, this work

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