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## High pressure single-crystal synthesis, structure and compressibility of the garnet $\text{Mn}^{2+}_3\text{Mn}^{3+}_2[\text{SiO}_4]_3$

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**Abstract** Single crystals of the garnet  $\text{Mn}^{2+}_3\text{Mn}^{3+}_2[\text{SiO}_4]_3$  and coesite were synthesised from  $\text{MnO}_2$ - $\text{SiO}_2$  oxide mixtures at 1000°C and 9 GPa in a multianvil press. The crystal structure of the garnet [space group  $Ia\bar{3}d$ ,  $a=11.801(2)$  Å] was refined at room temperature and 100 K from single-crystal X-ray data to  $R1=2.36\%$  and  $R1=2.71\%$ , respectively. In contrast to tetragonal  $\text{Ca}_3\text{Mn}^{3+}_2[\text{GeO}_4]_3$  (space group  $I4_1/a$ ), the high-pressure garnet is cubic and does not display an ordered Jahn-Teller distortion of octahedral  $\text{Mn}^{3+}$ . A disordered Jahn-Teller distortion either dynamic or static is evidenced by unusual high anisotropic displacement parameters. The room temperature structure is characterised by following bond lengths: Si-O=1.636(4) Å (tetrahedron),  $\text{Mn}^{3+}$ -O=1.995(4) Å (octahedron),  $\text{Mn}^{2+}$ -O=2.280(5) and 2.409(4) Å (dodecahedron). The cubic structure was preserved upon cooling to 100 K [ $a=11.788(2)$  Å] and upon compressing up to 11.8 GPa in a diamond-anvil cell. Pressure variation of the unit cell parameter expressed by a third-order Birch-Murnaghan equation of state led to a bulk modulus  $K_0=151.6(8)$  GPa and its pressure derivatives  $K'=6.38(19)$ . The peak positions of the Raman spectrum recorded for  $\text{Mn}^{2+}_3\text{Mn}^{3+}_2[\text{SiO}_4]_3$  were assigned based on a calderite

$\text{Mn}^{2+}_3\text{Fe}^{3+}_2[\text{SiO}_4]_3$  model extrapolated from andradite and grossular literature data.

### Introduction

The natural occurrence of garnets, spessartine and spessartine-almandine solid solutions with dodecahedral  $\text{Mn}^{2+}$ , are widespread in metamorphic and plutonic rocks. However  $\text{Mn}^{2+}$ -rich garnets with substantial substitution of  $\text{Al}^{3+}$  by  $\text{Fe}^{3+}$  or  $\text{Mn}^{3+}$  on the octahedral site are rare. Only the garnet calderite, ideally  $\text{Mn}^{2+}_3\text{Fe}^{3+}_2[\text{SiO}_4]_3$ , was reported in  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  rich metasediments from several occurrences (Lattard and Schreyer 1983; Reinecke 1987). The mixed-valence garnet  $\text{Mn}^{2+}_3\text{Mn}^{3+}_2[\text{SiO}_4]_3$  was described as “blythite-component” in natural garnets by Fermor (1926), but the name is not accepted by IMA. Recently, the hypothetical garnet mineral “blythite” was analysed as a minor component (8.5 mol%) in a natural calderite-andradite garnet formed at  $T<700^\circ\text{C}$  and  $P<0.5$  GPa (Bühn et al. 1995). The presence of octahedral  $\text{Mn}^{3+}$  in these garnets was confirmed by means of optical absorption spectroscopy (Amthauer et al. 1989).

The  $\text{Mn}^{3+}$ -ion with  $3d^4$  configuration in octahedral oxygen coordination is governed by the Jahn-Teller effect, e.g., by distortion from the ideal  $m\bar{3}m$  octahedral symmetry. The symmetry should be lower than cubic to allow the  ${}^5\text{B}_g$  ground-state to be lifted. Since favoured distortions are tetragonal elongation or compression, the incorporation of  $\text{Mn}^{3+}$  on the six coordinated Y-site of the cubic garnet structure was repeatedly disputed (Strens 1965; Rickwood 1968). Novak and Gibbs (1971) calculated several crystallographic data of garnets based on effective ionic radii. Due to reasonable bond lengths the “stability” of cubic  $\text{Mn}^{3+}$ -bearing garnets was predicted and the cell dimension of  $\text{Mn}^{2+}_3\text{Mn}^{3+}_2[\text{SiO}_4]_3$  was extrapolated to  $a=11.85$  Å.

$\text{Mn}^{3+}$ -bearing cubic garnets were first synthesised by Nishizawa and Koizumi (1975;  $\text{Ca}_3\text{Mn}^{3+}_2[\text{SiO}_4]_3$  with  $a=12.060$  Å and  $\text{Cd}_3\text{Mn}^{3+}_2[\text{SiO}_4]_3$  with  $a=11.987$  Å). Later, Fursenko (1983) synthesised the end-member “blyth-

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ite"  $\text{Mn}^{2+}_3\text{Mn}^{3+}_2[\text{SiO}_4]_3$  at 4–6 GPa and 1000–1100°C from an oxide mixture of  $3\text{MnO}/\text{Mn}_2\text{O}_3/3\text{SiO}_2$  composition. The resulting garnets were always accompanied by tephroite ( $\text{Mn}_2\text{SiO}_4$ ). From the X-ray powder pattern, that exhibited additional tephroite lines, Fursenko (1983) calculated the cubic cell dimension  $a = 11.807(2)$  Å. The crystal structure of a complex synthetic  $\text{Mn}^{3+}$ -bearing garnet with the composition  $(\text{Ca}_{2.43}\text{Mn}_{0.57})(\text{Al}_{1.28}\text{Mn}^{3+}_{0.72})[\text{SiO}_4]_3$  was refined by Arni et al. (1985) in space group  $Ia3d$  ( $a = 11.867$  Å). The cubic symmetry and the geometry of the  $\text{Mn}^{3+}\text{O}_6$  octahedron led the authors to conclude that  $\text{Mn}^{3+}$  does not cause an ordered Jahn-Teller distortion in this garnet structure.

Tetragonal symmetry for garnet structures due to Jahn-Teller distortion were reported for the natural  $\text{Mn}^{3+}$ -bearing hydrogarnet henritermierite  $\text{Ca}_3(\text{Mn}^{3+}_{1.5}\text{Al}_{0.5})(\text{SiO}_4)_2(\text{OH})_4$  (Gaudefroy et al. 1969; Aubry et al. 1969) and for some synthetic germanates. Recently Heinemann (1997) studied a  $\text{Ca}_3\text{Mn}^{3+}_2[\text{GeO}_4]_3$  garnet with octahedral sites fully occupied by  $\text{Mn}^{3+}$ . In contrast to  $\text{Mn}^{3+}$  garnets with Si on the tetrahedral site, this garnet shows tetragonal space-group symmetry ( $I4_1/a$ ) at ambient temperature and as a result of the Jahn-Teller effect, the  $\text{Mn}^{3+}$  octahedra are uniaxially elongated. In a temperature dependent study on  $\text{Ca}_3\text{Mn}^{3+}_2[\text{GeO}_4]_3$  Miletich et al. (1997) demonstrated that dynamic positional disorder of the orientation of the elongated direction of the  $\text{Mn}^{3+}$  octahedra increases above 270 K thus leading to cubic symmetry at about 500 K (personal communication to Armbruster).

It should be noted, that the synthetic high pressure garnet  $\text{Mn}^{2+}_3(\text{Mn}^{2+}\text{Si}^{4+})[\text{SiO}_4]_3$  (Ringwood and Major 1967; Akimoto and Syono 1972), the structure of which has been refined by Fujino et al. (1986), has a different stoichiometry and cation distribution. Si occupies half of the octahedral sites in an ordered fashion, whereas  $\text{Mn}^{2+}$  occupies the remaining sites. As a result of the cation order, the symmetry reduces to tetragonal (space group  $I4_1/a$ ;  $a = 11.774$  and  $c = 11.636$  Å). In the natural  $\text{V}^{3+}$ -garnet palenzonaite  $(\text{Ca}_2\text{Na})\text{Mn}_2[\text{VO}_4]_3$ , the octahedral site is completely occupied by  $\text{Mn}^{2+}$  (Basso 1987).

Almost all natural garnets are solid solutions between several end-members. Numerous garnet systematics stimulate the synthesis and study of end-member garnets in order to understand the physical properties of the solid solutions and their behaviour as a function of pressure and temperature. This is especially important in calderite – andradite or “blythite” – andradite solid solutions, since the stability ranges of the end-members are extremely different (Schreyer and Baller 1980; Lattard and Schreyer 1983). In this study we present the synthesis of the “blythite” end-member  $\text{Mn}^{2+}_3\text{Mn}^{3+}_2[\text{SiO}_4]_3$ , structure refinements from single crystal X-ray data at 100 K and 293 K, characterisation by Raman-spectroscopy, and in-situ compression data up to 11.8 GPa.

## Experimental technique

The starting material for the synthesis of  $\text{Mn}^{2+}_3\text{Mn}^{3+}_2\text{Si}_3\text{O}_{12}$  garnet (“blythite”) consisted of a mixture of  $\text{MnO}_2$  and excess  $\text{SiO}_2$ . Approximately 4 mg of finely ground oxide mix and 0.2 ml of  $\text{H}_2\text{O}$  (added by a micro-syringe) were welded into a Pt capsule with 1.6 mm outer diameter. The synthesis was performed at 9 GPa pressure and 1000°C for 8 h in a Walker-type multianvil apparatus (Walker et al. 1990). Tungsten-carbide cubes with truncated edge lengths of 12 mm were used. The pressure transmitting octahedron and gasket-fins were fabricated from MgO-based castable ceramics (Ceracast 584), and have been fired at 1150°C for at least 10 h. Stepped graphite heaters of 3.5 mm outer diameter were used to minimise thermal gradients. Pressure calibration is based on the following phase transitions:  $\text{CaGeO}_3$ : garnet – perovskite (6.1 GPa at 1000°C, Susaki et al. 1985),  $\text{TiO}_2$ : rutile –  $\alpha$ - $\text{PbO}_2$  structure (7.7 GPa at 1100°C, Akaogi et al. 1992),  $\text{SiO}_2$ : coesite – stishovite (9.1 GPa at 1000°C, Yagi and Akimoto 1976). The successful synthesis of blythite-garnet, containing divalent and trivalent Mn, is the result of an extremely oxidising starting material (all  $\text{Mn}^{4+}$ ) and a time dependent reduction during the high-pressure synthesis in the multianvil apparatus. The quenched sample consisted of orange-red “blythite” and colourless coesite crystals ranging in size up to 0.3 mm (identified by micro-Raman spectroscopy). Raman spectra were excited by the 632.8-nm line of a HeNe-laser. The Raman signal was analysed with a Dilor Labram II detection system. Spectra were collected at 293 K and measured from 100 to 4000  $\text{cm}^{-1}$ .

A “blythite” crystal of approximately  $50 \times 75 \times 100$   $\mu\text{m}$  in size was employed for the structure refinement. Data were collected on an ENRAF NONIUS CAD4 single-crystal X-ray diffractometer using graphite-monochromated  $\text{MoK}\alpha$  X-radiation. During the low-temperature measurement at 100 K the crystal was cooled with a liquid nitrogen cooling device. Diffraction data with an  $\omega$ -scan of

**Table 1** Refined atomic coordinates and displacement parameters for “blythite” garnet  $\text{Mn}^{2+}_3\text{Mn}^{3+}_2(\text{SiO}_4)_3$

	100 K	293 K
Oxygen		
x	0.0363(3)	0.0362(4)
y	0.0526(3)	0.0516(3)
z	0.6570(3)	0.6569(3)
$B_{\text{eq}}$	0.91(6)	1.13(8)
$U_{11}$	0.006(1)	0.010(2)
$U_{22}$	0.010(2)	0.013(2)
$U_{33}$	0.019(2)	0.020(3)
$U_{12}$	−0.001(1)	0.000(2)
$U_{13}$	−0.003(1)	−0.007(2)
$U_{23}$	0.002(2)	0.002(2)
$\text{Mn}^{2+}$ (0, 1/4, 1/8); $U_{11}=U_{22}$ ; $U_{13}=U_{23}=0$		
$B_{\text{eq}}$	0.52(2)	0.89(3)
$U_{11}$	0.0072(5)	0.0133(7)
$U_{33}$	0.0053(7)	0.007(1)
$U_{12}$	0.0015(7)	0.003(1)
$\text{Mn}^{3+}$ (0, 0, 0); $U_{11}=U_{22}=U_{33}$ ; $U_{12}=U_{13}=U_{23}$		
$B_{\text{eq}}$	0.39(1)	0.58(1)
$U_{11}$	0.0049(3)	0.0074(4)
$U_{12}$	−0.0003(4)	−0.0003(6)
Si (3/8, 0, 1/4); $U_{22}=U_{33}$ ; $U_{12}=U_{13}=U_{23}=0$		
$B_{\text{eq}}$	0.64(3)	0.79(4)
$U_{11}$	0.003(1)	0.008(2)
$U_{22}$	0.0105(9)	0.011(1)

Note: displacement parameters are of the form:  
 $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$

$1.5^\circ + 0.35 \tan\theta$  were collected up to  $\theta = 30^\circ$  yielding a total of 1243 reflections at 293 K of which 201 were unique and had  $I > 2\sigma(I)$ . A total of 1369 reflections were collected at 100 K of which 205 were unique and had  $I > 2\sigma(I)$ . Intensity data were empirically corrected for anisotropic absorption effects by using psi-scans. Data reduction, including background and Lorentz-polarisation corrections, was carried out with the SDP program system (Enraf-Nonius 1983). The structure was refined with the program SHELX-97 (Sheldrick 1997) using neutral atom scattering factors (International Tables for Crystallography 1992), and a weighting scheme of  $1/[\sigma^2(\text{Fo}^2) + (0.0233 \text{ P})^2 + 4.07 \text{ P}]$  at 293 K and  $1/[\sigma^2(\text{Fo}^2) + (0.0171 \text{ P})^2]$  at 100 K (with  $\text{P} = (\text{Max}(\text{Fo}^2, 0) + 2\text{Fc}^2)/3$ ). Test refinement indicated that both positions X (dodecahedral) and Y (octahedral) were fully occupied by  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$ , respectively. All atoms were refined with anisotropic displacement parameters, converging at  $\text{R1} = 2.36\%$  at 293 K and  $\text{R1} = 2.71\%$  at 100 K [ $\text{R1} = (\sum ||F_o| - |F_c||) / (\sum |F_o|)$ ;  $\text{Fo} > 4\sigma(\text{Fo})$ ].

For the high-pressure study a  $130 \times 70 \times 35 \mu\text{m}$  crystal fragment was loaded in a BGI-type diamond-anvil cell (Allan et al. 1996) together with a ruby chip for approximate pressure determination by the ruby-fluorescence technique (Mao et al. 1986) and a quartz crystal to act as internal diffraction standard (Angel et al. 1997). For the high-pressure experiment a T301 stainless steel gasket with a  $195 \pm 5 \mu\text{m}$  hole and a 4:1 methanol-ethanol mixture as pressure transmitting medium were used. Up to 9.4 GPa the peak profiles of both the sample and the quartz crystals showed no broadening, which would be indicative of non-hydrostatic stresses. In contrast, peak broadening was found at all pressures higher than 9.5 GPa. In these cases the whole diamond-anvil cell was externally heated to  $60 \pm 5^\circ\text{C}$  for 8 to 12 h to relax the deviatoric stresses within the pressure medium which causes peak broadening.

Unit-cell parameters of both the garnet and the pressure calibrant crystals were measured using a customised HUBER four-circle diffractometer operated with unmonochromatised Mo X-ray radiation. Details of the diffractometer and the centring procedure are given by Angel et al. (1997). In addition to the unit-cell parameters the profile parameters of the reflections 040, 004, 444, 080 and 008 were determined at each pressure. All reflections were measured using the technique of least attenuation (Finger and King 1978) in order to achieve maximum accessibility and minimum absorption effects. To prevent crystal-offset errors and diffractometer aberrations affecting the results, the technique of diffracted-beam centring (King and Finger 1979) was employed to obtain correct setting angles. The lattice parameters constrained to cubic symmetry were obtained by a vector-least-squares fit (Ralph and Finger 1982) to the corrected reflection positions. The unit-cell parameters were determined from the corrected positions of 21 to 27 accessible reflections within the  $14.0\text{--}26.6^\circ$  range in  $2\theta$ .

Equation-of-state parameters were determined by a fully weighted least-squares fit of a third-order Birch-Murnaghan equation of state (Birch 1947) to the  $P$ - $V$  data set (Table 3) with pressures determined from the quartz unit-cell volumes using the equation-of-state parameters of Angel et al. (1997) and  $V_0 = 112.990(10) \text{ \AA}^3$ .

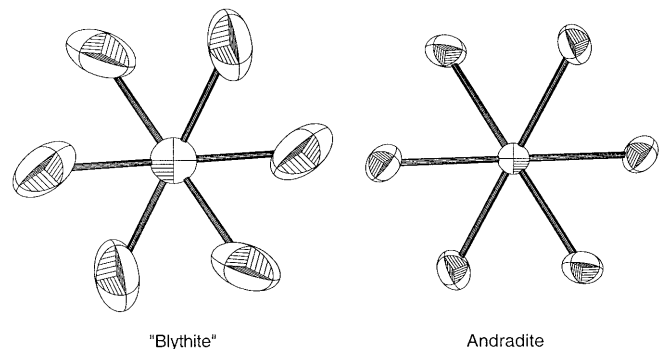
## Results

The results of our single-crystal refinements at 100 K and 293 K are given in Tables 1 and 2. In Table 1 the refined atom coordinates and the anisotropic displacement parameters are listed, whereas Table 2 shows selected interatomic distances and angles. Systematic extinctions are in agreement with the cubic space group  $Ia\bar{3}d$ . At ambient temperature the cell dimension refined to  $a = 11.801(2) \text{ \AA}$  and at 100 K to  $a = 11.788(2) \text{ \AA}$ . Although the Jahn-Teller ion  $\text{Mn}^{3+}$  prefers a distorted octahedral environment, neither peak splitting nor broadening of the reflections showed deviations from cubic symmetry. However, the anisotropic displacement parameters given in Table 1

**Table 2** Selected interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) of “blythite” garnet

Atoms	100 K	295 K
Si-O (4x)	1.636(3)	1.636(4)
O-Si-O (2x)	100.6(3)	100.4(3)
O-Si-O (4x)	114.1(1)	114.2(2)
$\text{Mn}^{3+}$ -O (6x)	1.998(3)	1.995(4)
O- $\text{Mn}^{3+}$ -O (6x)	88.7(1)	88.9(2)
O- $\text{Mn}^{3+}$ -O (6x)	91.3(1)	91.1(2)
$\text{Mn}^{2+}$ -O (4x)	2.280(4)	2.280(5)
$\text{Mn}^{2+}$ -O (4x)	2.396(3)	2.409(4)
O- $\text{Mn}^{2+}$ -O (2x)	67.0(1)	66.9(2)
O- $\text{Mn}^{2+}$ -O (2x)	71.2(2)	71.3(2)
O- $\text{Mn}^{2+}$ -O (4x)	72.0(1)	72.3(2)
O- $\text{Mn}^{2+}$ -O (4x)	73.3(1)	73.1(2)
$\rho_x$	4.468	4.454
$\phi$	50.27	50.19
$\alpha$	29.48	29.01

$\tan \alpha = y/z$ ;  $\cos \phi = (a \cdot x) / 1.636$  (Born and Zemmann 1964);  $\rho_x = 8 \text{ M} \cdot 1.66 / \text{\AA}^3$



**Fig. 1** The  $\text{Mn}^{3+}\text{O}_6$  octahedron (room temperature) of “blythite” projected parallel to the three-fold axis is compared with the corresponding  $\text{Fe}^{3+}\text{O}_6$  octahedron in andradite (Armbruster and Geiger 1993). Probability displacement ellipsoids are drawn in common but arbitrary scale. Notice that the disordered Jahn-Teller distortion in “blythite” leads to displacement ellipsoids which are increased by a factor of approximately three compared to andradite

show large amplitudes for all atoms compared to other end-member garnets (e.g., Armbruster and Geiger 1993; Geiger and Armbruster 1997). In Fig. 1, the  $\text{Mn}^{3+}\text{O}_6$  octahedron (room temperature) of “blythite” is projected parallel to the three-fold axis and compared with the corresponding  $\text{Fe}^{3+}\text{O}_6$  octahedron in andradite (Armbruster and Geiger 1993). The displacement ellipsoids of “blythite”, which are increased by a factor of approximately three compared to andradite, indicate a dynamic, fluctuating or statistically disordered Jahn-Teller distortion of octahedral  $\text{Mn}^{3+}$ .

In our high-pressure study, the  $\text{Mn}^{2+}_3\text{Mn}^{3+}_2[\text{SiO}_4]_3$  garnet did not undergo the expected pressure-induced cubic-to-tetragonal phase transition within the investigated pressure range of 0.0001 to 11.8 GPa. Neither the widths of the five reflections increased significantly which would indicate peak splitting according to non-merohedral twinning known for tetragonal garnets (Heinemann 1997), nor the unconstrained refinement of the lattice parameters in-

**Table 3** Variation of the unit-cell parameters of “blythite” garnet  $Mn^{2+}_3Mn^{3+}_2(SiO_4)_3$  with pressure

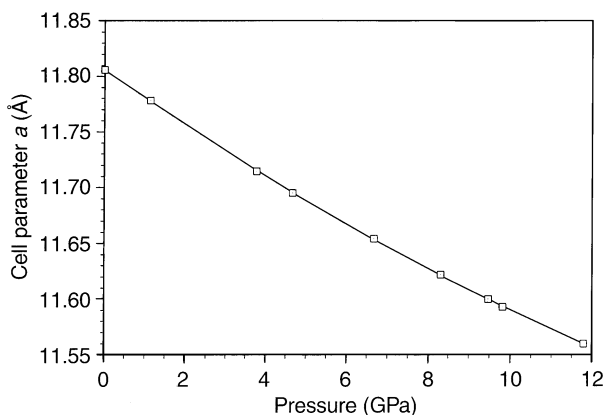
p (GPa)	Quartz		“Blythite”		
	V ( $\text{\AA}^3$ )	N <sub>refl</sub>	a ( $\text{\AA}$ )	V ( $\text{\AA}^3$ )	N <sub>refl</sub>
0.0001 <sup>a</sup>	n.d.	—	11.8057(4)	1645.43(17)	49
0.0001 <sup>b</sup>	112.990(10)	12	11.8060(3)	1645.54(10)	27
1.136(7)	109.855(12)	7	11.7781(4)	1633.64(15)	22
3.778(7)	104.289(12)	7	11.7148(4)	1607.71(15)	21
4.673(6)	102.763(10)	11	11.6953(4)	1599.68(13)	23
6.659(7)	99.813(14)	6	11.6545(3)	1582.99(11)	25
8.314(7)	97.705(13)	12	11.6218(4)	1569.73(13)	23
9.473(6)	96.377(8)	7	11.6000(3)	1560.90(10)	25
9.819(8)	96.000(18)	6	11.5929(4)	1558.03(15)	25
11.79(1)	94.007(23)	12	11.5596(5)	1544.66(20)	21

Note: pressures determined from unit-cell volumes of quartz internal diffraction standard by applying the EOS of Angel et al. (1997).

N<sub>refl</sub>=number of reflection used for the vector least-squares refinement of the unit-cell parameters

<sup>a</sup> Crystal in air

<sup>b</sup> Crystal in DAC; without pressure transmitting medium

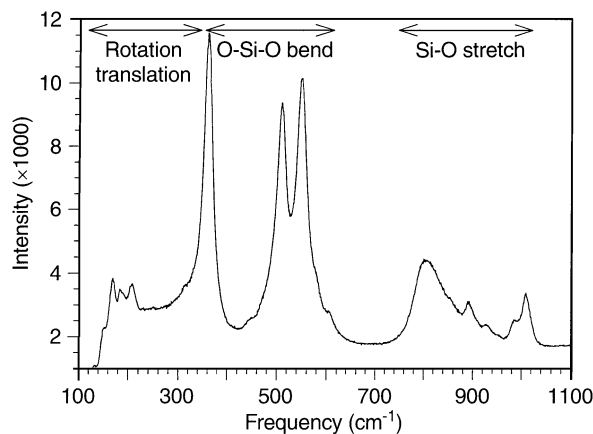
**Fig. 2** Variation of cell parameter *a* of “blythite” with pressure. The data are best fitted by a second-order polynomial equation

indicated significant deviations from the cubic symmetry within  $2\sigma$  esds. The variation of the unit-cell dimension *a* (Table 3) was found to be best described by a second-order polynomial equation (Fig. 2):

$$a = 11.8059(4) \text{ \AA} - 2.535(15) \times 10^{-2} \text{ \AA GPa}^{-1} \times P + 3.79(14) \times 10^{-4} \text{ \AA GPa}^{-2} \times P^2 \quad (r^2 = 0.999978)$$

The pressure dependency of *a* is significantly nonlinear. The pressure variation of the unit-cell parameters expressed by a formulation equivalent to the Murnaghan equation-of-state leads to linear modulus  $K_0 = 454.8$  (2.4) GPa and its pressure derivative  $K' = 19.1$  (6). For a third-order Birch-Murnaghan equation of state we obtain from the *P*-*V* data (Table 3) at  $T = 298(1)$  K,  $V_0 = 1645.52$  (8)  $\text{\AA}^3$ ,  $K_0 = 151.6(8)$  GPa, and  $K' = 6.38(19)$ .

Figure 3 and Table 4 show the results of the Raman spectroscopic study. The overall appearance of the spectrum is similar to that of andradite (Hofmeister and Chopelas 1991), with wavenumbers of the “blythite” bands shifted towards higher frequency due to the smaller

**Fig. 3** Raman spectrum of synthetic blythite end-member. For detailed band assignments see Table 4. The broad band at 780–850  $\text{cm}^{-1}$  is believed to reflect a dynamic distortion of the  $[\text{SiO}_4]$ -tetrahedra**Table 4** Calculated Raman-spectra of calderite and observed spectra of “blythite” garnet  $Mn^{2+}_3Mn^{3+}_2(SiO_4)_3$ 

Mode <sup>a</sup>	Calderite calculated [ $\text{cm}^{-1}$ ]	“Blythite” observed [ $\text{cm}^{-1}$ ]	Intensity observed
Si-O stretch, asym	1017	1009 985	Strong
Si-O stretch, sym	897	890	Broad
Si-O stretch, asym	887		
Si-O stretch, sym	884	780–850	Very broad
Si-O stretch, asym	871		
Si-O stretch, asym	840	605	Very strong
O-Si-O bend, asym	597		
O-Si-O bend, asym	580	570	Very strong
O-Si-O bend, sym	552		
O-Si-O bend, sym	522	509	Shoulder
O-Si-O bend, asym	486	ca. 480	
O-Si-O bend, sym	450	ca. 450	Shoulder
$[\text{SiO}_4]$ rotation	373	360	Very strong
O-Si-O bend, sym	355		
$[\text{SiO}_4]$ rotation	349	315	Shoulder
$[\text{SiO}_4]$ rotation	344		
$[\text{SiO}_4]$ translation	300	250	
$[\text{SiO}_4]$ rotation	293		
$[\text{SiO}_4]$ translation	284	208	
$[\text{SiO}_4]$ translation	217		
X-O translation	211	185	Sharp
$[\text{SiO}_4]$ translation	186		
X-O translation	169	150	Sharp
X-O translation	158		

<sup>a</sup> Assignments according to Hofmeister and Chopelas (1991)

cation  $Mn^{2+}$  on the dodecahedral site. Test measurements up to 4000  $\text{cm}^{-1}$  did not show further bands which confirms the absence of OH-groups in the structure.

## Discussion

Novak and Gibbs (1971) calculated the cell dimensions  $a = 11.85$   $\text{\AA}$  for “blythite”  $Mn^{2+}_3Mn^{3+}_2[\text{SiO}_4]_3$ ,  $a = 11.84$   $\text{\AA}$

for calderite  $\text{Mn}^{2+}_3\text{Fe}^{3+}_2[\text{SiO}_4]_3$  and  $a=12.07 \text{ \AA}$  for synthetic  $\text{Ca}_3\text{Mn}^{3+}_2[\text{SiO}_4]_3$ , based on the effective radii given in Shannon and Prewitt (1969). The revised data of Shannon (1976) do not show differences concerning the size of  $\text{Ca}^{2+}$ (VIII),  $\text{Mg}^{2+}$ (VIII) or  $\text{Al}^{3+}$ (VI), but the value of  $r(\text{Mn}^{2+},\text{VIII})$  was decreased from  $0.98 \text{ \AA}$  to  $0.96 \text{ \AA}$  and  $r(\text{Mn}^{3+},\text{VI})$  was given as  $0.645 \text{ \AA}$  identical to  $r(\text{Fe}^{3+},\text{VI})$ . Recalculation with the empirical equations by Novak and Gibbs (1971) based on the revised radii of Shannon (1976) yielded  $a=11.80 \text{ \AA}$  both for “blythite” and calderite and  $a=12.06 \text{ \AA}$  for the  $\text{CaMn}$ -silicate garnet in excellent agreement with the observed data:  $a=11.801(2) \text{ \AA}$  for “blythite” (this study),  $11.82$  for calderite (Lattard and Schreyer 1983) and  $12.060 \text{ \AA}$  for  $\text{Ca}_3\text{Mn}^{3+}_2[\text{SiO}_4]_3$  (Nishizawa and Koizumi 1975). The recalculated oxygen coordinates according to Novak and Gibbs (1971) for “blythite” are  $x=0.0362$ ,  $y=0.0528$  and  $z=0.6563$  in agreement with the observed values (Table 1).

Unfortunately no data are available concerning the structure of calderite  $\text{Mn}^{2+}_3\text{Fe}^{3+}_2[\text{SiO}_4]_3$ , but due to the similar size of  $\text{Mn}^{3+}$  and  $\text{Fe}^{3+}$  we do not expect large differences compared to “blythite”. As expected, the Y-O distance in “blythite” of  $1.995 \text{ \AA}$  at  $293 \text{ K}$  is close to the andradite value ( $2.020 \text{ \AA}$ , Armbruster and Geiger 1993) while the X-O distances ( $2.280 \text{ \AA}$  and  $2.409 \text{ \AA}$ ) and Si-O distances ( $1.636 \text{ \AA}$ ) are closer to those in spessartine ( $2.246 \text{ \AA}$ ,  $2.404 \text{ \AA}$  and  $1.639 \text{ \AA}$ ; Geiger and Armbruster 1997). The same correlations are valid for the  $100 \text{ K}$  data. Beside the chemical differences, the main difference between “blythite” and spessartine are the displacement parameters which are two to four times higher in the  $\text{Mn}^{3+}$ -garnet. In addition, the anisotropic displacement parameters found in “blythite” end-member are between  $50$  and  $120\%$  higher compared to the data of Arni et al. (1985) in which  $\text{Mn}^{3+}$  occupies only  $36\%$  of the Y-site. When compared with andradite at  $295 \text{ K}$  (Armbruster and Geiger 1993), the isotropic displacement parameters  $B_{\text{eq}}$  in “blythite” are approx. three times those in andradite (Fig. 1). The unusually large displacement parameters in “blythite” indicate an averaged structure of either static or dynamic Jahn-Teller disorder on the octahedral site. At the temperatures of our single-crystal data collections ( $100 \text{ K}$  and  $293 \text{ K}$ ) the tetragonal distortion is statistical, yielding cubic symmetry.

In garnet structures the rotation of a rigid  $\text{SiO}_4$  unit may be described with the rotation angle  $\alpha$  (Born and Zemmann 1964) that reflects the dodecahedral distortion. In “blythite” the angle  $\alpha$  is  $29.01^\circ$  at  $293 \text{ K}$  which is  $1.8^\circ$  higher compared to that in andradite at ambient temperature ( $27.18^\circ$ , Armbruster and Geiger 1993). The rotation angle increases at  $100 \text{ K}$  to  $\alpha=29.48^\circ$ . Comparable differences are observed in the Al-garnets spessartine and grossular (Geiger and Armbruster 1997). The tetrahedral distortion in “blythite” is characterised by the angle  $\varphi$  which is  $50.19^\circ$  at  $293 \text{ K}$  and  $50.27^\circ$  at  $100 \text{ K}$  ( $\varphi$  is the angle between an Si-O vector and the 4-fold axis). In an ideal tetrahedron  $\varphi$  is  $54.75^\circ$  and therefore the  $[\text{SiO}_4]$  unit in “blythite” forms a slightly stretched tetragonal “disphenoid” (Born and Zemmann 1964).

In contrast to the cubic  $\text{Mn}^{3+}$ -orthosilicate garnets  $\text{X}_3(\text{Mn}^{3+})_2[\text{SiO}_4]_3$  with ( $\text{X}=\text{Ca},\text{Cd},\text{Mn}$ ), two tetragonal  $\text{Mn}^{3+}$ -garnets are described: henritermiérite  $\text{Ca}_3(\text{Mn}^{3+}_{1.5}\text{Al}_{0.5})(\text{SiO}_4)_2(\text{OH})_4$  and synthetic  $\text{Ca}_3\text{Mn}^{3+}_2[\text{GeO}_4]_3$ . Henritermiérite belongs to the hydrogarnet-group, generally  $\text{X}_3\text{Y}_2[(\text{Si},\text{H}_4)\text{O}_4]_3$ . Four of the six oxygen atoms of  $[\text{MnO}_6]$  groups are common with the  $[\text{SiO}_4]$  tetrahedron ( $\text{Mn-O}=1.97$  and  $2.13 \text{ \AA}$ ), and the remaining two oxygen atoms are common with  $(\text{O}_4\text{H}_4)$  tetrahedra ( $\text{Mn-O}=1.90 \text{ \AA}$ ). Therefore, the coordination with four short bonds and two long ones may be approximated as uniaxially elongated. The  $(\text{O}_4\text{H}_4)$  tetrahedra are larger and more flexible than the rigid  $\text{SiO}_4$  tetrahedra and allow the  $\text{Mn}^{3+}$  cation to stabilise its electronic structure by polyhedral distortion.

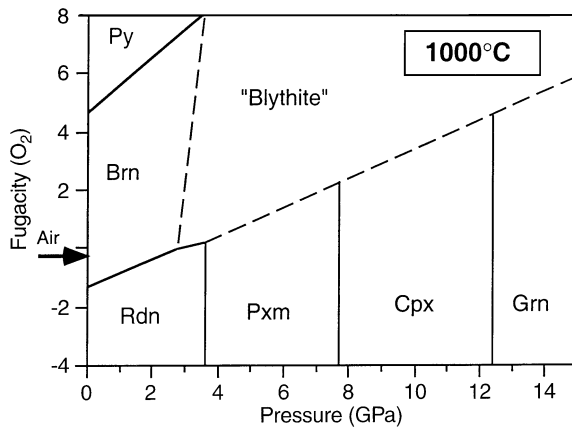
In the tetragonal garnet  $\text{Ca}_3\text{Mn}^{3+}_2[\text{GeO}_4]_3$ , the effect of pressure was found to increase the uniaxial distortion of  $\text{Mn}^{3+}$  octahedra (Miletich et al. 1997). Therefore a pressure induced cubic-to-tetragonal phase transition could be expected also in  $\text{Mn}^{2+}_3\text{Mn}^{3+}_2[\text{SiO}_4]_3$ . However, “blythite” remained cubic to the maximum pressure achieved ( $11.8 \text{ GPa}$ , Fig. 2). It is remarkable that the pressure derivative ( $K'=6.38$ ) of “blythite” is significantly larger relative to the values determined for other silicate garnets (Zhang et al. 1993). Together with the comparatively lower bulk modulus ( $K_0=151.6$ ) this garnet appears to be somewhat softer giving rise to a higher compressibility and a larger pressure dependence of  $(dK/dP)_T$ . A very similar compressional behaviour has recently been determined for “skiagite” garnet,  $\text{Fe}^{2+}_3\text{Fe}^{3+}_2[\text{SiO}_4]_3$ , for which the equation-of-state parameters were determined to be  $K_0=157.4\pm 3.0 \text{ GPa}$  and  $K'=6.7(8)$  (Koch et al. 1997).

The “blythite” Raman spectrum at ambient conditions is given in Fig. 3. Since Hofmeister and Chopelas (1991) showed that the wavenumbers of the bands largely depend on the lattice parameter  $a$ , a hypothetical calderite spectrum was calculated from the shift of the wave numbers ( $1/\lambda$ ) between grossular and andradite:

$$1/\lambda_{\text{cald}}=[(a_{\text{cald}}-a_{\text{spes}})\cdot(1/\lambda_{\text{andr}}-1/\lambda_{\text{gros}})]/(a_{\text{andr}}-a_{\text{gros}})$$

Due to similar lattice parameters of calderite and “blythite”, the calculated bands of calderite correlate well with the observed ones in “blythite” and were used for the band assignment (Table 4). According to Hofmeister and Chopelas (1991) 25 first order Raman bands are mandated by symmetry for the  $Ia3d$  garnet structure. For aluminous garnets, the  $A_{1g}$  modes are the three most intense features in the spectra. However, “blythite” shows similarities with andradite since the strongest peak at about  $890 \text{ cm}^{-1}$  is dramatically decreased. A very broad band is monitored between  $780$  and  $850 \text{ cm}^{-1}$  which is assumed to represent asymmetric Si-O stretching modes. Similar to andradite, the frequency of O-Si-O bending is lower in “blythite” compared to the Al garnets, because the heavier mass of the  $\text{Mn}^{3+}$  ion damps the bending.

The similarity of Raman spectra and IR-spectra in the high frequency range (Hofmeister and Chopelas 1991) allow us to compare our results with the IR-data of  $\text{Ca}_3\text{Mn}^{3+}_2[\text{SiO}_4]_3$  and  $\text{Cd}_3\text{Mn}^{3+}_2[\text{SiO}_4]_3$  given by Ni-



**Fig. 4** The system Mn-Si-O with excess SiO<sub>2</sub> phases. *Py*, pyrolusite; *Brn*, braunite; *Rdn*, rhodonite; *Pxm*, pyroxmangite; *Cpx*, clinopyroxene (*C2/c*); *Grn*, garnet Mn<sup>2+</sup><sub>3</sub>(Mn<sup>2+</sup>Si)[SiO<sub>4</sub>]<sub>3</sub>, “Blythite”=garnet Mn<sup>2+</sup><sub>3</sub>Mn<sup>3+</sup><sub>2</sub>[SiO<sub>4</sub>]<sub>3</sub>

shizawa and Koizumi (1975). In a series of Cd<sub>3</sub>Y<sub>2</sub>-garnets (Y: Al, Ga, Cr, Mn, Fe, V) these authors observed the bands between 810 and 840 cm<sup>-1</sup> shifted to abnormally low frequencies in the Mn<sup>3+</sup>-garnets, indicating highly distorted SiO<sub>4</sub> tetrahedra. They suggested that the tetrahedra are strongly affected by the Jahn-Teller distortion of the Mn<sup>3+</sup>O<sub>6</sub> octahedra. In “blythite” we also observed a broad band at 780–850 cm<sup>-1</sup> assigned to asymmetric Si-O stretch (Fig. 3, Table 4). Compared to other garnets and the calculated calderite-spectra, this band appears to be shifted also to lower frequencies. The broadening of the band is in agreement with the strong displacements of Si and O outlined and further supports a disordered dynamic or static Jahn Teller distortion of the Mn<sup>3+</sup>O<sub>6</sub> octahedra.

In contrast to calderite which may form during the amphibolite facies metamorphism, “blythite” is only described as a component in natural garnets (e.g., Amthauer et al. 1989). In Fig. 4 we estimated the position of “blythite” in a pressure versus  $f(\text{O}_2)$  plot at 1000°C. Although Fig. 4 is highly approximate, it is consistent with the MnSiO<sub>3</sub>-polymorphism (Akimoto et al. 1972; Arlt et al. 1998), the reactions between rhodonite, braunite and pyrolusite under metamorphic conditions (Abs-Wurmbach et al. 1983) and the synthesis runs performed at 4, 5, 6 and 9 GPa (Fursenko 1983 and this study). The phase boundary between braunite and “blythite” is assumed to have a positive slope because the reaction: 5 Brn+16 Qtz→7 Bly+4 O<sub>2</sub> produces oxygen. Since the stability of garnets are largely dependent on the cation radii (Schreyer and Baller 1980), we expect a similar stability field as for calderite, but shifted to higher  $f(\text{O}_2)$ . Lattard and Schreyer (1983) showed that the end-member composition of calderite is not stable below 2.2 GPa, although the slight substitution of other ions (Ca, Al, Mg) decreases this pressure limit. We expect the same behaviour for “blythite” although the crystal field stabilisation energy CFSE in calderite might shift the stability field towards lower pressures. However, extrapolation of the re-

action: 2 Brn+ 12 Qtz→14 Rdn+3 O<sub>2</sub> (Abs-Wurmbach et al. 1983) to higher pressures suggest that the oxygen fugacity, necessary for the formation of “blythite”, is above atmospheric conditions. These unusual conditions, high oxygen fugacity together with high pressure and the absence of Fe<sup>3+</sup> seem to be the reason for the lack of “blythite” as a mineral on earth.

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