Raman scattering study on pressure-induced phase transformation of marokite (CaMn$_2$O$_4$)

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Abstract

An in-situ Raman Spectroscopic study was conducted to explore the pressure-induced phase transformation of CaMn$_2$O$_4$ to pressures of 73.7 GPa. Group theory yields 24 Raman active modes for CaMn$_2$O$_4$, of which 20 are observed at ambient conditions. With the slight compression below 5 GPa, the pressure-induced contraction compensates the structural distortion induced by a Jahn–Teller (JT) effect, resulting in the occurrence of the zero pressure shifts of the JT-related Raman modes. Upon elevation of pressure to nearby 35 GPa, these Raman modes start to display a significant variation in pressure shift, implying the appearance of a pressure-induced phase transformation. Group factor analyses on all possible structure polymorphs indicate that the high-pressure phase is preferentially assigned to an orthorhombic structure, having the CaTi$_2$O$_4$ structure. The cooperative JT distortion is continuously reduced in the CaMn$_2$O$_4$ polymorph up to 35 GPa. Beyond 35 GPa, it is found that the JT effect was completely suppressed by pressure in the newly formed high-pressure phase. Upon release of pressure, this high-pressure phase transforms to the original CaMn$_2$O$_4$ phase, and continuously remains stable to ambient conditions.

1. Introduction

A considerable effect has been devoted to understanding the physical properties of the 3d transition-metal oxides, in particular the Mn-related oxides with the chemical formula of NMn$_2$O$_4$ (N = Ni, Zn, Ca, Cu, Li, etc.) [1–4]. The distribution and valencies of the metal ions in those oxides are of great importance for the interpretation of the magnetic, electric, and crystallographic properties of these materials [1,2]. Those properties can significantly be influenced by the external conditions, in particular temperature and pressure, which ultimately tune to the interplay between lattice and electronic degrees of the freedom. Studies indicate that a large number of those oxides crystallize in the cubic spinel structure ($Fd3m$-O_h^7) at high temperatures, and exhibit an antiferromagnetic property; at low temperature, they distort to a tetragonal structure (D_{2h} *point group*), and in turn display a

ferromagnetic property [2,3]. Although their properties have extensively been studied at one atmosphere, little study, however, was yet conducted under pressure. With advancement of high-pressure techniques, particularly Diamond Anvil Cell (DAC), considerable attention has been paid to explore the pressure-induced effect of solids [5]. Thus, this allows one to obtain a possibility for investigating the properties of those Mn-related oxides under compression.

Marokite CaMn$_2$O$_4$ crystallizes in an orthorhombic structure at one atmosphere [1]. Such a structure is different from that in the general NMn$_2$O$_4$ oxides and the most AB$_2$O$_4$ solids [2–4,6–10], which crystallize either in the cubic spinel structure ($Fd3m$) or in the tetragonal structure ($I4_1/amd$). High-pressure studies on the cubic spinels indicate that a cubic-to-orthorhombic phase transformation takes place under pressure [6–10]. This observed high-pressure orthorhombic polymorph was preferentially assigned to one of the three structural polymorphs, including CaTi$_2$O$_4$, CaFe$_2$O$_4$ and CaMn$_2$O$_4$ structures [6,7,11]. However, the resolution of the obtained X-ray diffraction pattern combined

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to Rietveld analysis is still not enough to make a precise crystal assignment due to the similarity between the above three polymorphs [6]. Raman spectroscopy is a powerful technique for detecting the subtle structural distortion between the several structure-related polymorphs. Since the difference between the above three polymorphs was only reflected in slight distortion of the structure [12], it is expected that the Raman spectra may be able to cast a significant constraint for characterizing the structural symmetry of the high-pressure post-spinel polymorph.

The tetragonal spinel structure was observed in a large number of NMn_2O_4 solids, such as $NiMn_2O_4$, $CuMn_2O_4$, Mn_3O_4 and $ZnMn_2O_4$ [2–4,13]. The formation of such a structure was previously interpreted by a Jahn–Teller-effect-induced spin order because of the existence of the Mn^{3+} ions [3]. Since the tetragonal-to-cubic phase transformation was observed in those spinels with increase in temperature, it is thus expected that the same phase transformation also be induced by pressure. However, the pressure studies indicate that those solids exhibit another phase transformation, showing that another tetragonal structure was obtained at high pressure. Difference between the two tetragonal polymorphs was reflected only in the variation of the unit-cell parameter of a and c, rather than a remarkable alteration in compressibility [2,3]. Such an observable effect was assumed as being caused by a combination of the pressure-induced structural contraction and the strong Jahn–Teller electron phonon coupling effect. Thus, a novel pressure-induced effect is also expected to occur in $CaMn_2O_4$.

As a result, we are motivated to use Raman spectroscopic technique to cast a further constraint on the structural characteristics of $CaMn_2O_4$, and thus to explore the possible pressure-induced phase transformation. The obtained result might also be able to reconcile the existing argument for determining precisely the structure of the pressure-induced post-spinel polymorph, and therefore obtain a full understanding of the transition dynamics in the Mn-related spinels. Below, we presented the in-situ high-pressure Raman spectra of $CaMn_2O_4$ at pressures ranging from 0 to 73.7 GPa. A detailed discussion was also given.

2. Experimental

The $CaMn_2O_4$ polycrystalline sample was synthesized by mixing stoichiometric amounts of $CaCO_3$ and MnO_2 with a mortar and pestle for 10 min followed by reaction for 20 h at 1100°C. The sample was reground for 10 min and reacted at 1200°C [1]. Three subsequent regrindings and 20 h reactions at 1300°C were conducted. X-ray diffraction and Raman spectroscopy characterized that the recovered $CaMn_2O_4$ specimen crystallizes in an orthorhombic structure [1].

High-pressure Raman measurements were conducted at room temperature by using a gasketed high-pressure Diamond Anvil Cell (DAC) and Raman spectrometer in the back scattering configuration. Ti^{3+}–sapphire laser pumped by an argon ion laser was tuned at 785 nm. This design can effectively suppress the strong fluorescence of diamond. To avoid a heating effect, lasers were operated at 3 mW (after filter), and the sample without pressure medium was loaded. However, such a sample loading may lead to a large pressure gradient across the sample chamber. Raman spectra were collected by using high throughput holographic imaging spectrograph with volume transmission grating, holographic notch filter and thermoelectrically cooled CCD detector (Physics Spectra) with the resolution of 4 cm^{-1} [14]. The spectrometer was regularly calibrated by using the neon lines. Pressures were determined from the ruby fluorescence R_1 line [15]. The sample was placed in a 301 stainless-steel gasket hole 60 μm in initial thickness and 150 μm in diameter with a few ruby chips as the pressure makers. The laser beam was focused on the sample with a spot size of 5 μm. To avoid a possible laser heating induced chemical reaction between the sample and the ruby, the exposure spot on the sample is only close to the ruby chip, in which the pressure difference does not exceed ± 0.5 GPa. A 15-min exposure time was used for Raman collection at each run.

3. Results and discussion

Refinements of the neutron diffraction data of marokite ($CaMn_2O_4$) collected at room temperature were carried out using the GSAS Rietveld program [1]. The refined results indicate that $CaMn_2O_4$ has an orthorhombic structure, belonging to the D_{2h}^{11}-$Pbcm$ space group ($Z = 4$) with the unit-cell parameters of $a_0 = 3.15886(8)$ Å, $b_0 = 9.9958(2)$ Å and $c_0 = 9.6776(2)$ Å [1]. Group theory analysis expects 24 Raman active modes arising from the orthorhombic $CaMn_2O_4$ phase, as represented below

$$\Gamma = 6A_g(R) + 7B_{1g}(R) + 6B_{2g}(R) + 5B_{3g}(R).$$

At 1 atm, 20 of these 24 Raman active modes were observed and presented in Fig. 1 and in Table 1. Since the $CaMn_2O_4$ specimen is one polycrystalline powder, we cannot precisely assign these observed modes using a combination of the single-crystal orientation and the polarized Raman scattering. However, these observed Raman modes can be classified into four general families of lattice vibrations: Ca-related external modes, as well as rotational modes of the oxygen octahedra at frequencies below 300 cm^{-1}, bending vibrations of the octahedra at 300–500 cm^{-1}, and oxygen-stretching modes at frequencies above 500 cm^{-1} [16,17]. Indications of the significant typical peaks are well shown
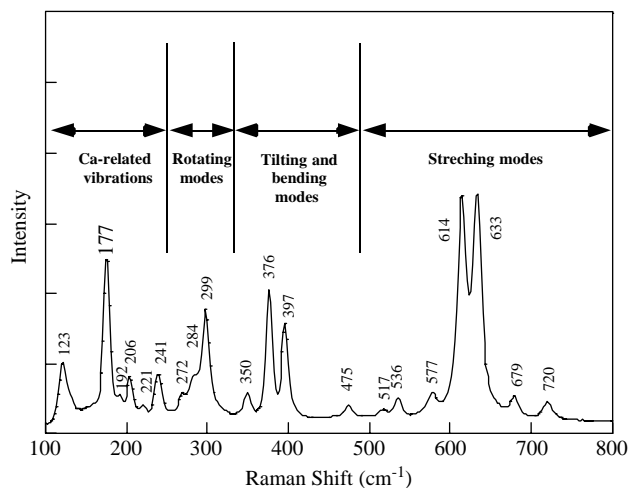
Fig. 1. Raman spectrum of $CaMn_2O_4$ at ambient conditions.

Table 1
Observed Raman modes of $CaMn_2O_4$ at high pressures and their pressure shifts

Observed modes at 1 atm (cm^{-1})	Pressure shifts (cm^{-1}/GPa)		
	<5 GPa	5–35 GPa	>35 GPa
123	1.46 (5)	1.53 (9)	0.51 (5)
177	1.11 (3)	1.13 (4)	0.32 (3)
192	—	—	—
206	0.69 (6)	0.83 (9)	0.39 (3)
221	—	—	—
241	1.46 (7)	1.45 (11)	0.43 (4)
272	0	—	—
284	0	1.49 (8)	0.68 (2)
299	0	3.09 (11)	0.93 (3)
350	0	2.77 (13)	0.83 (7)
376	0	2.92 (7)	2.01 (14)
397	0	2.87 (9)	—
475	0	2.13 (4)	—
517	0	2.21 (4)	2.94 (14)
536	0	1.96 (13)	1.21 (2)
577	0	2.41 (8)	—
614	0	2.35 (11)	1.02 (5)
632	0	2.81 (13)	—
679	0	3.82 (7)	−0.08 (4)
720	0	4.26 (15)	0.93 (17)

Note: The wavelengths in column (1) have the error estimation of $\pm 4\,cm^{-1}$, because of the resolution of $4\,cm^{-1}$.

Fig. 2. Raman spectra of $CaMn_2O_4$ upon elevation of pressure to 73.7 GPa. The lines guide eyes for better comparison.

at frequencies nearby 177, 299, 376 and $620\,cm^{-1}$, respectively.

High-pressure Raman spectra of $CaMn_2O_4$ are shown in detail in Fig. 2. The pressure shifts of the observed Raman modes are plotted in Figs. 3(a–c). At pressures lower than 5 GPa (Figs. 2 and 3a), the pressure shifts of the modes below $250\,cm^{-1}$ (Table 1) did not exhibit any observable variation. Because the existence of the Mn^{3+} ions in $CaMn_2O_4$, a Jahn–Teller (JT) effect can lead to a significant structural distortion. Simultaneously, pressure results in a structural contraction, most likely
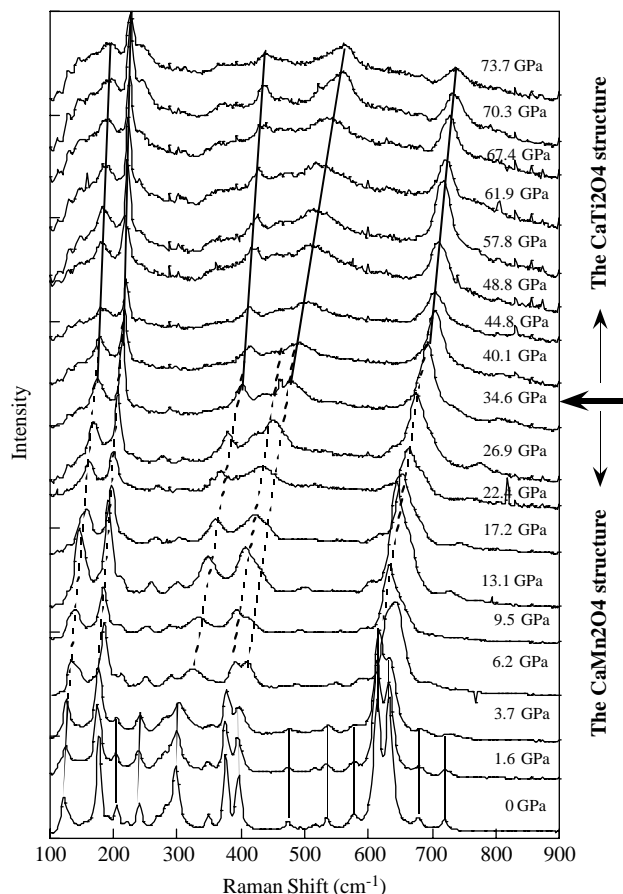
making the structure symmetry be higher. In this case, the two controversial effects compensate each other, leading to an unobservable modification in the compressed structure. In turn, such a combinational effect results in the zero pressure Raman shifts for several observed Raman modes, which are closely related to the JT effect. Upon a continuous enhancement of pressure, the remarkable variations are characterized in the broadening of the characteristic Raman peaks and the merging of several modes with close frequencies. These can be easily recognized from that the three peaks at nearby $299\,cm^{-1}$, the two at $\sim 376\,cm^{-1}$ and the two at high frequencies nearby $620\,cm^{-1}$ start to overlap and then to merge together at a pressure of 6.2 GPa (Fig. 2). Consequently, these merged peaks become broad and lose intensity upon continuous compression. All observed modes initially display the pressure dependences ranging from 0.69 to $3.09\,cm^{-1}$/GPa [Figs. 3(a–c) and Table 1], and remain constant to pressures as high as 35 GPa. Beyond 35 GPa, almost all observed peaks exhibit the lower pressure shifts ranging from −0.08 to $1.21\,cm^{-1}$/GPa relative to those at pressures below 35 GPa except the two modes as shown in Table 1. Such a variation in mode pressure dependence suggests the
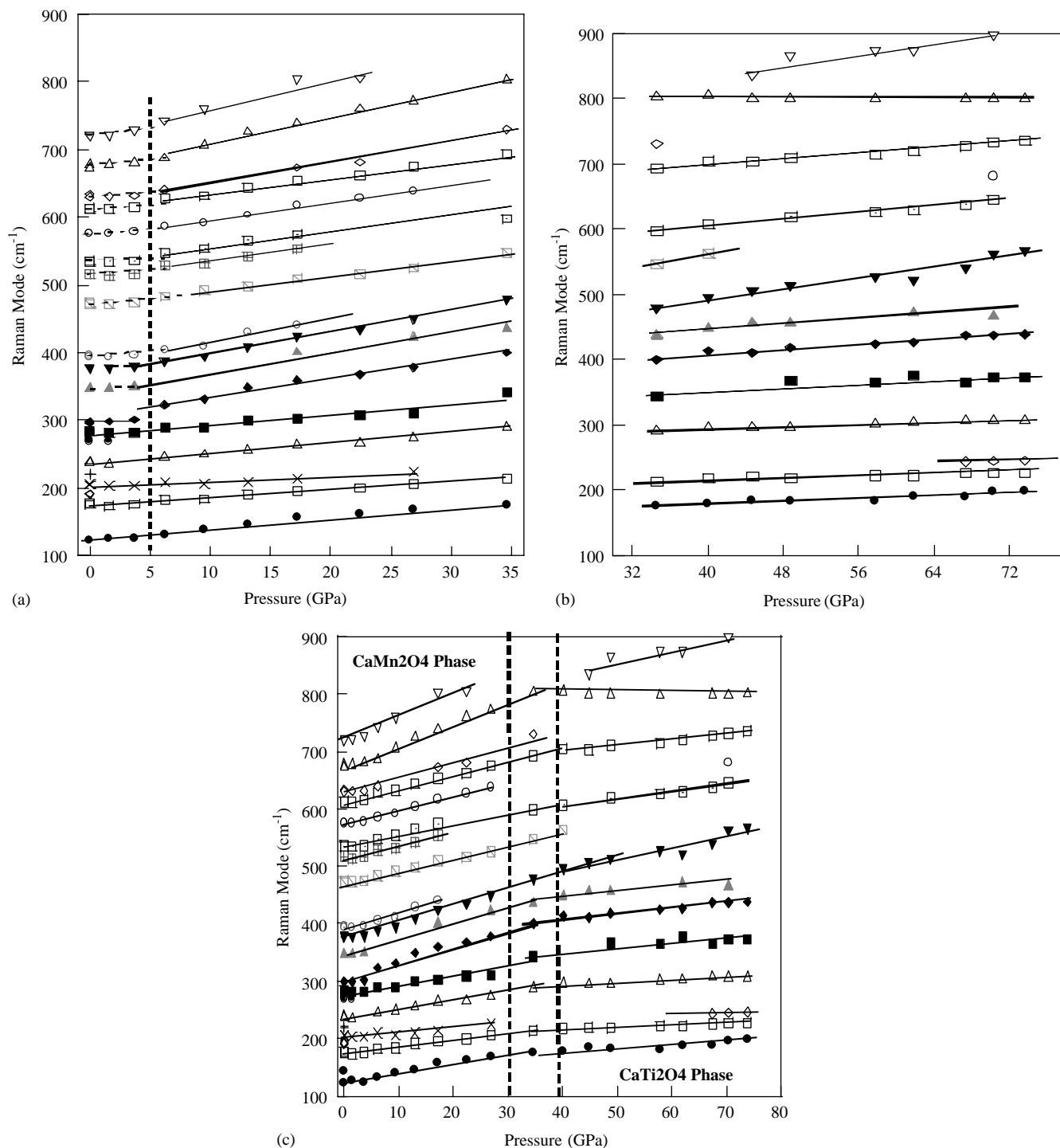
Fig. 3. The pressure shifts of the observed modes of CaMn$_2$O$_4$ under compression. (a) Plot at 0–35 GPa. The vertical dotted line represents the critical pressure for the pressure-induced spectroscopic change; (b) plot at 32–73.7 GPa; (c) plot at the whole investigated pressure range of 0–73.7 GPa. The marked zone between the two vertical dotted lines represents the coexistence of the two phases.

occurrence of a pressure-induced phase transformation at nearby 35 GPa. Since pressure can lead to a suppressing effect on the intensity of the vibrational spectrum, which is usually reflected in either the generation of the overlapping of several peaks or the extinction of the weak peaks, so we believe that no other

significant spectroscopic variation upon phase transformation occurs, such as the occurrence of any new peak or the disappearance of the strong characteristic modes. Accordingly, it is suggested that such a phase transformation most likely originates from a slight distortion within the two similar structure symmetries at

~ 35 GPa. The most possibility is the substitution of a new orthorhombic polymorph to the original $CaMn_2O_4$ structure. Nonetheless, such a tentative assumption still needs a fully structural analysis by using a combination of the obtained Raman spectra and the group theory for the possible structure candidates.

High-pressure studies on the cubic spinels indicate that a pressure-induced post-spinel phase has an orthorhombic structure, which was previously assigned to one of the three similar polymorphs, including $CaMn_2O_4$, $CaFe_2O_4$ and $CaTi_2O_4$ structures (6–10 m [18]). Both the $CaMn_2O_4$ and $CaFe_2O_4$ structures actually originate from the $CaTi_2O_4$ polymorph in terms of a slight structural distortion [6]. This implies that the structural symmetry taken by the $CaTi_2O_4$ polymorph is somewhat higher than those by the $CaMn_2O_4$ and $CaFe_2O_4$ polymorphs. The significant evidence can be found in the previous high-pressure studies on the spinel $MgAl_2O_4$ [18], whereby the spinel $MgAl_2O_4$ initially transforms either to the $CaMn_2O_4$ or to the $CaFe_2O_4$ structure, and in turn to the $CaTi_2O_4$ structure. Difference between the $CaFe_2O_4$ and $CaMn_2O_4$ polymorphs can be distinguished by a structural distortion with a variety of degrees due to the occurrence of one more MnO_6 and FeO_6 octahedral site, respectively, in these two polymorphs, as compared to the $CaTi_2O_4$ structure [6,11,13]. The existence of Mn^{3+} ions in $CaMn_2O_4$ leads to a significant Jahn–Teller effect, and such an effect can effectively induce somewhat a large degree of the structural distortion. Therefore, the modification to a lower symmetry for $CaMn_2O_4$ is usually preferentially formed to compare the $CaFe_2O_4$ polymorph. Applying such a finding to this study, the high-pressure polymorph of $CaMn_2O_4$ may take either the $CaTi_2O_4$ or $CaFe_2O_4$ structure. Studies on $NiMn_2O_4$ and $ZnMn_2O_4$ at in-situ temperature and high-pressure conditions indicate that these two solids crystallize in the tetragonal structures at low temperature, and transform to a cubic spinel structure upon an elevation of temperature [2,3]. Under compression, the two solids transform to another tetragonal structural polymorph, rather than an orthorhombic structure as observed in other cubic spinel solids [6,7,18]. Such a result was caused by a combination of the pressure-induced structural contraction and the Jahn–Teller induced distortion in the case of the existence of the Mn^{3+} ions [4]. Previous studies reveal that the Jahn–Teller effect usually leads to the spin order along one direction [1]. If such an effect could stabilize the structure in the tetragonal point group, it is expected that the $CaMn_2O_4$ also possibly transform to a tetragonal polymorph at high pressure. However, because previous X-ray diffraction pattern collected by an energy synchrotron radiation source had a low resolution, a precise space group was not assigned. The third possibility might be the dissociation of the $CaMn_2O_4$ phase to their compositional mixture either of the $CaMnO_3$ perovskite and MnO or of the layer perovskite $Ca_2Mn_2O_7$ and MnO. All these expected potential candidates of the high-pressure phase of $CaMn_2O_4$ have been summarized in Table 2.

In the $CaMn_2O_4$ structure, the two independent sites are located by the Ca and Mn ions, respectively, whereas the other three sites are taken by the oxygen ions [1]. Because of the modification of MnO_6 polyhedron within the structure induced by the JT effect, one more MnO_6 site is reasonably led to occur in this structure, whereas one oxygen site instead disappears simultaneously [6]. Group theory analysis yields 24 Raman active modes $(6A_g + 7B_{1g} + 6B_{2g} + 5B_{3g})$ in the $CaMn_2O_4$ structure (Table 2), of which 20 modes were observed in this Raman study. A reduced Raman mode number observed here was possibly caused by our particular Raman design system. Because a notch filter with the cutoff at ~ 100 cm^{-1} was added to avoid a plasma effect arising at nearby the laser position [10], some Raman modes at low frequencies were eventually led only to display either the weak characteristics or the extinction of some Raman modes. High-pressure $CaTi_2O_4$ modification also has an orthorhombic structure [6], belonging to the *Bbnm* space group (D_{2h}^{17}-*Bbnm*, $Z = 4$). Such a structural polymorph includes the three independent atomic sites, in which the two metal ions compete with the two oxygen ions to take the 4c and 8f sites, and another oxygen ion independently takes the 4a site [6]. Total of eight Raman active modes $(6A_g + 4B_{1g} + 2B_{2g} + 6B_{3g})$ is expected in such a structure (Table 2). Correlating the corresponding translation

Table 2
Comparison of the structures and Raman spectra between $CaMn_2O_4$ and the possible high-pressure polymorphs

Structure polymorph	$CaMn_2O_4$	$CaFe_2O_4$	$CaTi_2O_4$	$NiMn_2O_4$	$CaMnO_3$	$Ca_2Mn_2O_7$	MnO
Structure system	Orthorhombic	Orthorhombic	Orthorhombic	Tetragonal	Orthorhombic	Cubic	Cubic
Formula per unit cell	4	4	4	4	4	8	1
Space group	D_{2h}^{11}-*Pbcm*	D_{2h}^{16}-*Pbnm*	D_{2h}^{17}-*Bbmm*	$I4_1/amd$	D_{2h}^{16}-*Pbnm*	$Fd3m$-O_h^7	$Fd3m$-O_h^5
Expected Raman modes	$6A_g + 7B_{1g} + 6B_{2g} + 5B_{3g}$	$7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}$	$6A_g + 4B_{1g} + 2B_{2g} + 6B_{3g}$	$2A_g + 1A_{2g} + 3B_{1g} + 4E_g$	$7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}$	$A_{1g} + E_g + 4F_{2g}$	0

relation of the structures between the two space groups, we enable to observe the overlapping and the merging of the correlative modes. These characteristics can be discerned from the collected pressure Raman spectra of $CaMn_2O_4$, in which 20 modes belonging to the original phase were reduced to 14 modes originating from the newly formed high-pressure phase (Figs. 2 and 3). Previous high-pressure studies reveal that the $CaTi_2O_4$ polymorph has a larger incompressibility than the $CaMn_2O_4$ structure [7,10,18]. This can equally be recognized from Raman study with a low-pressure shift in the corresponding modes. Thus, the above tentative assumption for the formation of the $CaTi_2O_4$ polymorph is strongly supported by our Raman spectra, in which a low-pressure Raman shift was observed in all modes observed from the high-pressure phase (Table 1 and Fig. 4c), as compared to those of the initial $CaMn_2O_4$ polymorph. The $CaFe_2O_4$ structure is similar to the $CaMn_2O_4$ structure, and also includes the two types of FeO_6 polyhedral sites [6,7,11]. This usually results in the appearance of the equal number of Raman modes to the $CaMn_2O_4$ polymorph (Table 2). The pressure studies on those two types of structural polymorphs reveal that the $CaFe_2O_4$ phase has almost the same or somewhat lower bulk modulus (incompressibility) [6,18]. Applying such a finding to the Raman spectroscopic study, the mode pressure dependences of the $CaFe_2O_4$ could be very close or somewhat higher than those of the $CaMn_2O_4$ polymorph. Therefore, the expected Raman mode number and their pressure shifts are apparently incompatible with the collected Raman spectra of the newly formed high-pressure phase, in case of assuming the crystallization of the $CaFe_2O_4$ structural polymorph. Hence, the possibility for the $CaFe_2O_4$ polymorph can be excluded. If the $CaMn_2O_4$ phase transforms to a tetragonal polymorph as that observed in $NiMn_2O_4$ and $ZnMn_2O_4$ [2,3], the high-pressure phase should belong to the D_{2h} point group and most likely has $I4_1/amd$ space group, in which only nine Raman active modes ($2A_g + 1A_{2g} + 3B_{1g} + 4E_g$) could occur (Table 2). Even a pressure-induced suppressing effect could result in a significant extinction of the Raman modes, the reduced mode number of 13 observed from this study, however, is still higher and apparently incompatible to the above analyzed result on the tetragonal polymorph. Hence, such an assumption for the crystallization of a tetragonal structure is not acceptable. If $CaMn_2O_4$ dissociates to their compositional mixture of the $CaMnO_3$ perovskite and MnO or of the layer perovskite $Ca_2Mn_2O_7$ and MnO, a different Raman spectrum is expected (Table 2) [16,17,19]. X-ray diffractions indicate that the $CaMnO_3$ perovskite crystallizes in an orthorhombic structure, belonging to the D_{2h}^{16}-$Pbnm$ space group (57, $Z = 4$) [19], and that MnO crystallizes in the cubic B_1 (NaCl type) structure. The B_1 structure oxide has no Raman active mode, and the $CaMnO_3$ perovskite has 24 Raman active modes ($7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}$). However, the key characteristic modes originating from such a perovskite phase should occur at the frequency range differing from those of the $CaMn_2O_4$ structure [18]. As for the layer perovskite $Ca_2Mn_2O_7$ structure, it crystallizes in the face-centered cubic structure with space group $Fd3m$-O_h^7 including eight formula units per unit cell [16], in which six Raman active modes ($A_{1g} + E_g + 4F_{2g}$) are yielded. Such an expected mode number is apparently inconsistent to those observed from this newly formed high-pressure phase of $Ca_2Mn_2O_4$. Summarizing those analyses on the possibilities for the observed high-pressure phase of the $CaMn_2O_4$, a conclusion can be logically made as that the $CaMn_2O_4$ phase transforms to another orthorhombic phase, most likely having the $CaTi_2O_4$ structure. However, in order to confirm the reliability of such an analysis, an in-situ high-resolution X-ray diffraction is urgently waiting to be conducted. Because of the low resolution of the existing synchrotron source and the need of a large sample for neutron source, an ongoing project is currently planning being undertaken to this end, when the newly constructed HP-CAT beamline at APS is opened for users.
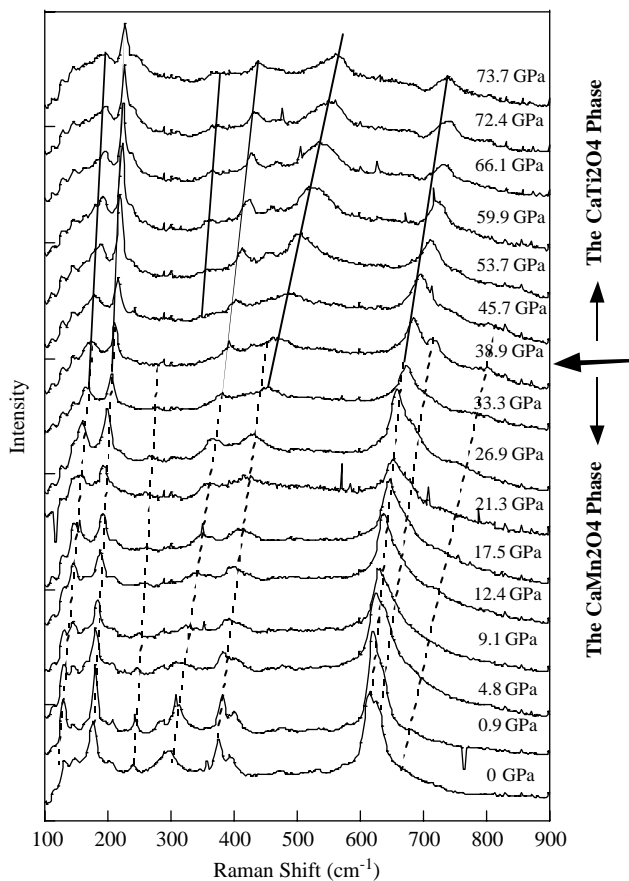

Fig. 4. Raman spectra of $CaMn_2O_4$ upon release of pressure to ambient conditions. The two types of lines guide our eyes for recognizing the significant variation of the mode pressure shifts.

Furthermore, several significant implications can also be discovered from the collected Raman spectra of $CaMn_2O_4$. It can be found from Fig. 3a and Table 1 that the pressure shifts at frequencies higher than $250 \, cm^{-1}$ do not exhibit any observable variation. This has previously been explained by a combination of the pressure-induced contraction and the JT-induced structural distortion, in which the two controversial effects compensate each other. This further implies that these high-frequency modes are truly related to the JT-induced structure distortion effect. It can also be found that pressure does not lead to a remarkable losing of the intensity of the key peak at the frequency of $177 \, cm^{-1}$, but exhibit an observable pressure shift (Table 1). Because such a peak was assigned to the Ca-site-related vibration, this observation suggests that only pressure play a significant role on a pure contraction of the CaO_8 polyhedron, also strongly supporting the reliability of the above assignment and explanation in which the Ca-site really has no close relation to the Jahn–Teller-induced effect. The other three key characteristic peaks at frequencies nearby 299, 376, $620 \, cm^{-1}$ exhibit the remarkable variation both in profile and in intensity, as shown in their merging and broadening before the phase transformation (Table 1 and Fig. 2). Since these modes are closely related to the modification of the MnO_6 polyhedra and the corresponding vibrations, including the rotating, bending and stretching, the observable variation in these modes, in particular the peak profile, may imply a combinational effect of the pressure-induced structural contraction and the Jahn–Teller-induced distortion. The modes at nearby $299 \, cm^{-1}$ attribute to the rotating of the MnO_6 polyhedron, and thus, it is only slightly influenced by the Jahn–Teller effect, as shown in which only the intensity was somewhat reduced, rather than a remarkable change in peak profile. The modes at nearby 380 and $620 \, cm^{-1}$ are closely related to the Jahn–Teller-induced distorted effect, as shown in which several modes at nearby the above two frequencies merge together, and in turn become broad and lose intensity. However, we cannot exclude the possibility that these observable results originate from the pressure-induced structure disorder. As is well known, pressure can lead to a significant contraction of structure, and hence, the structural contraction can reduce the Jahn–Teller-induced distortion. It means that the JT effect was initially compensated by the pressure-induced structural compaction, and exhibit the zero pressure shifts in the JT-related Raman modes. And then, pressure started to cast the main influence on the structural change. When the JT effect was completely suppressed as pressure was increased to a certain limit, the pressure-induced effect leads to the occurrence of a new structural polymorph with somewhat higher symmetry. This is supported by the observed Raman evidence in which the newly

formed phase exhibits only the weakening of the observed Raman peaks, rather than the variation either in profile or in number of the Raman modes. Such an effect has been found in the high-pressure study of $LaMnO_3$ [12], in which a strong compression ultimately led to a complete disappearance of the Jahn–Teller effect. Upon continuous compression, the newly formed high-pressure polymorph of $CaMn_2O_4$ stabilizes in the $CaTi_2O_4$ structure to the peak pressure of 73.7 GPa.

Upon release of pressure, the Raman spectra of $CaMn_2O_4$ were also collected as shown in Fig. 4. The pressure shifts of all observed Raman modes were plotted in Fig. 5. As decreasing pressures to 40 GPa, the high-pressure $CaTi_2O_4$ polymorph of $CaMn_2O_4$ transforms to the original $CaMn_2O_4$ structure. Because the reduction of pressure leads to a significant relaxing effect, a large pressure gradient across the sample chamber exists [8–10]. Such an effect usually results in the weakening of the Raman modes, so the intensities of the collected Raman spectra as shown in Fig. 4 are reduced relative to those in the compression run. However, no novel spectroscopic characteristic was observed at this decompressed pressure range (Figs. 4 and 5). Upon release of pressure to 1 atm, the obtained Raman spectrum is consistent to that collected from the original specimen. Thus, it is suggested that the high-pressure phase transforms to the original $CaMn_2O_4$ polymorph, which remains stable to ambient conditions. This was supported by the X-ray diffraction pattern collected from the recovered sample, which was well refined to the orthorhombic $CaMn_2O_4$ structure [1].
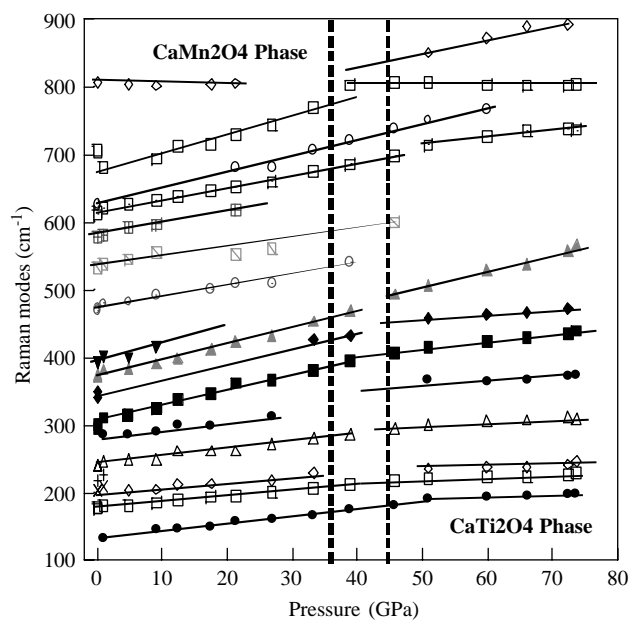

Fig. 5. The pressure shifts of the observed modes in $CaMn_2O_4$ upon release of pressure. The marked zone between the two vertical dotted lines donates to the coexistence of the two phases.

Since no pressure medium was loading into the DAC cell with the sample, a large pressure gradient may be generated across the sample chamber. Thus, we have to clarify any possible effect caused by the non-hydrostatic conditions. As is well known, a large pressure gradient may significantly lead to a reduction of the transition pressure of the pressure-induced phase transformation. However, it is difficult to maintain a hydrostatic condition in DAC cell up to very high pressure. Because any pressure medium takes a significant effect on maintaining a hydrostatic condition only at pressures below 20 GPa, but at above 20 GPa, the pressure mediums can lead to only a quasi-hydrostatic conditions due to the solidification of the liquid and gas. Thus, applying to this study, since the observed phase transformation takes place at above 35 GPa, which is beyond the pressure range of any pressure medium for maintaining the hydrostatic condition, it is not significant to use any pressure medium for our investigation on $CaMn_2O_4$. As a result, the possible effect may result in a lower pressure for the initial occurrence of the phase transition relative to that at hydrostatic conditions, further reflecting with a large pressure range of the phase transition. This has been exactly displayed by our Raman investigation. Upon release of pressure at decompression run, a relax effect always takes place, and thus result in a quite larger pressure gradient as compared to that at compression run. In this case, even the whole DAC body was completely released, the resident stress can still maintain a pressure of 5 GPa, so the observed Jahn–Teller effect at pressures below 5 GPa in compression run is hardly repeated upon release of pressure to 5 GPa in this study.

4. Conclusion

An in-situ Raman spectroscopic study has been carried out to explore the pressure-induced phase transformation to pressures as high as 73.7 GPa. Below 5 GPa, the pressure-induced compaction compensates the JT-induced structure distortion, leading to the occurrence of the zero pressure shifts in the JT-related Raman modes. Upon enhancement of compression, a pressure-induced phase transformation was observed at a pressure of ~ 35 GPa. The newly formed high-pressure phase was assigned to an orthorhombic $CaTi_2O_4$ structure, which remains stable to the peak pressure. Before the occurrence of the phase transformation at nearby 35 GPa, the pressure-induced structural contraction reduced the Jahn–Teller-induced distortion in the original $CaMn_2O_4$ structure polymorph. At above 35 GPa, the JT effect was completely suppressed by pressure in the high-pressure $CaTi_2O_4$ phase. Upon release of pressure to ~ 40 GPa, the high-pressure $CaTi_2O_4$ phase transforms to the low-pressure $CaMn_2O_4$ structure, which remains stable to ambient conditions.

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