Equation of state of $Ca_3Fe_2Ge_3O_{12}$ garnet

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HIGHLIGHTS

We study We study powdered single crystals of $Ca_3Fe_2Ge_3O_{12}$ garnet phase. The crystals were grown using the flux method. Powder X-ray diffraction analysis shows the expected cubic structure (*Ia-3d* space group). The equation of state is determined using the synchrotron radiation.

INTRODUCTION

•Crystals of garnet-type structure are of interest in the fields of mineralogy, solid state physics, chemistry and in technology [Baxter]. They exhibit unique magnetic and optical properties; some of them have been shown to exhibit low-thermal conductivity, or high resistance for plastic flow even at high temperatures. Among them fast ion conductors have been identified.

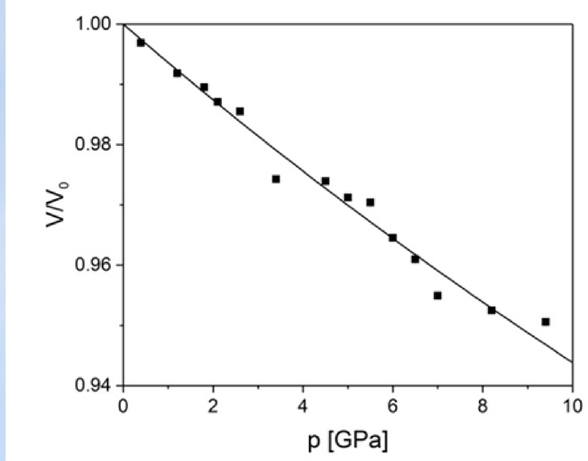
Mechanical properties of garnets are of interest for the field of Earth science, as the minerals of garnet structure are considered as components of the deep interior of the Earth; their EOS' have been reviewed in [Hawthorne1981]. Synthetic garnets can be applied as solid state electrolytes, scintillators, phosphors, as components of solid-state lasers, as optical high-pressure sensors. They can be used as substrates for epitaxy of superconducting films, and for semiconducting films.

•In this work we study the equation of state of powdered synthetic $Ca_3Fe_2Ge_3O_{12}$ garnet single crystal.

The studied $Ca_3Fe_2Ge_3O_{12}$ single crystal usig the flux method. The in-situ X-ray diffraction experiments were carried out using the angle-dispersive mode at ESRF ID15B beamline. The ab-initio total-energy simulations were carried out within the framework of density functional theory (DFT).

GENERAL

$Ca_3Fe_2Ge_3O_{12}$ garnet is a representative of four-component garnets, $X_3Y_2Z_3O_{12}$, where X, Y, Z are di-, tri- and tetravalent cations. The material is known for its oxygen conductivity, antiferromagnetism, and occurrence of spin waves. A preliminary study showed that $Ca_3Fe_2Ge_3O_{12}$ as well as the compositionally related $Ca_3Ga_2Ge_3O_{12}$ retain their garnet-type structure up to at least 8.7 GPa [3]. Presently, we describe a combined *in-situ* high-pressure X-ray diffraction and *ab-initio* study for $Ca_3Fe_2Ge_3O_{12}$.



•Figure 1. Relative unit cell volume as a function of pressure for $Ca_3Fe_2Ge_3O_{12}$. Experimental points are shown together with the result of second-order Birch-Murnaghan equation of state fitting (solid line).

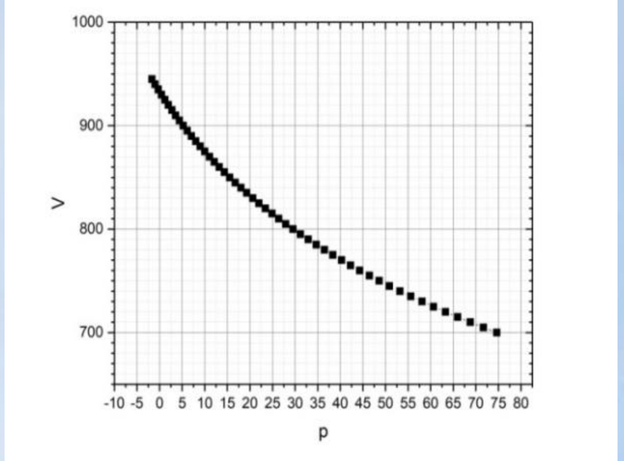


Figure 2. Figure... Theoretical V(p). Variation of unic cell volumes with pressure – DFT results.

Table 1. Experimental lattice parameter $Ca_3Fe_2Ge_3O_{12}$..

Lattice parameter [Å]	Remarks	Ref	Year
12.325(3)		(a) Hawthorne1984	1984
12.32		[iBrueckel1988]	1988
12.262		[iiBruckel1990]	1990
12.321(9)	SCXRD at 300 K	(i) Levy1999	1999
12.3288(2) Å.		(f) Werner2010	2010
12.32823(3)		(h) Tajima2021	2021
12.327(*)		(g) He2023	2023
12.3317	DAC SCXRD	this work	2024
12.31830(10)	DAC SCXRD p=0.39 GPa	this work	2024

(*) exact value depends on sintering conditions.

Table 2. Theoretical lattice parameter $Ca_3Fe_2Ge_3O_{12}$.

Lattice parameter [Å]	Calculation method	Ref.	Year
12.355	DFT	Meyer2010	2010
12.469	DFT	Meyer2010	2010
12.48	GGA+U	Lee2019	2019
12.316671	DFT	this work	2024

Table 3. Birch Murnagan EOS fitting results and DFT calculation for $Ca_3Fe_2Ge_3O_{12}$.

V_0 [Å^3]	K_0 [GPa]	K'	Method
1875.3(3)	153.9(8)	4	experiment, BM2
1868.46	135.52	4.49	theory, BM3

RESULTS AND CONCLUSIONS

The phase analysis shows that the garnet structure is preserved in the studied pressure range, 0 – 9.5 GPa.

The structure was refined using the Rietveld procedure.

The lattice parameter is in line with literature data (see Tables 1 and 2, showing the comparison with experimental and theoretical values reported.

The experimental *V*(*p*) variation was modelled through fitting the Birch-Murnaghan equation. The fitting result is illustrated in Fig. 1. The theoretical *V*(*p*) variation obtained using the density functional theory (Fig. 2) coincides with experimental data. The bulk modulus (Table 3) obtained experimentally, 153,9 GPa agrees well with that derived using the DFT theoretical approach, 135,5 GPa (12% discrepancy).

Our results show the information on elastic properties of calcium iron germanate garnet.

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