

# Spectroscopic study of the vibrational modes of magnesium nickel chromite, $\text{Mg}_x\text{Ni}_{1-x}\text{Cr}_2\text{O}_4$

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## ABSTRACT

Raman and infrared spectroscopy were performed on synthesized spinel oxide powders of solid solution  $\text{Mg}_x\text{Ni}_{1-x}\text{Cr}_2\text{O}_4$ , over the full range of composition  $0 \leq x \leq 1$ , to determine the dependence of the vibrational modes on the divalent cation, which occupies the tetrahedral site of the normal spinel lattice. X-ray diffraction shows a nearly linear change in the lattice parameter of the solid solution. Our data agree with literature values for the pure chromites,  $\text{NiCr}_2\text{O}_4$  and  $\text{MgCr}_2\text{O}_4$ . Solid solution data are reported here for the first time. All observed vibrational modes exhibit one-mode behavior and increase in wavenumber when nickel is replaced by magnesium. The wavenumbers of the highest-wavenumber Raman mode,  $A_{1g}$ , and the two higher-wavenumber infrared modes,  $\nu_1$  and  $\nu_2$ , do not significantly change with substitution of the divalent cation, while the lower-wavenumber Raman and infrared modes are affected by this cation substitution on the tetrahedral site. The  $E_g$  and  $F_{2g}(1)$  modes exhibit a nonlinear increase in wavenumber.

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## 1. Introduction

Metal oxides adopting the spinel structure,  $\text{AB}_2\text{O}_4$ , named after the gemstone spinel,  $\text{MgAl}_2\text{O}_4$ , are important materials of technological and geological interest.  $\text{MgCr}_2\text{O}_4$  refractories are important to the steel, cement, and copper industries [1,2]. Magnesiocromite,  $\text{MgCr}_2\text{O}_4$ , is also an important component of spinel in upper mantle peridotites. Other common geological spinels are  $\text{MgAl}_2\text{O}_4$ ,  $\text{FeCr}_2\text{O}_4$ , and  $\text{Fe}_3\text{O}_4$ . Nickel chromite,  $\text{NiCr}_2\text{O}_4$ , is a common product in the oxidation of high nickel alloys [3–5].

Investigation of the vibrational modes of  $\text{Mg}_x\text{Ni}_{1-x}\text{Cr}_2\text{O}_4$  can provide experimental data necessary to test theoretical models. Theory is in good agreement with experiment for the vibrational modes of pure spinels [6–8]. However, less work has been performed on solid solutions. Gupta et al. calculated the vibrations of mixed chalcogenide spinels, and found agreement between theory and experimental data [9]. Wakamura et al. modeled the one- and two-mode behavior of the vibrational modes of  $\text{Zn}_{1-x}\text{Cd}_x\text{Cr}_2\text{S}_4$  [10]. Calculations on  $\text{Cu}_x\text{Mg}_{1-x}\text{Cr}_2\text{O}_4$  by Sinha show good agreement with the two higher-wavenumber infrared modes [11]. However, these calculations disagree with the experimental data for the  $\nu_3$  mode.

The spinel structure belongs to the cubic space group  $Fd\bar{3}m$ . The unit cell, shown in Fig. 1, contains 56 atoms, while the smallest

asymmetric unit contains just 14 atoms. There are 42 normal modes at the Brillouin zone center: three  $F_{1u}$  acoustic modes and 39 optical modes, belonging to the symmetry species

$$\Gamma = A_{1g}(\text{R}) + E_g(\text{R}) + F_{1g} + 3F_{2g}(\text{R}) + 2A_{2u} + 2E_u + 4F_{1u}(\text{IR}) + 2F_{2u}, \quad (1)$$

where (R) and (IR) denote Raman-active and infrared-active vibrational species, respectively. Both  $\text{NiCr}_2\text{O}_4$  and  $\text{MgCr}_2\text{O}_4$  are normal spinels [12], with  $\text{Mg}^{2+}$  or  $\text{Ni}^{2+}$  cations occupying the tetrahedral sites and  $\text{Cr}^{3+}$  cations occupying the octahedral sites, though  $\text{NiCr}_2\text{O}_4$  exhibits a tetragonal distortion below 310 K [13–15]. Spinel having +2 and +3 cations are denoted II–III spinels. All oxygen anions within the spinel lattice are bonded to a single tetrahedral cation and three octahedral cations.

Earlier work by Waldron assumes that the primitive cell of spinel was composed of two tetrahedral  $\text{AO}_4$  units and a  $\text{B}_4$  unit [16]. White and DeAngelis share this assumption for their factor group analysis of spinel, which shows that the trivalent cations constructing the  $\text{B}_4$  unit remain stationary during all vibrations [17]. Many other researchers also make this assumption in assigning all vibrational modes to motions involving the  $\text{AO}_4$  unit [18–21]. However, as Preudhomme and Tarte show in their series of infrared studies on spinels, although only the tetrahedral cations may be involved in the actual motion of vibration, the assumption that higher-wavenumber vibrations are most influenced by the tetrahedral A–O bond may be incorrect, and the octahedral B–O bond may be the main contributor to these vibrations [22]. Gupta et al. show that the octahedral bond is more influential than the tetrahedral, for some sulfides and

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selenides [6]. Recent calculations of Co, Mn, and Zn chromites also report a larger B–O force constant [23,24].

The  $\text{Mg}_x\text{Ni}_{1-x}\text{Cr}_2\text{O}_4$  series provides a good opportunity to examine how substitution of the divalent cation affects the Raman and infrared modes of this normal II–III spinel system.  $\text{Cr}^{3+}$  has a greater preference for the octahedral site [25] and occupies this site for all  $x$  in the series.

## 2. Experimental setup

The Raman microscope system uses a Lexel Ramanlon krypton ion laser (647.1 nm) as the excitation source for most spectra. A Spectra-Physics Beamlok argon ion laser (514.5 nm) was also used as an excitation source for two additional spectra of  $\text{NiCr}_2\text{O}_4$  and  $\text{MgCr}_2\text{O}_4$ . A Nikon MM-40 measuring microscope creates a backscattering geometry, focusing the laser beam onto the sample and collecting the scattered light. This light is filtered by a Jobin-Yvon TRIAX 550 monochromator with a 1200 lines/mm grating blazed at 500 nm, and detected by a Princeton Instruments Spec-10 liquid-nitrogen-cooled CCD. The resolution of the system is  $3.5\text{ cm}^{-1}$ . The Raman system is calibrated using emission lines from a neon lamp.

Infrared data were acquired with a Varian FTS FTIR spectrometer fitted with a photoacoustic detector. Three of the four infrared-active vibrational modes are reported here. The lowest-wavenumber infrared mode, reported by Preudhomme and Tarte at  $182\text{ (253)}\text{ cm}^{-1}$  for  $\text{NiCr}_2\text{O}_4$  ( $\text{MgCr}_2\text{O}_4$ ) [22] is below the  $375\text{ cm}^{-1}$  limit of the FTIR system.

X-ray diffraction data were acquired with a Bruker AXS D8 Advance diffractometer equipped with a Johansson-type primary monochromator. The X-ray source is the  $\text{K}\alpha_1$  emission line of a copper source, with wavelength  $1.54063\text{ \AA}$ . Diffraction spectra were calibrated using a silicon powder standard mixed with the sample. Topas software was used for the Rietveld refinement.

## 3. Sample preparation

Synthesis of the spinels closely follows a simple combustion method [26]. Stoichiometric amounts of metal nitrates are mixed with urea and a small amount of water in a 100 ml beaker. The solution is then placed in a  $375\text{ }^\circ\text{C}$  furnace for 15–20 min. The reaction produces a light, fragile foam which is crushed into a

powder. All samples were synthesized twice to check for consistency of the combustion reaction.

The spinel structure of the synthesized powder is confirmed using XRD, and the lattice parameter of the cubic unit cell is determined. All samples contain less than 3% of the corundum-phase  $\text{Cr}_2\text{O}_3$ . The lattice parameters,  $a$ , of the end member chromites agree well with the literature values, as shown in Table 1.

$\text{NiCr}_2\text{O}_4$  exhibits a tetragonal distortion to space group  $I4_1/amd$  below a temperature of approximately 310 K [13–15]. This phase transition has a relatively large temperature range in which cubic and tetragonal phases coexist [15,28,29]. XRD patterns of the powder sample show that these two phases occur in a cubic:tetragonal ratio of approximately 3:1. The lattice parameter of the spinel phase of the  $\text{NiCr}_2\text{O}_4$  sample is reported in Table 1. The  $c/a$  ratio of the tetragonal phase is 1.020, in agreement with previous work indicating the coexistence of both phases [15,28]. Only the  $\text{NiCr}_2\text{O}_4$  sample,  $x=0$ , exhibits this tetragonal distortion.

The lattice parameter of the entire  $\text{Mg}_x\text{Ni}_{1-x}\text{Cr}_2\text{O}_4$  series, shown as a function of  $x$  in Fig. 2, increases as the nickel is replaced by magnesium. The increase in the lattice parameter is nearly linear, given (in Ångstroms) by:  $y=8.31882(9) + 0.02054(4)x - 0.00506(4)x^2$ , where  $x$  is the magnesium content in  $\text{Mg}_x\text{Ni}_{1-x}\text{Cr}_2\text{O}_4$ .

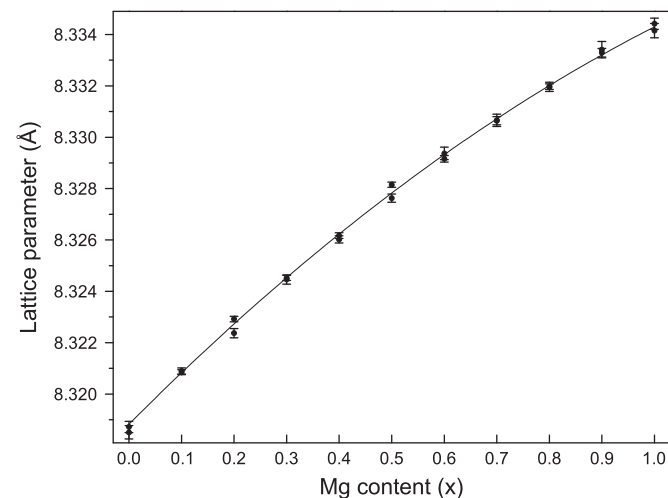
## 4. Results and discussion

Four Raman spectra were acquired for each sample in order to check spectral uniformity throughout the powder. Reported Raman peak positions and linewidths are averaged from the four spectra. The Raman spectra of the  $\text{Mg}_x\text{Ni}_{1-x}\text{Cr}_2\text{O}_4$  series can be seen in Fig. 3. Table 2 shows the agreement with the literature for the Raman modes of the end members,  $\text{NiCr}_2\text{O}_4$  and  $\text{MgCr}_2\text{O}_4$ . All five expected Raman vibrations are detected in the  $\text{Mg}_x\text{Ni}_{1-x}\text{Cr}_2\text{O}_4$  series, though some modes are difficult to

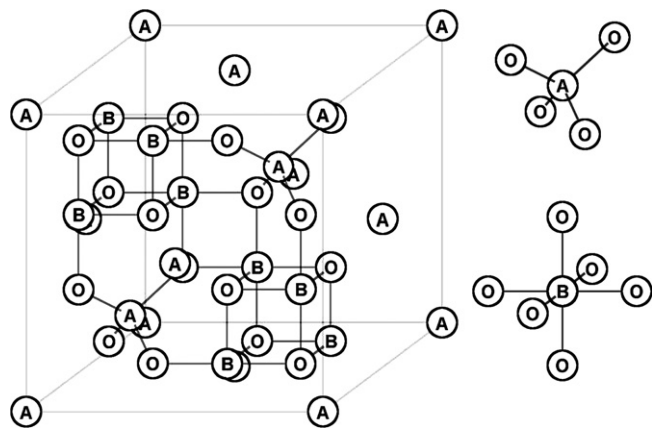
**Table 1**

Lattice parameters (in Ångstroms) of synthesized  $\text{MgCr}_2\text{O}_4$  and  $\text{NiCr}_2\text{O}_4$ . Numbers in parentheses represent error in the last digit.

Spinel	This work	Literature [12,27]
$\text{NiCr}_2\text{O}_4$	8.3186(2)	8.3186
$\text{MgCr}_2\text{O}_4$	8.3343(3)	8.3341



**Fig. 2.** Lattice parameters of  $\text{Mg}_x\text{Ni}_{1-x}\text{Cr}_2\text{O}_4$  as a function of magnesium content,  $x$ .



**Fig. 1.** The unit cell of the  $\text{AB}_2\text{O}_4$  normal spinel lattice contains 56 atoms. To simplify the image, only the front half of the unit cell interior is shown. The  $\text{A}^{2+}$  and  $\text{B}^{3+}$  cations occupy the tetrahedral and octahedral sites, respectively, in the lattice.  $\text{AO}_4$  and  $\text{BO}_6$  units are contained throughout the lattice and are displayed beside the unit cell.

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