

High-Pressure Raman Spectroscopic Study of Spinel (ZnCr₂O₄)

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An *in situ* Raman spectroscopic study was conducted to investigate the pressure-induced phase transformation in the synthetic ZnCr₂O₄ spinel up to pressures of 70 GPa at room temperature. Results indicate that ZnCr₂O₄ spinel starts to transform to the CaFe₂O₄ (or CaTi₂O₄) structure at 17.5 GPa, and such a phase transformation is complete at 35 GPa. The coexistence of two phases over a wide range of pressure implies a sluggish mechanism upon phase transformation. No experimental evidence was observed to support the theoretical simulation with the dissociation of ZnCr₂O₄ to ZnO and Cr₂O₃ at 34 GPa. Moreover, enhancement of the intensity of the Raman peak at 642 cm⁻¹ at either elevated pressures or temperatures is most likely caused by an enhanced order–disorder effect. Upon release of pressure, the recovered phase may exhibit an inverse spinel structure, which differs from the initial normal spinel structure. © 2002 Elsevier Science

(USA)

INTRODUCTION

Spinel with AB₂O₄ formula are binary oxides, which have important technological applications, including use as magnetic materials (1), superhard materials (2), high-temperature ceramics (3), as well as high-pressure sensors by Cr³⁺ doping (4). From the view point of geophysics, silicates with spinel structure are stable in the upper mantle of the Earth, and consequently, the prediction of high-pressure phases of silicate spinels may provide critical information for a detailed understanding of the dynamics of the Earth's interior (5). However, silicates remain stable in the spinel structure over a wide range of pressure, and application of high pressure often results in the disappearance of spectroscopic peaks, and then to a misinterpretation of high-pressure phase transformations. Moreover, similarity between several post-spinel phases underlies the need for a precise refinement with X-ray diffraction (6), and for good-quality spectroscopic data on high-pressure phases of spinels. In general, solids with large ionic radius have lower transition

pressure, so use of large ionic radius solids should be expected to avoid the pressure-induced spectroscopic extinction within the range of transition pressure. The results obtained can be further used to predict the high-pressure behavior of similar solids (7). As a result, the physical properties of the prototype spinel ZnCr₂O₄ are of general interest to be studied experimentally with potential applications in fields ranging from material physics to geophysics.

ZnCr₂O₄ spinel has the crystal group *Fd3m*, with 56 atoms per unit cell (*Z* = 8). Zn²⁺ and Cr³⁺ ions occupy the tetrahedral and octahedral sites, respectively. At one atmosphere, the temperature-induced order–disorder effect in numerous spinels has been studied by X-ray and neutron diffractions (8–12), which indicate that temperature can lead to a significant enhancement of the disorder effect of two ions over the tetrahedral and octahedral sites. However, the pressure-induced order–disorder effect has not been widely recognized (13). So far, only one *ab initio* calculation has been carried out to investigate the pressure-induced phase transformation in ZnCr₂O₄ spinel (14). This simulation predicts that ZnCr₂O₄ spinel dissociates to the mixture of ZnO and Cr₂O₃ at a pressure of 34 GPa at room temperature. Previous studies on the spinel groups reveal two types of high-pressure behaviors: one shows that the spinel transforms to a novel denser phase; another dissociates. Basically, the dissociation of a spinel is of high-energy hindrance (7), so a high-temperature treatment is theoretically needed. Therefore, the reliability of theoretical simulation on the dissociation of ZnCr₂O₄ spinel at room temperature is questionable. In order to clarify the high-pressure dynamics of ZnCr₂O₄ spinel, an *in situ* Raman spectroscopic study was conducted up to pressures of 70 GPa in Diamond Anvil Cell (DAC) at room temperature, and the detailed discussion is given below.

EXPERIMENTAL PROCEDURE

The ZnCr₂O₄ sample was synthesized by a high-temperature solid reaction with a stoichiometric mixture of

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analytical grade ZnO and Cr₂O₃. Both X-ray diffraction and Raman spectroscopy indicate that ZnCr₂O₄ crystallizes in a cubic spinel structure.

High-pressure Raman measurements were carried out at room temperature by using a gasketed high-pressure diamond anvil cell (DAC) and Raman spectrometer in the back-scattering configuration. Ti³⁺:sapphire laser pumped by an argon ion laser was tuned at a near-infrared wavelength of 785 nm, which significantly suppresses the strong fluorescence of diamond. Laser power for probing the vibrations was set at 10 mW at ambient conditions, and at 50–200 mW (after filter) at high-pressures. Raman spectra were collected by using high-throughput holographic imaging spectrograph with volume transmission grating, holographic notch filter and thermoelectrically cooled CCD detector with a resolution of 4 cm⁻¹ (15). Pressures were determined from the shift of the ruby fluorescence R₁ line (16), excited by an argon laser with a wavelength of 514.5 nm. The sample was placed in a 301 stainless-steel gasket hole 65 μm in initial thickness and 150 μm in diameter without pressure medium and with the ruby chip as a pressure marker. In addition, Raman spectra were also collected at variable laser powers at 1 atm.

RESULTS AND DISCUSSIONS

ZnCr₂O₄ spinel has a cubic structure belonging to the space group O_h⁷ (*Fd3m*). Although the full unit cell contains 56 atoms, the smallest Bravais cell contains only 14 atoms. As a result, one should expect 42 vibrational modes. The factor group analysis predicts the following modes in ZnCr₂O₄ spinel:

$$A_{1g}(R) + E_g(R) + F_{1g} + 3F_{2g}(R) \\ + 2A_{2u} + 2E_u + 4F_{1u}(IR) + 2F_{2u}.$$

There are five Raman active modes, all of which were observed in this study at ambient conditions, as shown in Table 1 and Fig. 1. These modes are in agreement with the previous measurements and calculations using different models (17–19). Moreover, three very weak and broad Raman modes were observed at 567, 642, and 804 cm⁻¹, and a strong peak at 1051 cm⁻¹. The origin of these modes remains unclear. The strong peak lies at approximately twice the frequency of the peak at 511 cm⁻¹. Its assignment to an overtone mode seems unlikely because the second-order scattering is typically 10–100 times weaker than the first-order one. The second-order mode contains contributions throughout the Brillouin zone, so it is usually broad. Instead, the peak at 1051 cm⁻¹ could indicate the presence of an impurity. However, the X-ray diffraction pattern of the starting sample does not support this possibility. For some spinel characters, the tetrahedral ZnO₄ groups have frequencies near 1000 cm⁻¹. In this spinel, Zn ions are incorp-

TABLE 1
The Observed Raman Modes and Previous Data at Ambient Conditions

Observed modes (cm ⁻¹)	Symmetry	Lutz	Gupta	Himmrich and Lutz (18)	
		<i>et al.</i> (19)	<i>et al.</i> (17)		
180	<i>F</i> _{2g}	186	159	181	164
430	<i>E</i> _g	457	457	456	474
511	<i>F</i> _{2g}	515	552	529	513
567					
605	<i>F</i> _{2g}	610	631	614	610
642					
687	<i>A</i> _g	692	692	690	679
804					
1051					

Note. Data in Column (1) were measured in this study; data in Column (3) measured by Lutz *et al.* (1991); data in columns (3–5) calculated with Short-range Force Model (SFM), Polarizable Ion Model (PIM) and Short-range Rigid Model (SRM), respectively, by the given authors.

orated in the tetrahedral site, which might result in the appearance of this unexpected strong peak. Previous studies indicate that the order-disorder of the two ions (*A* and *B*) over the tetrahedral and octahedral sites exists in the spinel structure (*AB*₂O₄), and that temperature leads to a significant enhancement of this order-disorder effect (7–12). The strong absorption of laser by ZnCr₂O₄ may result in an elevation of temperature. To this end, Raman spectra were collected at elevated laser powers to check the temperature-induced structural change. The obtained data are shown in

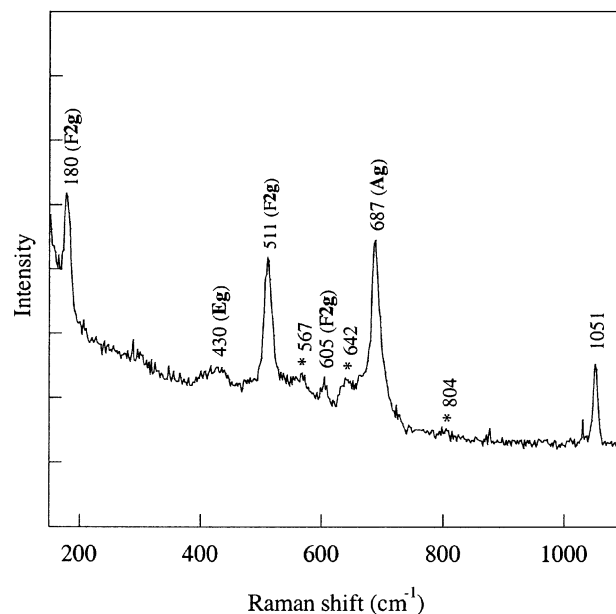


FIG. 1. Raman spectrum of ZnCr₂O₄ spinel collected at ambient conditions.

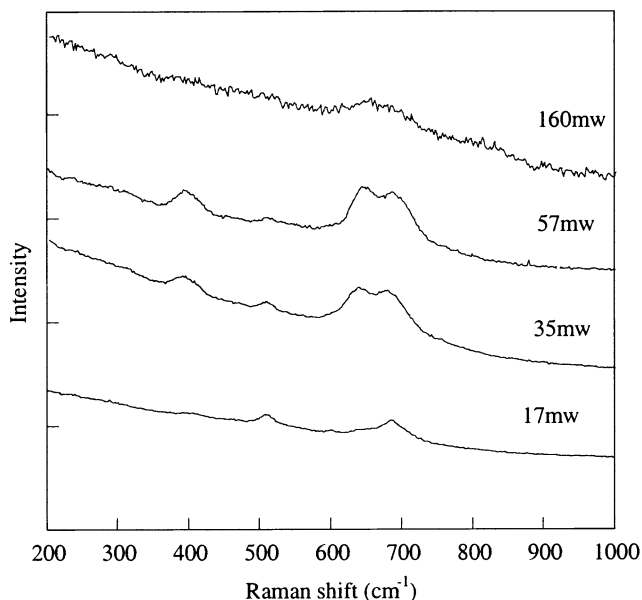


FIG. 2. Raman spectra of ZnCr_2O_4 spinel collected at elevated temperatures at one atmosphere.

Fig. 2. Upon elevation of laser power, the intensity of the peak at 642 cm^{-1} is significantly enhanced. In analogy with the Raman results on MgAl_2O_4 by Cynn *et al.* (8), we suggest that this peak originates from the increase of the degree of the disorder of Zn^{2+} and Cr^{3+} over the two crystal sites. The two weak modes at 567 and at 804 cm^{-1} still remain unclear. Taking into account that the sample was prepared by a high-temperature procedure, they most likely result from a partial disorder in the sample. Among the vibrational symmetry species involving Cr ions, the stretching modes of Cr–O–Cr have been observed at 500 – 850 cm^{-1} (20). This may also represent a plausible interpretation for the above two modes.

Figure 3 shows the Raman spectra of ZnCr_2O_4 spinel at high pressures and at room temperature. We observed that, upon elevation of pressure to 17.5 GPa , new additional peaks start to arise, whereas the initial modes of the spinel phase reduce in their intensities. At a pressure of 35 GPa , all peaks belonging to the spinel structure completely disappear. The pressure dependences of all Raman modes are plotted in Fig. 4. Among these Raman peaks of the spinel phase, the two low-wavenumber modes (F_{2g} and E_g) exhibit pressure dependences of 2.05 and $2.67\text{ cm}^{-1}\text{ GPa}^{-1}$; three high-wavenumber modes (two F_{2g} and one A_g) exhibit the pressure dependences of 4.07 , 4.11 and $4.61\text{ cm}^{-1}\text{ GPa}^{-1}$, respectively. The highest wavenumber mode at 1051 cm^{-1} has a pressure dependence of $2.59\text{ cm}^{-1}\text{ GPa}^{-1}$. Such an observation implies that a phase transformation starts to occur at 17.5 GPa , and is complete at about 35 GPa^{-1} . This new phase exhibits different pressure dependences in all the observed Raman modes as compared to those of the spinel

phase. The two strong modes have the pressure dependences of 1.85 and $1.06\text{ cm}^{-1}\text{ GPa}^{-1}$, respectively, whereas the weak mode has a pressure shift of $0.13\text{ cm}^{-1}\text{ GPa}^{-1}$. The coexistence of two phases over a wide range of pressure of 17.5 – 35 GPa suggests a sluggish mechanism in this pressure-induced phase transformation. The disappearance of the strong peak at 1051 cm^{-1} upon phase transformation can also imply the occurrence of a high Zn–O coordination (> 4) after the disappearance of the ZnO_4 species. If this mode is really caused by an impurity, the peak at 1051 cm^{-1} should be expected to remain. In this case, the possibility of an impurity in the sample can be excluded.

Figure 3 also reveals the pressure-induced enhancement of the intensity of the Raman peak at 642 cm^{-1} . Correlating

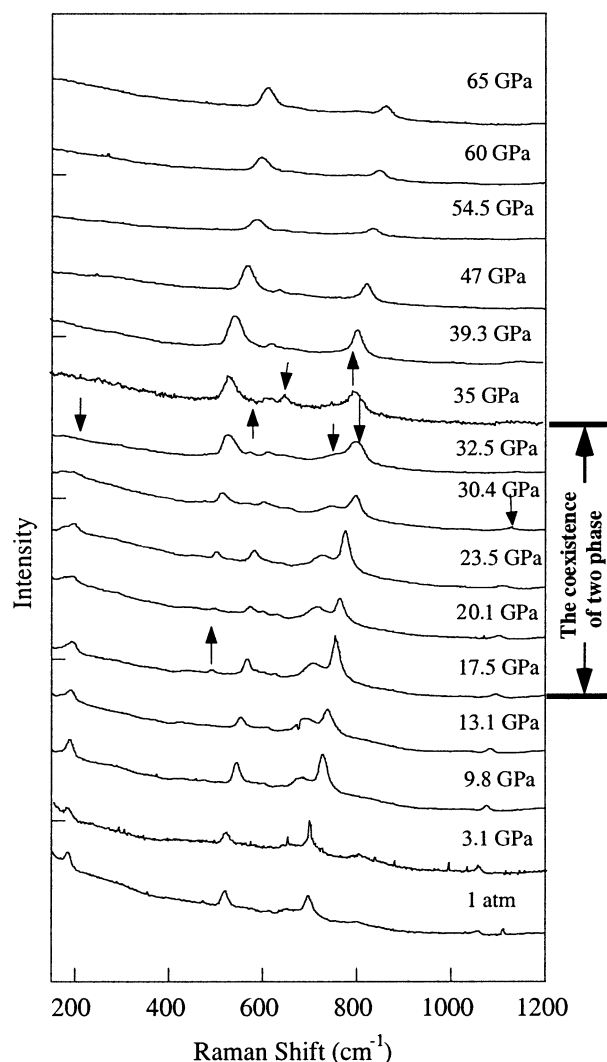


FIG. 3. Raman spectra of ZnCr_2O_4 spinel collected up to pressures of 70 GPa at room temperature. The downward arrow (\downarrow) and upward arrow (\uparrow) represent the disappearance of the peaks of the initial phase and the appearance of the peaks of the new phase, respectively.

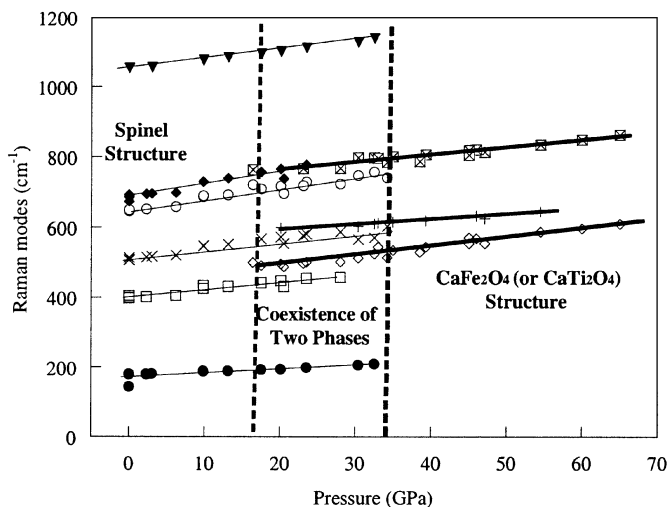


FIG. 4. The pressure dependences of Raman modes observed from the spinel phase and from the high-pressure phase of ZnCr_2O_4 .

this observation with the Raman results on the spinel MgAl_2O_4 at elevated temperatures and the corresponding interpretations (8), it is suggested that pressure may play a similar role, which also results in a significant disorder of Zn^{2+} and Cr^{3+} ions over the two atom occupancies in the spinel structure. However, even the possibility of the pressure-induced diffusion of defects cannot be excluded. When such a disorder or defect-diffusion effect approaches a certain limit in the spinel ZnCr_2O_4 upon elevation of pressure, a new phase starts to crystallize. A sluggish mechanism upon phase transformation also supports such an explanation, in which the diffusion mechanism of defects leads to a wide range of pressure for the coexistence of the two phases. Controversially, if a diffusionless kinetics upon phase transformation exists, the Raman spectra should exhibit an abrupt change at a certain pressure (corresponding to the transition pressure). Such a phenomenon has been observed in the pressure-induced olivine-spinel phase transformation in $(\text{Mg,Fe})_2\text{SiO}_4$ (21).

Catti *et al.* (14) have carried out a series of *ab initio* simulations on pressure-induced phase transformations of Cr-bearing spinels ($M\text{Cr}_2\text{O}_4$; $M = \text{Zn, Mg, Mn}$). This simulation predicts that ZnCr_2O_4 spinel dissociates to the mixture of ZnO and Cr_2O_3 at pressures over 34 GPa. Previous studies indicate that ZnO crystallizes in the wurtzite structure at ambient conditions, which remains stable up to 9 GPa, and then transforms to a rocksalt structure (B_1) phase at pressures larger than 9 GPa (22). Cr_2O_3 is stable in the corundum (Al_2O_3) structure at pressures < 30 GPa, and then likely transforms to a new Rh_2O_3 -II phase with moderate spectroscopic evidence (23). Raman analyses on high-pressure phases of ZnO and Cr_2O_3 indicate that the rocksalt ZnO phase is silent in Raman vibrations, and that the high-pressure phase of Cr_2O_3 exhibits a few Raman

active modes (23). In comparison with our high-pressure Raman spectra, no Raman peak is in coincidence with those of either the corundum phase or the high-pressure polymorphism of Cr_2O_3 . Therefore, we are quite confident that ZnCr_2O_4 spinel directly transforms to a single high-pressure phase without any compositional dissociation.

Based on the high-pressure studies in which MgAl_2O_4 crystallizes in a perfect spinel structure, this compound undergoes a phase transformation at pressures above 25 GPa, with a similar structure to that of calcium ferrite (CaFe_2O_4) or calcium titanite (CaTi_2O_4) structure (24, 25). Difference between the spinel structure and these two types of structures can be found with atomic arrangements denser in the two new high-pressure phases (Fig. 5). In these two high-density structures, the coordination around the cations is higher compared to the spinel, and Ca^{2+} is observed in a dodecahedral site (CaO_8), whereas Fe and Ti ions are found in octahedral sites. A more compact three-dimensional network is formed by edge- and corner-sharing octahedra, with hollow channels parallel to the c -axis, where the Ca cations are located. The difference between these denser structures lies in a slight modification of the polyhedral linkage, which results in the presence of two types of FeO_6 octahedral sites in CaFe_2O_4 , and a more symmetric CaO_8 polyhedron in CaTi_2O_4 . The CaFe_2O_4 and CaTi_2O_4 structures belong to the D_{2h}^{16} ($Pnam$) and D_{2h}^{18} ($Cmcm$) space groups, respectively. The unit cell consists of four formula units ($Z = 4$). According to group theory, one should expect four types of Raman active modes ($A_g, B_{1g}, B_{2g}, B_{3g}$) and three types of IR active modes (B_{1u}, B_{2u} and B_{3u}). On the basis of the correlation between the Raman active modes of

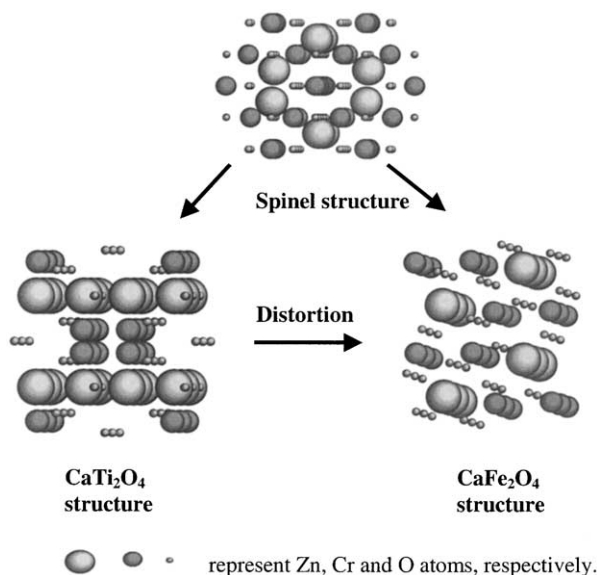


FIG. 5. The schematic view of three structures: spinel, CaTi_2O_4 and CaFe_2O_4 .

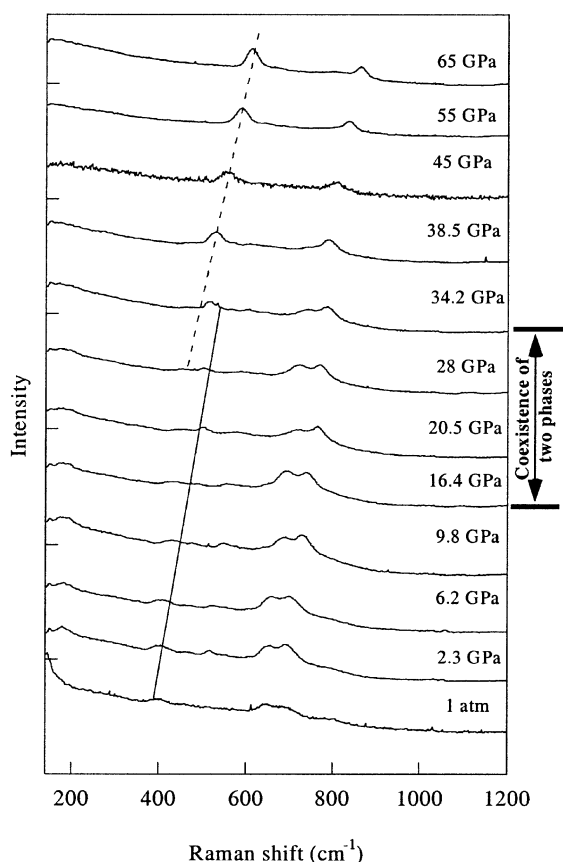


FIG. 6. Raman spectra of ZnCr_2O_4 collected upon release of pressure to ambient conditions.

the two point groups (O_h and D_{2h}), the A_{1g} and E_g modes in the O_h representations transform to the A_g modes in the D_{2h} representation, and the F_{2g} modes transform to the $B_{1g} + B_{2g} + B_{3g}$ modes. As observed in ZnCr_2O_4 , the parallel behavior of the new mode at 800 cm^{-1} and the A_g mode of the spinel upon pressure increase and decrease allows us to assume that the mode at 800 cm^{-1} is of A_g symmetry. Two additional new modes, at 550 and 600 cm^{-1} , exhibit similar behavior. They correlate to the F_{2g} spinel mode and as such they should have $B_{(1,2,3)g}$ symmetry. The structure assignment upon the above analysis has been confirmed by the recent X-ray diffraction data (unpublished data).

As shown in Fig. 6, the Raman spectra of ZnCr_2O_4 were also collected upon release of pressure. A pressure of about 35 GPa corresponding to the inverse phase transformation from the CaFe_2O_4 (or CaTi_2O_4) structure to the spinel phase was observed to be the same as that observed at the compression run (Fig. 3). It can be concluded that the high-pressure CaFe_2O_4 (or CaTi_2O_4) phase is unquenchable as pressure decreases. Upon release of pressure to 32 GPa , a spinel phase was recovered, and remains stable up to ambient conditions. However, it is noted here that the recovered spinel ZnCr_2O_4 exhibits neither the weakness of

the mode at 642 cm^{-1} nor the appearance of the mode at 1051 cm^{-1} (Fig. 6). Such an observation may imply that the recovered spinel ZnCr_2O_4 does not include the ZnO_4 groups, and in turn, may suggest the existence of an inverse ZnCr_2O_4 spinel structure, in which Zn ions are incorporated in the octahedral sites. It is suggested that the pressure-induced effect leads to a final phase with an inverse spinel structure, differing from the initial spinel phase with a normal spinel structure.

CONCLUSION

A Raman spectroscopic study was carried out to explore the pressure-induced phase transformation in ZnCr_2O_4 spinel up to pressures of 70 GPa . The ZnCr_2O_4 spinel starts to transform to the CaFe_2O_4 (or CaTi_2O_4) structure at a pressure of 17.5 GPa . Upon elevation of pressure to $\sim 35\text{ GPa}$, the spinel-to- CaFe_2O_4 (or CaTi_2O_4) phase transformation is complete. The sluggish nature of the transition may originate from a diffusion-controlled kinetics. Temperature and pressure play important roles in the order-disorder (or defect diffusion) effect of Zn^{2+} and Cr^{3+} ions over the tetrahedral and octahedral sites in the spinel structure. Upon decompression, a new phase with an inverse spinel structure was recovered.

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