

1 Raman spectra and phase composition of MnGeO₃ crystals

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9 Abstract

10 MnGeO₃ single crystal samples have been synthesized by optical zonal melting and spon-
11 taneous crystallization. X-ray crystal analysis showed the first sample to be a two-phase one with
12 phase ratio: 17% - monoclinic *C2/c* and 83% - orthorhombic *Pbca*; the phase ratio of the second
13 sample was unknown. Raman spectra have been produced for these samples. Lattice dynamics
14 has been simulated and polarization dependencies of lines' intensities have been analyzed to in-
15 terpret experimental Raman spectra and to attribute lines to the spectra of monoclinic and ortho-
16 rhombic phases.

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18 Author keywords

19 Raman spectroscopy, lattice dynamics, Raman tensor analysis

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21 1. INTRODUCTION

22 To predict crystal structures and physical properties of minerals under high pressure and
23 temperature is among the most exciting problems of modern structural mineralogy; to solve this
24 problem would be a gain in the knowledge of composition, structure and evolution of the earth
25 shells. Pyroxenes are widely occurring components of the Earth crust; they comprise about 4%
26 of its continental mass. The main motif of the pyroxene structure are chains of SiO₄ tetrahedra
27 extending along *c* axis. Pyroxenes can be divided into orthorhombic (orthopyroxenes) and mon-
28 oclinic (clinopyroxenes). Intimate relationship between monoclinic and orthorhombic pyroxenes
29 is crystallographically due to simple polysynthetic twinings and polysymmetry of the parts of
30 elementary structural units. The knowledge about regularities of the structure of silicates can be
31 substantially expanded by investigation of germanium-containing analogs. Proceeding from sim-
32 ple crystallochemical principles many germinates can be considered structural models of corre-
33 sponding silicates of abyssal origin. Under high pressure the radii of anions composing the struc-
34 ture reduce differently. In oxygen compounds large O²⁻ anions are more compressible than
35 smaller cations, therefore, the ratio of ion radii (r_{cat}/r_o) increases with pressure. Under normal

36 pressure the radius of Ge^{4+} is more than the radius of Si^{4+} by about 20%. So, because of initial
37 ratio of Ge^{4+} and O^{2-} , bigger compared to the silicates, the germinates need smaller pressure for
38 analogous phase transitions; many of them crystallize even under normal pressure in structural
39 forms which occur in the silicates under high pressures only [1]. MnGeO_3 is the closest germani-
40 um-containing substitute of widely occurring pyroxene MgSiO_3 . Recently silicates and oxide
41 compounds have been taking up new areas of applications, driving in some cases metals out. For
42 a long time the silicate structures have been studied mostly by X-ray analysis, however, in recent
43 20 years the interest has been rising to their vibrational spectra. This is due to development of
44 more efficient spectrometers and methods of interpreting vibrational spectra of crystals with
45 complex ions. This paper discusses Raman scattering applied to investigate the structure of
46 MnGeO_3 germinate. Particular emphasis is given to methods of interpreting the spectra with ac-
47 count of crystal symmetry and polarization of Raman lines.

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49 **2. EXPERIMENTAL**

50 **2.1. Preparation of samples**

51 MnGeO_3 crystal samples under study were synthesized by two methods at the Kirensky In-
52 stitute of Physics (Russian Academy of Sciences, Siberian Branch).

53 The first single crystal MnGeO_3 sample was synthesized by optical zonal melting on FZ-
54 4000 unit (Crystal System Co, Japan). Polycrystalline MnGeO_3 powder was hydrostatically
55 pressed into a rod 5 mm in diameter and 10 cm long and annealed at 1200 °C for 8 hours. Then,
56 the produced rod was placed into optical zonal melting furnace to recrystallize. The crystal
57 grown in the air under normal pressure at growth rate 1 mm/hour and rotation rate of rods – 30
58 rpm turned into MnGeO_3 single crystal rod. However, after 2 days the surface of the single crys-
59 tal developed cracks, and in one day more the entire single crystal rod disintegrated into small
60 needle-shaped fragments 1-2 mm long. This behavior was also noted by the authors of [2], in
61 which single crystal of the same composition synthesized by optical zonal melting disintegrated
62 immediately after crystallization.

63 The second single crystal MnGeO_3 sample was synthesized by spontaneous crystallization
64 from flux-melt. For solvent we used MnCl_2 with melting temperature 615°C [4]. Crystals were
65 grown from flux-melt under normal pressure. Initial components of MnO , GeO_2 in stoichio-
66 metric ratio were thoroughly mixed with solvent MnCl_2 and placed in a specially designed alun-
67 dum crucibles [4]. This device was placed into an automatically controlled furnace with silit
68 heaters. To crystallize the charge was heated to maximum temperature (1050°C) to completely
69 dissolve followed by holding for 2 hours to homogenize the flux and cool it gradually at the rate

70 of 20°/h. This resulted in production of transparent brown needle-shaped single crystals extend-
71 ing along *c* axis. The produced crystals are shown in Figure 1.

72 **2.2. Powder X-ray diffraction and crystal structures**

73 The powder X-ray diffractogram of samples synthesized by optical zonal melting (sample
74 1), was obtained at room temperature with D8 ADVANCE diffractometer (Bruker), VANTEC
75 beam detector and Cu-K α radiation. The X-ray diffractogram was made in angular range 2θ : 5–
76 140° with 0.016° step and point exposure time 7.5 s. Structures and mass fraction of phases in
77 the sample were refined by Rietveld method with TOPAS 4.2 software [4]. Refining of structure
78 parameters was stable and yielded low *R*-factor; basic parameters obtained are presented in Ta-
79 ble 1. The compound crystallizes mostly in orthorhombic modification with *Pbca* space group,
80 present is also the monoclinic *C2/c* modification analogous to [2]. Structures of orthorhombic
81 and monoclinic phases of MnGeO₃ described in detail in [2] are shown in Figure 2.

82 X-ray diffraction analysis of samples synthesized by spontaneous crystallization (hereinaf-
83 ter 2) showed them to feature pyroxene structure of orthorhombic modification with *Pbca* space
84 group, its parameters were shown earlier in [4].

85 **2.3. Raman measurements**

86 Raman measurements have been performed with triple monochromator T64000 Raman
87 spectrometer (Horiba Jobin Yvon) operating in a double subtractive mode then detected by a
88 charge-coupled device cooled at 140 K. The spectral resolution for the recorded Stokes side Ra-
89 man spectra was set to ~ 2 cm⁻¹ (this resolution was achieved by using gratings with 1800 mm⁻¹
90 grooves and 100 mm slits). The microRaman system based on Olympus BX41 microscope with
91 a 50x objective lens $f = 1.2$ mm with 0.75 numerical aperture provides a focal spot diameter of
92 about 2 μ m on the sample. Single-mode argon 514.5 nm from a Stabilite 2017 (Spectra-Physics)
93 Ar+ laser of 1 mW on the sample was used as excitation light source.

94 To study angular dependence of intensities of Raman spectra lines on polarization direction
95 of incident and scattered radiation two experiment series were conducted with parallel and cross-
96 polar polarizations of incident and scattered beams. Back scattering geometry was used. The
97 shift of the incidence point of exciting radiation was not more than 2 μ m in complete revolution
98 by 2π .

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100 **3. RESULTS AND DISCUSSION**

101 **3.1. Lattice dynamics simulation**

102 The Raman spectra produced from different points of sample 1 are shown in Figure 3. It is
103 apparent that spectra 2 and 3 notably differ, especially in the low-frequency (below 400 cm⁻¹)
104 range, while spectrum 1 is their superposition. The full Raman spectrum of both phases can be

105 divided into four parts: I – $< 200 \text{ cm}^{-1}$ is the range of lattice vibrations, II – $200\text{--}450 \text{ cm}^{-1}$ is the
 106 range of bending vibrations, III – $480\text{--}580 \text{ cm}^{-1}$ is the range of GeO_4 bridging vibrations, IV –
 107 $700\text{--}850 \text{ cm}^{-1}$ is the range of ν_1 and ν_3 stretching vibrations of GeO_4 groups (denotations of in-
 108 ternal vibration modes of GeO_4 groups are given in accordance with [6]).

109 To interpret the Raman spectra of orthorhombic and monoclinic phases of MnGeO_3 were
 110 simulated within the framework of empirical lattice dynamics model with LADY software [7].

111 Vibrational representation for the orthorhombic phase in the center of Brillouin zone has
 112 the following form:

$$113 \quad \Gamma(Pbca) = 30A_g + 30B_{1g} + 30B_{2g} + 30B_{3g} + 30A_u + 30B_{1u} + 30B_{2u} + 30B_{3u}. \quad (1)$$

114 Modes active in Raman:

$$115 \quad \Gamma_{\text{Raman}}(Pbca) = 30A_g + 30B_{1g} + 30B_{2g} + 30B_{3g}, \quad (2)$$

116 For the monoclinic phase:

$$117 \quad \Gamma(C2/c) = 14A_g + 16B_g + 14A_u + 16B_u. \quad (3)$$

118 Modes active in Raman:

$$119 \quad \Gamma_{\text{Raman}}(C2/c) = 14A_g + 16B_g. \quad (4)$$

120 Interatomic interactions were described with simplified Born-von Karman model. This
 121 model represents potential function as the sum of $\varphi(r)$ potentials of pair interactions of structural
 122 units which depend on the distance between them only. This takes into consideration the stretch
 123 interactions only. Parameters of the model were refined to bring into agreement experimentally
 124 observed and calculated vibration frequencies. Table 3 presents comparison of experimental and
 125 calculated spectra frequencies for the monoclinic phase.

126 Because of the difference in the length of Ge–O bonds normal vibrations of GeO_4 tetrahe-
 127 dra are distorted. Numerical simulation shows that the lines in the Raman spectra of monoclinic
 128 phase 836 and 791 cm^{-1} correspond to stretching vibrations of Ge–O, the line at frequency 703
 129 cm^{-1} – to distorted vibration ν_3 of GeO_4 tetrahedron. The range of $480\text{--}580 \text{ cm}^{-1}$ corresponds to
 130 vibrations of oxygen atoms through which the tetrahedral chains are connected. In the case of
 131 monoclinic chain the spectral band at 541 cm^{-1} corresponds to bridging (i.e. linking one tetrahe-
 132 dron to the other) Ge–O–Ge vibration.

133 Both ν_2 and ν_4 vibrations of GeO_4 tetrahedra present in range II $280\text{--}450 \text{ cm}^{-1}$, according
 134 to [6] for most compounds with tetrahedral ReO_4 ions frequency $\nu_2 < \nu_4$, and intensity of ν_2 vi-
 135 brations should be higher than of ν_4 . Range $200\text{--}280 \text{ cm}^{-1}$ corresponds to mixed bending vibra-
 136 tions of octahedral and tetrahedral groups.

137 Raman spectrum of sample 2 was compared to the spectra of sample 1. On the basis of
 138 simulated lattice dynamics the spectrum corresponds to monoclinic phase shown in Figure 4.

139 This fact attracted special attention because by the X-ray diffraction analysis this sample corre-
 140 sponds to the orthorhombic phase.

141 When interpreting the experimental spectrum within the framework of semi-empirical
 142 models the lines have not always been unambiguously attributed to symmetry types in complex
 143 spectra. Above 300 cm^{-1} we gained good agreement with the number of lines and their frequen-
 144 cies, while in the low-frequency range the spectral bands were observed to notably overlap – this
 145 makes unambiguous interpretation difficult.

146 Generally, symmetry types of vibrations are attributed by polarization measurements of
 147 spectra made on oriented samples. However, small size of samples and inhomogeneity of phase
 148 composition of sample 1 deny their orientation. Nevertheless, the lines corresponding to vibra-
 149 tions of different symmetry should manifest at different polarizations of incident and scattered
 150 radiation. This makes attributing symmetry of spectral lines with non-oriented samples possible
 151 by their dependencies intensities vs. direction of radiation polarization [8-15]. This approach was
 152 used to analyze the spectrum of single phase sample 2.

153 3.2 Raman tensor analysis

154 Spectral lines can be attributed to symmetry types for non-oriented samples by Raman
 155 tensor analysis, described in [8-15].

156 Relative intensities of scattered light have form:

$$157 \quad I \propto |e_i \mathbf{R} e_s|^2, \quad (5)$$

158 where e_i and e_s are unit vectors of polarization of electric field for incident and scattered light, R
 159 is the Raman tensor [16]. For the monoclinic ($C2/c$) structure the Raman tensors have form:

$$160 \quad R_{A_g} = \begin{pmatrix} a & 0 & d \\ 0 & b & 0 \\ d & 0 & c \end{pmatrix}, \quad R_{B_g} = \begin{pmatrix} 0 & f & 0 \\ f & 0 & e \\ 0 & e & 0 \end{pmatrix}, \quad (6)$$

161 Converting the Raman tensors (6) into laboratory system of coordinates and substituting
 162 them into (5), in analogy with [9] have expressions for the dependence of spectral intensity on
 163 orientation of the sample, for parallel and cross-polar directions of polarization of exciting and
 164 scattered radiations. Angular dependencies for intensities of A_g and B_g vibration modes have
 165 form:

$$166 \quad I_{A_g}^{\parallel} \propto |\sin \theta \sin \psi [-d \sin \varphi \cos \psi + (-d \cos \theta \cos \varphi + a \sin \theta) \sin \psi] \\ + (\cos \psi \sin \varphi + \cos \theta \cos \varphi \sin \psi) [c \sin \varphi \cos \psi + (c \cos \theta \cos \varphi - d \sin \theta) \sin \psi] \\ + b(\cos \psi \cos \varphi + \cos \theta \sin \varphi \sin \psi)^2|^2, \quad (7)$$

$$167 \quad I_{B_g}^{\parallel} \propto \left| -2[f \sin \varphi \cos \psi + (f \cos \theta \cos \varphi - e \sin \theta) \sin \psi] \right. \\ \left. \times (\cos \varphi \cos \psi - \cos \theta \sin \varphi \sin \psi) \right|^2, \quad (8)$$

$$168 \quad I_{A_g}^{\perp} \propto \left| \sin \theta \cos \psi [d \sin \varphi \cos \psi + (d \cos \theta \cos \varphi - a \sin \theta) \sin \psi] \right. \\ \left. - (\cos \theta \cos \varphi \cos \psi - \sin \varphi \cos \psi) [c \sin \varphi \cos \psi + (c \cos \theta \cos \varphi - d \sin \theta) \sin \psi] \right. \\ \left. + b(\cos \theta \sin \varphi \sin \psi + \cos \varphi \sin \psi)(\cos \varphi \cos \psi - \cos \theta \sin \varphi \sin \psi) \right|^2, \quad (9)$$

$$169 \quad I_{B_g}^{\perp} \propto \left| -2f \cos^2 \theta \sin \varphi \cos \varphi \sin \psi \cos \psi \right. \\ \left. + \cos \varphi (-e \sin \theta \cos^2 \psi - 2f \sin \varphi \sin \psi \cos \psi + e \sin \theta \sin^2 \psi) \right. \\ \left. + \cos \theta [f \cos^2 \varphi \cos(2\psi) + \sin \varphi (-f \sin \varphi \cos^2 \psi + f \sin \varphi \sin^2 \psi + e \sin \theta \sin(2\psi))] \right|^2. \quad (10)$$

170 The expressions produced are in agreement with results in [9].

171 According to (7–10), the angular dependencies of spectral intensities (Figure 5) for lines
 172 of different symmetry types should correspond to different pattern pairs for the parallel and
 173 crossed-polar geometries of the experiment. Classification of produced dependencies of spectral
 174 intensities by patterns yielded the following result: active in the spectrum are 14 modes of A_g
 175 type, this agrees with the selection rules for the monoclinic structure, and 5 modes of B_g type.
 176 Inconsistency by the number of B_g modes is probably due to their smaller intensity. The number
 177 of vibrational modes found by analysis of angular dependencies of the Raman tensor corresponds
 178 to the number of vibrations of the monoclinic structure. Figure 6 shows comparison of experi-
 179 mental and calculated dependencies in cross-polar polarizations for spectral lines at 542 cm^{-1} and
 180 431 cm^{-1} corresponding to A_g and B_g vibration modes by lattice dynamics simulation. Figure 7
 181 shows 3d graph of intensity of spectral line at 542 cm^{-1} vs. angle of rotation in cross-polar
 182 ization.

183 So, according to selection rules, lattice dynamics simulation and produced angular de-
 184 pendencies of the Raman tensor the structure of sample 2 is monoclinic.

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186 4. CONCLUSIONS

187 Raman spectra of MnGeO_3 synthesized by two methods: optical zonal melting (sample 1)
 188 and spontaneous crystallization (sample 2) have been studied. X-ray diffraction analysis showed
 189 the first sample to contain 83% of orthorhombic and 17% of monoclinic phase. Comparison of
 190 experimental spectra to lattice dynamics simulations confirms the two-phase nature of this sam-
 191 ple. Polarization dependencies of Raman lines' intensities for sample 2 have been obtained and
 192 symmetries of vibration modes have been found by analysis of Raman tensor. Thus, having sim-
 193 ulated the lattice dynamics, having analyzed Raman spectrum and selection rules considered we
 194 come to conclusion that the structure of the second sample is nowadays monoclinic. However,
 195 the X-ray diffraction analysis [3] conducted six years ago yielded orthorhombic modification. It

196 can be assumed that under normal conditions the orthorhombic phase of MnGeO_3 is metastable
197 and with time transits into the monoclinic one; the rate of this transition depends on the method
198 of synthesizing the single crystal.

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Table 1. Fundamental crystallographic characteristics and parameters of structure of crystal synthesized by optical zonal melting.

Chemical formula	MnGeO ₃	MnGeO ₃
Syngony	orthorhombic	monoclinic
Space group	<i>Pbca</i>	<i>C2/c</i>
<i>a</i> , Å	19.2979(3)	9.9227(5)
<i>b</i> , Å	9.2448(2)	9.2794(7)
<i>c</i> , Å	5.4800(1)	5.2775(3)
β , °	–	101.768(5)
<i>V</i> , Å ³	977.65(3)	475.73(5)
Weight fraction of phase, wt., %	83.1(5)	16.9(5)
Number of reflections	935	460
Number of refined parameters	102	
<i>R</i> _B , %	1.08	0.84
<i>R</i> _{wp} , %	1.72	
<i>R</i> _{exp} , %	0.989	
<i>R</i> _p , %	1.28	
χ^2	1.743	

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Table 2. Comparison of calculated and experimental frequencies of vibrations

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for the monoclinic structure

№	Symm. type	ω , cm ⁻¹ (calc.)		ω , cm ⁻¹ (exp.)
1	<i>Bg</i>	839		
2	<i>Ag</i>	836	}	836
3	<i>Bg</i>	811		
4	<i>Ag</i>	790		790
5	<i>Ag</i>	703		703
6	<i>Bg</i>	664		
7	<i>Bg</i>	570	}	541
8	<i>Ag</i>	541		
9	<i>Ag</i>	442		444
10	<i>Bg</i>	438		431
11	<i>Bg</i>	383		401
12	<i>Ag</i>	381		381
13	<i>Ag</i>	353	}	351
14	<i>Bg</i>	336		
15	<i>Ag</i>	318		316
16	<i>Bg</i>	306		306
17	<i>Bg</i>	291		276
18	<i>Ag</i>	269		268
19	<i>Bg</i>	205		241
20	<i>Ag</i>	185		232
21	<i>Bg</i>	181		
22	<i>Ag</i>	176		211
23	<i>Bg</i>	140		
24	<i>Bg</i>	133		
25	<i>Bg</i>	124		
26	<i>Ag</i>	114		146
27	<i>Bg</i>	113		
28	<i>Ag</i>	110		126
29	<i>Ag</i>	80		88
30	<i>Bg</i>	67		

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Caption of figure

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Figure 1. Photograph of crystals synthesized by a –optical zonal melting, b – spontaneous crystallization.

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Figure 2. Polyhedral representation of MnGeO_3 structure for orthorhombic Pbca (a) and monoclinic C2/c (b) phases.

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Figure 3. Three Raman spectrum types for the sample synthesized by optical zonal melting obtained from different points of its surface. Components of monoclinic C2/c , orthorhombic Pbca and mixed phases defined by lattice dynamics simulation within the framework of semi-empirical model with LADY software.

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Figure 4. Raman spectra of samples 1 and 2 corresponding to the simulated spectra of monoclinic phase.

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Figure 5. Dependencies of spectral intensity on polarization direction of exciting radiation.

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Figure 6. Angular dependencies in parallel (HH) and cross-polar (HV) polarization of incident and scattered radiation for 542 cm^{-1} and 431 cm^{-1} spectral lines, corresponding to A_g and B_g vibration modes. Solid curves are the calculation, dots are the experimental results.

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Figure 7. 3D graph of intensity of spectral line at 542 cm^{-1} vs. angle of rotation in cross-polar polarization.

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