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An in situ Raman spectroscopic study of pressure induced dissociation of spinel $NiCr_2O_4$

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Abstract

An in situ Raman spectroscopic study was conducted to investigate the pressure induced phase transformation of spinel $NiCr_2O_4$ to pressures of 57.1 GPa. Results indicate that $NiCr_2O_4$ spinel dissociates to the mixture of Cr_2O_3 and NiO at 13.1 GPa. Such a dissociation is complete at 25.1 GPa. The coexistence of Cr_2O_3 and NiO remains up to the peak pressure of 57.1 GPa. Upon release of pressure to 33.3 GPa, the Cr_2O_3 starts to react with NiO to form the spinel phase, and such a reaction is complete at 18.9 GPa. The recovered spinel phase may exhibit an inverse spinel structure, which differs from the initial normal spinel structure. Combined with the results obtained from other end member chromites, it is suggested that the variation of high-pressure behavior of chromites (ACr_2O_4) significantly depends on the average A–O bond length of the A–O tetrahedron.
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Keywords: C. Raman spectroscopy; A. Ceramics; D. Phase transformation; E. High-pressure

1. Introduction

Spinel with general formula AB_2O_4 has a cubic structure with the crystal group *Fd*3*m* [1,2]. There are two types of spinel structures at ambient conditions: the normal and inverse spinel. In the ideal normal spinel, A and B ions occupy the tetrahedral (T) and octahedral sites (M), respectively; in the inverse spinel, half of the B ions enter the fourfold coordination, with the consequent migration of all the A ions to the octahedral sites [3,4]. A variety of studies have been conducted to investigate the pressure induced phase transformations of the spinels to date [3,5–9]. Results reveal two types of high-pressure behaviors in the spinel solids: one undergoes a pressure induced phase transformation from the spinel structure to its single high-pressure polymorph [3,5,8,9]; another dissociates to the mixture of the constituent oxides [5,6].

Due to the geophysical interest, previous high-pressure investigations only focused on the particular spinels, mostly relevant to the constituents of the Earth's interior, including Fe, Mg, Al, Si, and Ge [5,8,9,10]. With these scare data, it is hard to obtain a complete understanding of the high-pressure behavior of these spinels. From the viewpoint of the technique, a pressure reached by the traditional large compress apparatus is quite low and far from the critical pressure of the phase transformation [5]. Even though advancements of the diamond anvil cell (DAC) techniques allow one to reach several orders of magnitude in pressure, low resolutions of the old techniques, however, were not able to detect the pressure induced phase variation, possibly leading to a wrong conclusion. In particular, a pressure induced peak extinction effect often happens, most likely originating in a misinterpretation of an order phase as the occurrence of amorphization. Chromites are considered as a significant spinel system with potential applications in fields ranging from applied physics, material sciences to geophysics [6]. Due to the large ionic radii of the Cr cation, it is expected that the phase transformation occur at lower

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pressure relative to that in other spinel solids. Thus, below the peak pressure of the pressure induced spectroscopic extinction, the possible phase transformation in chromites, similar to that found in several studied spinels [5], might be able to be observed using the current techniques, particularly Raman spectroscopy [11,12]. So far, one ab initio calculation has been conducted to investigate the phase transformation of the chromites [6], and the simulation predicts that the chromites dissociate to their constituent oxides at high-pressure and at room temperature. But, those results are not consistent with recent pressure Raman investigations on $ZnCr_2O_4$ and $MgCr_2O_4$ spinel, whereby a pressure induced phase transformation from the spinel structure to the single high-pressure polymorph was observed [11,12]. Such a disagreement implies that the transition mechanism suggested by the theoretical simulation is not critical. Therefore, a systematical study is needed to provide clarity.

From the chemical formula of chromites (ACr_2O_4), the remarkable distinction between the end member chromites can be found in variation of the A ion of the AO_4 tetrahedron. The substitution of the A cation can lead to a significant modification of the AO_4 tetrahedron, which is simply shown by the variation of the average A–O bond length. The noticeable evidence caused by such a variation can be identified by the change of the compressibility of tetrahedron, which in turn impacts the elasticity of the two octahedra, ultimately inducing modification of the whole spinel structure [1,4,13]. On the basis of the above analyses, the pressure induced phase relations are expected to differ between the end member chromites. In previous pressure studies on the end member chromites, including $CdCr_2O_4$, $ZnCr_2O_4$ and $MgCr_2O_4$, a pressure induced phase transformation from the spinel structure to the single polymorph was observed [5,11,12]. This effect most likely originates from the existence of the longer average A–O bond length of the AO_4 tetrahedron. Thus, if the cation A of the AO_4 tetrahedron is substituted by one with the shorter average A–O bond length, such as Ni^{2+}, it could be expected to exhibit novel high-pressure behavior, most likely resulting in a pressure induced compositional dissociation. To test the reliability of such a hypothesis, we are motivated to investigate the pressure induced phase transformation of spinel $NiCr_2O_4$ for comparison. In this study, an in situ Raman spectroscopic study was conducted to pressures as high as 57.1 GPa with the DAC at room temperature. The results and discussion are presented in detail later.

2. Experimental procedure

The $NiCr_2O_4$ sample was synthesized by a high temperature solid reaction with a stochiometric mixture of analytical grade NiO and Cr_2O_3, which was heated and maintained at a temperature of 1200 °C for 24 h with a gas fugacity of $CO/CO_2 = 3.297$ [14]. X-ray diffraction and Raman spectroscopy indicate that $NiCr_2O_4$ crystallizes in a cubic spinel structure.

High-pressure Raman measurements were conducted at room temperature by using a gasketed high-pressure DAC and Raman spectrometer in the back scattering configuration. Ti^{3+}: sapphire laser pumped by an argon ion laser was tuned at 785 nm, in which the strong fluorescence of diamond was effectively suppressed. To avoid a heating effect, lasers were operated at 3 mW (after filer) to excite the sample, which keeps in direct touch with the tips of the low fluorescence diamonds. Raman spectra were collected by using high throughput holographic imaging spectrograph with volume transmission grating, holographic notch filter and thermoelectrically cooled CCD detector with the resolution of $4 \, cm^{-1}$ [15,16]. The spectrometer was regularly calibrated with the well-known neon lines. Pressures were determined by the calibrated ruby R_1 peak [17]. The sample was placed in a 301 stainless steel gasket hole 62 μm in initial thickness and 120 μm in diameter with a few ruby chips as pressure makers. The laser beam was focused on the sample with a spot size of 5 μm. To avoid a chemical reaction between the sample and the ruby, the exposed spot on the sample is only close to the ruby chip, in which the pressure difference does not exceed ± 0.5 GPa between the pressure of the focused sample spot and the exactly measured pressure. A 15 min exposure time was used to collect the Raman spectrum at each run.

3. Results and discussions

$NiCr_2O_4$ spinel has a cubic structure belonging to the space group $O_h^7(Fd3m)$. It contains 32 equivalent oxygen anions in a site with point symmetry $3m$, having coordinates (u, u, u). One Ni and two Cr cations of one $NiCr_2O_4$ formula are arranged in a tetrahedral (T) site and two octahedral (M) sites, respectively. T site has point symmetry $\bar{4}3m$, multiplicity 8 and coordinates $(0,0,0)$; M site has point symmetry $\bar{3}m$, multiplicity 16 and coordinates $(1/2,1/2,1/2)$. A full description of spinel structure geometry includes cell edge, u, T–O and M–O bond distances, a tetrahedral unshared edge, an octahedral unshared edge, an octahedral edge shared with other octahedra, and an octahedral O–M–O angle. The above structural description indicates that the full unit cell with eight formulas of $NiCr_2O_4$ contains 56 atoms, but the smallest Bravais cell consists only of 14 atoms ($Z = 2$). Therefore, one should expect 42 vibrational modes. The factor group analysis predicts the following modes in spinel $NiCr_2O_4$:

$$A_{1g}(R) + E_g(R) + F_{1g} + 3F_{2g}(R) + 2A_{2u}$$

$$+ 2E_u + 4F_{1u}(IR) + 2F_{2u}$$

There are five Raman active modes ($A_{1g} + E_g + 3F_{2g}$), and all of them are observed at ambient conditions, as shown in

Table 1
Observed Raman modes of three end member chromites including $NiCr_2O_4$, $MgCr_2O_4$, $ZnCr_2O_4$ at ambient conditions, and their assignment and pressure shifts

Chromite	$NiCr_2O_4$		$MgCr_2O_4$		$ZnCr_2O_4$	
Symmetry	Observed modes (cm^{-1})	Pressure shift (cm^{-1}/GPa)	Observed modes (cm^{-1})	Pressure shift (cm^{-1}/GPa)	Observed modes (cm^{-1})	Pressure shift (cm^{-1}/GPa)
F_{2g}	181	5.81	227	–	180	2.05
E_g	425	3.70	447	1.98	430	2.67
F_{2g}	511	1.96	544	2.66	511	4.07
F_{2g}	580	3.11	614	3.38	605	4.11
A_{1g}	686	2.67	687	3.01	687	4.61
	796	1.21	792	–	804	–

Note: Data of $MgCr_2O_4$ and $ZnCr_2O_4$ are from Wang et al. [11,12], respectively and data of $NiCr_2O_4$ are from this study.

Table 1 and Fig. 1. One broad mode was observed at 796 cm^{-1}. Taking into account that the second-order scattering is typically 10–100 times weaker than the first-order one, and that the contributions of the second-order mode throughout the Brillouin zone usually lead to an broad Raman character, the peak at 796 cm^{-1} can, thus, be reasonably assigned to an overtone mode [12]. Compared to our studies on $MgCr_2O_4$ and $ZnCr_2O_4$ spinel, $NiCr_2O_4$ spinel exhibits all expected first-order Raman peaks, which have the wavelengths almost same as those of the two studied spinels (Table 1) [11,12]. Such a result may be logically explained from the structural factor by the substitution of the A cation of AO_4 tetrahedron. From the viewpoint of the spinel structure, the substitution of cation A does not originate in a significant variation of the M–O distance of the octahedron [18]. This can be found in which the T site has $\bar{4}3m$ symmetry with six equivalent unshared edges and no angular freedom, and consequently in which the cation in the T site can only modify the T–O distance. On the contrary, cations entering the M site can modify not only the M–O distance but also the octahedral angle, because the M site has $\bar{3}m$ symmetry with six unshared edges, pertaining to the faces perpendicular to the threefold axis, and six shared edges; the octahedral angle O–M–O (O–O is a shared edge) is 90° only for $u = 1/4$.
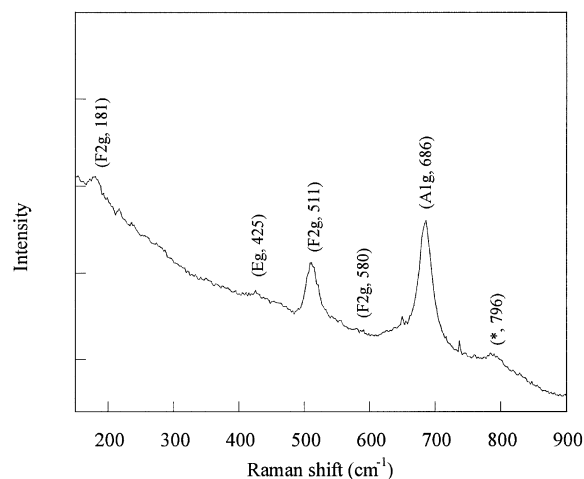

Fig. 1. Raman spectra of $NiCr_2O_4$ spinel collected at ambient conditions. All the peaks are marked with the frequencies and factor assignments.
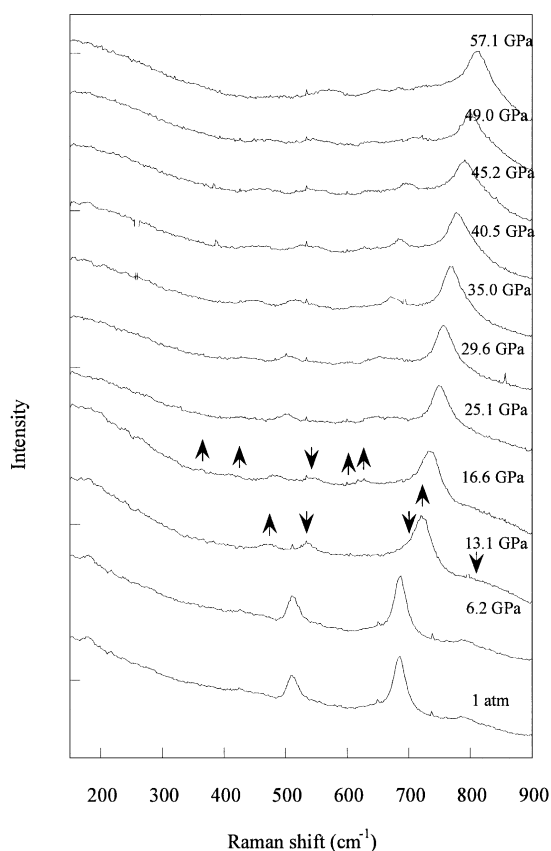

Fig. 2. Raman spectra of $NiCr_2O_4$ spinel collected to pressures of 57.1 GPa at room temperature. The downward (↓) and upward arrows (↑) represent the disappearance (or weakening) of the Raman modes of spinel phase and the occurrence of the Raman modes of the new phase, respectively.

Table 2
Comparison of Raman data between three observed phases

Spinel structure			Al$_2$O$_3$ structure ($R3c$)			Rh$_2$O$_3$ (II) structure		
Observed modes at 1 atm (cm^{-1})	Symmetry	Recovered phase at 1 atm (cm^{-1})	Previous data at 1 atm (cm^{-1})	Symmetry	Previous data at 16.6 GPa (cm^{-1})	Previous data at 16.6 GPa (cm^{-1})	Observed modes at 16.6 GPa (cm^{-1})	Recovered phase at 16.6 GPa (cm^{-1})
181	F_{2g}	181	235	E_g	–	–		
425	E_g	411	266	A_{1g}	–	–		390
511	F_{2g}	507	296	E_g	286	286	321	
580	F_{2g}	580	350	E_g	365	360	410	460
		639				415	485	540
686	A_{1g}	685	529	E_g	572	490	589	601
796		795	554	A_{1g}	598	568	624	702
			615	E_g	694	595	735	
						691		

Note: Previous data of the two polymorphs (Al$_2$O$_3$ and Rh$_2$O$_3$ II) of Cr$_2$O$_3$ are from Mougin et al. [19]. The other data are from this study.

Among the end member chromites, the significant variation is reflected only in the cations of the AO$_4$ tetrahedra, rather than those of octahedra, because the octahedra are taken only by the Cr ions. Therefore, this may represent the favorable interpretation on the appearance of the similar wavelength modes in those end member chromites (Table 1).

Fig. 2 shows the Raman spectra of NiCr$_2$O$_4$ spinel at high-pressure and at room temperature. Upon elevation of pressure, the observed Raman modes exhibit the pressure dependences ranging from 1.21 to 5.81 cm^{-1}/GPa (Table 1). At a pressure of 13.1 GPa, two strong proceeding modes at 511 and 686 cm^{-1} became weak, and consequently disappeared at 25.1 GPa. Simultaneously, several additional modes start to arise clearly at 321, 410, 485, 589, 624 and 735 cm^{-1} at 16.6 GPa, respectively, exhibiting different pressure shifts relative to those of the spinel phase (Table 2). Such a noticeable observation suggests that NiCr$_2$O$_4$ spinel undergoes a phase transformation at the pressure range of 13.1–25.1 GPa. This can be easily recognized from Fig. 3, plot with the pressure shifts of the observed Raman modes. Furthermore, those observed modes initially giving rise at a pressure of ~16.6 GPa remain stable to the peak pressure of 57.1 GPa.

Catti et al. have conducted a series of ab initio calculations on the pressure induced phase transformations of the Cr-bearing spinels (MCr$_2$O$_4$: M = Zn, Mg, Mn) [6]. This simulation predicts that the three end member chromites dissociate to the mixture of their constituent oxides (MO + Cr$_2$O$_3$), in which the transition pressures are 15.7–18.8 GPa in MgCr$_2$O$_4$, 19.6–22.7 GPa in MnCr$_2$O$_4$ and 30.7–34.7 GPa in ZnCr$_2$O$_4$, respectively. Therefore, it is expected that NiCr$_2$O$_4$ spinel may also dissociate to the mixture of NiO and Cr$_2$O$_3$. However, our recent pressure Raman studies on MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ indicate that those
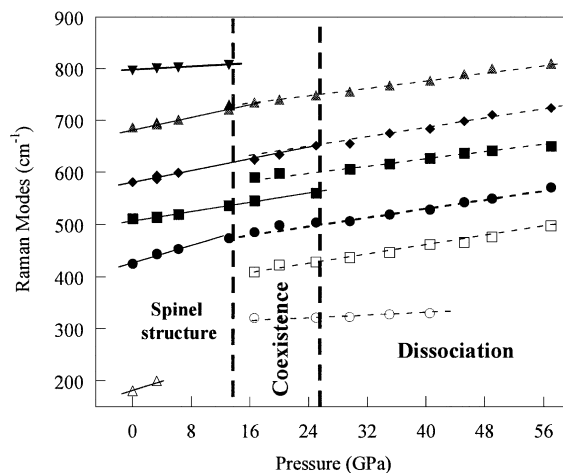

Fig. 3. The pressure dependences of the Raman modes observed from NiCr$_2$O$_4$ upon elevation of pressure.

two spinels transform to a single high-pressure polymorph with either a $CaFe_2O_4$ or $CaTi_2O_4$ structure [11,12], rather than a predicted decomposition. As seen from the composition, the difference among the end member chromites is reflected only in the variation of the cation A of the AO_4 tetrahedron. Combination of the theoretical simulation and experimental investigations allows one to assume that the high-pressure behavior of chromite may significantly depend on the variation of the average A–O bond length of the AO_4 tetrahedron. As for the $NiCr_2O_4$ spinel, the average A–O bond length of the NiO_4 tetrahedron is typically shorter than others, including MgO_4, CdO_4 and ZnO_4 tetrahedron. Thus, the $NiCr_2O_4$ spinel may exhibit the high-pressure behavior differing from $MgCr_2O_4$, $CdCr_2O_4$, and $ZnCr_2O_4$ spinel [5,11,12].

In the pressure Raman studies, only two and three remarkable Raman modes were observed in the corresponding high-pressure polymorph of $MgCr_2O_4$ and $ZnCr_2O_4$ spinel, respectively, [11,12]. The pressure dependences of the observed modes obviously differ from those of the spinel phase. With group factor theory and the transformation relation to the spinel structure, the observed high-pressure polymorph was logically assigned to either the $CaFe_2O_4$ or $CaTi_2O_4$ structure. In this study, six Raman modes were observed in the newly formed phase of $NiCr_2O_4$ at a pressure of 16.6 GPa. Hence, a novel high-pressure behavior differing that of $MgCr_2O_4$ and $ZnCr_2O_4$ is expected to response the pressure induced phase transformation of the spinel $NiCr_2O_4$. As combined the theoretical simulation to this study, it is most likely that $NiCr_2O_4$ spinel dissociates to the mixture of NiO and Cr_2O_3. Numerous high-pressure studies indicate that NiO and Cr_2O_3 crystallize in the rocksalt (B_1) and the corundum (Al_2O_3) structure at one atmosphere, respectively [19,20]. The high symmetry with the cubic structure leads NiO to be Raman inactive [20], whereas the relative low symmetry with the hexagonal group originates in the occurrence of seven Raman active modes ($2A_{1g} + 5E_g$) in Cr_2O_3 [19]. Upon elevation of pressure, NiO stabilizes in the B_1 structure at least to 140 GPa [20]; the corundum polymorph of Cr_2O_3 transforms to the Rh_2O_3 (II) structure at pressures above 13 GPa [19]. The group factor theory predicts that the Rh_2O_3 (II) polymorph of Cr_2O_3 could exhibit 30 Raman modes ($7A_g + 8B_{1g} + 8B_{2g} + 7B_{3g}$), but only six modes were observed in the pioneering Raman study [19]. Difference between the two polymorphs of Cr_2O_3 can be found in which the two additional modes appear at 415 and 490 cm^{-1} in the Rh_2O_3 (II) polymorph at 16.6 GPa, relative to the Al_2O_3 polymorph (Table 2). In this study, two modes at 410 and 485 cm^{-1} were observed at 16.6 GPa, in good agreement with the finding in the Rh_2O_3 (II) polymorph (Table 2). Therefore, it is reasonable to assume that pressure significantly induces the breakdown of the spinel $NiCr_2O_4$ at a pressure of 16.6 GPa, which results in the crystallization of the orthorhombic Rh_2O_3 (II) polymorph of Cr_2O_3 and the cubic NiO phase (Figs. 2 and 3).
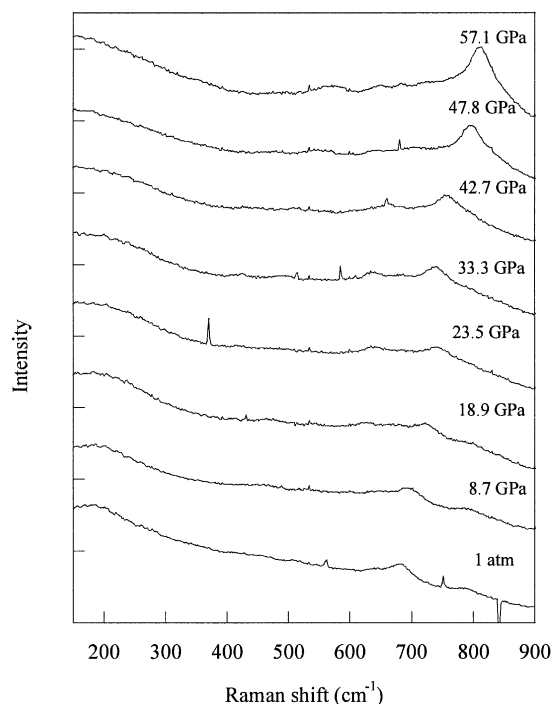

Fig. 4. Raman spectra of $NiCr_2O_4$ collected upon release of pressure to ambient conditions. The very sharp peaks are due to the high noises.

Upon release of pressure, the Raman spectra of $NiCr_2O_4$ were also collected, as shown in Fig. 4. The pressure shifts of the observed Raman modes are plotted in Fig. 5. The significant variation can be found in the pressure range of 18.9–33.3 GPa. Such a noticeable variation may imply that a pressure induced phase
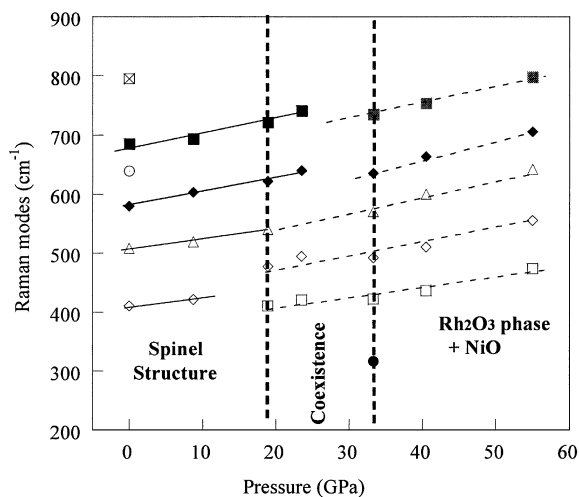

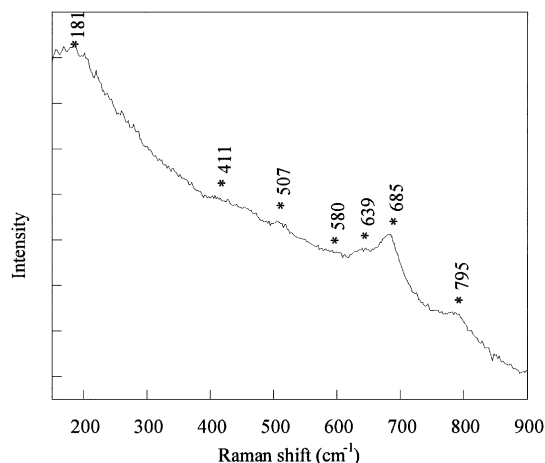Fig. 5. The pressure dependences of the Raman modes observed from $NiCr_2O_4$ upon release of pressure.

Fig. 6. The Raman spectra of the recovered spinel NiCr$_2$O$_4$ at ambient conditions.

transformation takes place at the above pressure range. As compared to the Raman spectra of spinel NiCr$_2$O$_4$ and the Rh$_2$O$_3$ (II) polymorph of Cr$_2$O$_3$, this phase transformation can correspond to the crystallization of spinel NiCr$_2$O$_4$ in term of the recombination of NiO and Cr$_2$O$_3$. It is mentioned here that the transition pressure range of this reverse phase transformation is somewhat higher than that of the normal phase transformation in the compressed run. Such a difference may be reasonably explained by the variation of stress states between the compressed and decompressed runs. With increasing pressure, a large pressure gradient may lead to a significant reduce of transition pressure, but upon release of pressure, a relax effect usually occurs and correspondingly result in a decrease of pressure gradient across the sample chamber, ultimately originating in an enhancement of the transformation pressure. At ambient conditions, seven Raman modes were observed (Fig. 6 and Table 2), in which six modes are in good agreement with those of the starting spinel phase. However, one additional broad mode at 639 cm^{-1} was found nearby the high frequency A$_{1g}$ mode at 685 cm^{-1}. Such a Raman peak was also found in ZnCr$_2$O$_4$ and MgAl$_2$O$_4$ spinel [11,22]. Based on the temperature Raman studies [11,22], the disorder effect of the two metal cations in the tetrahedral and tetrahedral sites was significantly enhanced by increasing temperature, consequently resulting in the appearance of one mode nearby the high frequency A$_{1g}$ mode [11,22]. Moreover, such an effect was also observed in the pressure Raman investigation of ZnCr$_2$O$_4$ spinel [11], in which an inverse structure spinel was found in the recovered ZnCr$_2$O$_4$ phase at ambient conditions. Therefore, it is reasonable to assume that the NiCr$_2$O$_4$ spinel at pressure-quenched conditions could have a large ratio of disorder of Ni and Cr cations over the octahedral and tetrahedral sites, implying the formation of an inverse spinel structure.

Such a finding in NiCr$_2$O$_4$ which differs from that in MgCr$_2$O$_4$ and ZnCr$_2$O$_4$ spinel casts a question in which factor exactly causes such a noticeable difference between the pressure induced phase transformations of the end member chromites. To this end, a systemic investigation is needed. As viewed from the structure and composition of the end member chromites, the significant characteristic can be found in the tetrahedral site (AO$_4$) [2], in which the substitution of A cation of the AO$_4$ tetrahedron may cast a crucial constraint on the pressure induced phase transformation. The obvious evidence can be seen from the variation of the average A–O bond lengths of the AO$_4$ tetrahedra among the end member chromites (ACr$_2$O$_4$). Thus, the most possibility resulting in such a noticeable difference may be due to the cation-A-induced effect. The relationship between the high-pressure behavior of the end member chromites and the average A–O bond radii of the AO$_4$ tetrahedron were shown in Fig. 7. As observed in the previous studies, upon phase transformation from the spinel structure to the high-pressure polymorph, the AO$_4$ coordination of the spinel was significantly increased to the AO$_6$ coordination [3,21]. Thus, the promising response might be obtained by comparing the average A–O bond lengths of the AO$_4$ tetrahedron to that of CrO$_6$ octahedron of the spinel. It can be found from Fig. 7 that, when the average A–O bond radius of the AO$_4$ tetrahedra are close or longer than that of the CrO$_6$ octahedron, the corresponding end member chromite transforms to the single high-pressure polymorph; otherwise, the corresponding one breaks down to its constituent oxides, such as the finding in NiCr$_2$O$_4$. In the case of the first type of chromites, with increase in
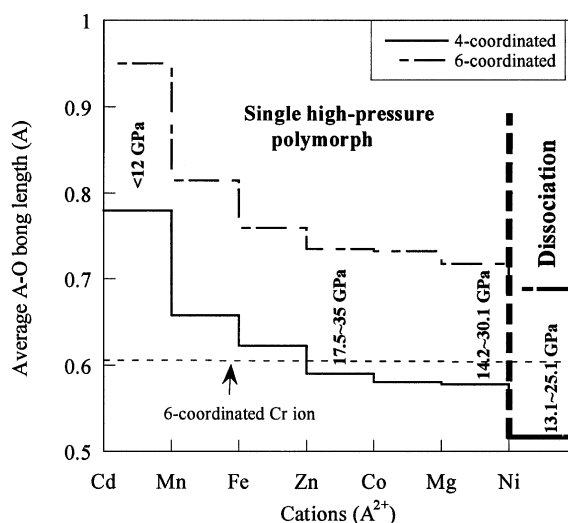

Fig. 7. The schematic of relationship between the high-pressure behaviors of the end member chromites and their average A–O bond radius of the AO$_4$ tetrahedra. Data are from this study and Refs. [1,2,5,11,12]. As for comparison, the data of the six coordinated ionic radius are also plotted.

the average A–O bond length of the AO_4 tetrahedron, the transition pressure was somewhat elevated. Thus, it can be predicted that the Fe-, Mn- and Co-bearing chromites most likely transform to the single high-pressure polymorph at the pressure range of 12–30 GPa. However, the detailed experimental studies are still needed to judge such a prediction.

4. Conclusion

An in situ Raman spectroscopic study was carried out to explore the pressure induced phase transformation in $NiCr_2O_4$ spinel to pressures of 57.1 GPa. $NiCr_2O_4$ spinel initially dissociates to the mixture of Cr_2O_3 and NiO at a pressure of 13.1 GPa. Such a decomposition is complete at 25.1 GPa, and then remains stable to the peak pressure of 57.1 GPa. Upon release of pressure, a reverse phase transformation was found at the pressure range of 18.9–33.3 GPa, whereby the newly formed spinel phase coexists with the constituent oxides of NiO and Cr_2O_3. At ambient conditions, the obtained spinel phase exhibits a large ratio of disorder of Ni and Cr cations over the octahedral and tetrahedral sites. Moreover, the high-pressure behavior of chromites significantly depends on the average A–O bond lengths of the AO_4 tetrahedra in the spinel chromites. As compared to the Cr cation in the CrO_6 octahedron, the chromites with the similar or longer ionic radius transform to the single high-pressure polymorph. Otherwise, the chromites dissociate to the mixture of their constituent oxides.

Acknowledgments

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