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LETTER TO THE EDITOR

Cation migration and magnetic ordering in spinel CoFe$_2$O$_4$ powder: micro-Raman scattering study

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Abstract
Micro-Raman scattering was used to characterize spinel CoFe$_2$O$_4$ at high temperature up to 870 K and under an external magnetic field up to 6.0 kOe. It was found that the rapid increase in the linewidth of the Raman modes was related to the inter-site cation migration starting at $\sim$390 K. A red-shift of the Raman peaks induced by the magnetic ordering was observed upon applying a magnetic field at room temperature. Phase analysis of CoFe$_2$O$_4$ powder was also carried out by means of x-ray diffraction and micro-Raman spectroscopy in this work.

As an important candidate for use in magnetic and magneto-optical recording media, spinel CoFe$_2$O$_4$, a cubic ferromagnetic oxide with high coercivity, moderate saturation magnetization, as well as remarkable chemical stability and mechanical hardness, has been extensively studied [1–4]. Spinels can be divided into two kinds according to their structures. One is ‘normal’ spinel, with all the divalent (A) cations on the tetrahedral (T-) sites and the trivalent (B) cations on the octahedral (O-) sites, which can be represented by the formula A(BB)O$_4$. The other is ‘inverse’ spinel, B(AB)O$_4$, in which the divalent cations occupy the O-sites and the trivalent cations are equally divided among the T- and remaining O-sites. CoFe$_2$O$_4$ is predominantly an inverse spinel with formula

Co$_x$Fe$_{1-x}$((Co$_{1-x}$Fe$_{1+x}$))O$_4$ (with $x \to 0$)

where $x$ is the cation distribution factor which describes the fraction of tetrahedral sites occupied by Co$^{2+}$ cations [5]. As is well known, uniaxial anisotropy with high remanence ratio, which makes spinel CoFe$_2$O$_4$ more promising as a permanent magnetic material, can be induced by magnetic annealing [6]. Several models have been proposed including the ion migration model, in which the distribution of the cations is changed, i.e. Co ions migrate from O-sites to T-sites while irons migrate from T-sites to O-sites. However, the mechanism governing the formation of uniaxial anisotropy still needs further investigation. Ion migration in spinel
CoFe$_2$O$_4$ has also been experimentally studied by Mössbauer spectroscopy [7]. However, the poor resolution caused by the severe overlapping of the T-site and O-site peaks in Mössbauer spectroscopy forbids a detailed study. As a powerful tool for lattice and structural study, Raman spectroscopy may provide useful information on the cation migration in spinel CoFe$_2$O$_4$.

Due to its high sensitivity to many lattice effects, such as structure transition [8], lattice distortion [9], charge–lattice and spin–lattice couplings [10], local cation ordering [11], and magnetic ordering [12], Raman scattering is uniquely suited for probing magnetic oxides. However, to the best of our knowledge, no Raman scattering study has been carried out for CoFe$_2$O$_4$. In this work, we carried out an in situ micro-Raman scattering study of CoFe$_2$O$_4$ powder between 300 and 870 K, and under an external magnetic field (up to 6.0 kOe).

The CoFe$_2$O$_4$ powder was prepared by co-precipitation and further calcination at 1300°C for 2 h in air. The structure and phase purity of the calcined powder was characterized using x-ray diffraction (XRD). Scanning electron microscopy (SEM) was employed for characterization of the morphology of spinel CoFe$_2$O$_4$ powder. All micro-Raman spectra were measured in the backscattering geometry using a Spex 1702/04 Raman spectrometer with an Olympus microscope attachment and equipped with a liquid-nitrogen-cooled CCD detector. The 488 nm line of an argon-ion laser was used as the excitation source. The spot size of the laser on the sample is ~1 µm in diameter. The in situ high-temperature Raman experiments were carried out using a TMS 93 Linkam thermal stage capable of maintaining temperature over the range between 300 and 870 K.

Figure 1(a) shows the XRD pattern of the CoFe$_2$O$_4$ powder. Six peaks at 2θ angles of 29.9°, 35.2°, 42.8°, 53.3°, 56.7°, and 62.3° were observed, corresponding to the (220), (311), (400), (422), (511), and (440) planes of the polycrystalline CoFe$_2$O$_4$ spinel structure respectively [13]. The appearance of these diffraction peaks demonstrates that single-phase polycrystalline CoFe$_2$O$_4$ powder can be formed by calcination of the precursor derived from the co-precipitation process.

Figure 1(b) shows the SEM micrograph of CoFe$_2$O$_4$ powder. As shown, some small protrusions, assumed to be Fe$_2$O$_3$ in the previous study [5], appeared at the CoFe$_2$O$_4$ grain boundaries. In order to identify whether they are of the second phase (Fe$_2$O$_3$), a micro-Raman scattering study was carried out by critically focusing the laser beam on these protrusions. Because of the small spot size of the laser (~1 µm), we were able to focus the laser exclusively on the protrusions. Noting the fact that Fe$_2$O$_3$ has strong and sharp Raman peaks at ~240 and ~300 cm$^{-1}$ [14] that are stronger than those of CoFe$_2$O$_4$, we would have no problem in identifying them if the protrusions were of Fe$_2$O$_3$. Our Raman results indicate that these protrusions are of CoFe$_2$O$_4$, not Fe$_2$O$_3$.

CoFe$_2$O$_4$ has a cubic inverse-spinel structure with O$^7_h$ (Fd$3$m) space group, which gives rise to 39 normal modes:

$$\Gamma = A_{1g} + E_g + F_{1g} + 3F_{2g} + A_{2u} + 2E_u + 4F_{1u} + 2F_{2u},$$

where five optic modes are Raman active ($A_{1g} + E_g + 3F_{2g}$) and four are infrared active (4$F_{1u}$) [15]. Figure 2(a) (bottom spectrum) shows the Raman modes of spinel CoFe$_2$O$_4$ powder at room temperature. Due to the polycrystalline nature of the CoFe$_2$O$_4$ powder, polarized measurements were not performed and the assignments of all degenerate irreducible representations to each of the Raman-active modes were also not carried out. According to the previous study [16], we assigned the highest-frequency Raman mode at 695 cm$^{-1}$ to the T-site mode, which reflects the local lattice effect in the tetrahedral sublattice, and the peak at 470 cm$^{-1}$ to the O-site mode, which reflects the local lattice effect in the octahedral sublattice. This is consistent with the Raman study on Fe$_3$O$_4$ [8], in which the T-site mode is found at 670 cm$^{-1}$, and NiFe$_2$O$_4$ [18], with the T-site mode at 701 cm$^{-1}$ and the O-site mode at 585 cm$^{-1}$.
Figure 2(a) also shows the in situ high-temperature Raman spectra of CoFe$_2$O$_4$ powder. Over the temperature range between 300 and 870 K, the only obvious change is the dramatic increase in linewidth of the Raman peaks at elevated temperature. In order to study the lattice effect in the CoFe$_2$O$_4$ polycrystalline phase, a least-squares fit with the Lorentzian line-shape was used to fit the Raman peaks of the T-site and O-site modes. Figure 2(b) shows the fitted full width at half-maximum (FWHM) as a function of temperature. Interestingly, the FWHM of the two modes increased only slightly over the low-temperature range between 300 and 370 K and started to increase rapidly from 32 cm$^{-1}$ at 370 K to 38 cm$^{-1}$ at 410 K for the T-site mode and from 48 to 55 cm$^{-1}$ for the O-site mode. This tendency of increasing FWHM with increase of temperature remained, though at a slower rate, and the FWHMs at 870 K are 1.66 times (T-site) and 1.48 times (O-site) their initial values at room temperature. The normal anharmonic effect on the phonon linewidth alone does not explain the unusual increase of FWHM with increasing temperature, in particular the rapid increase observed at $\sim$390 K. Considering the cation migration in spinel CoFe$_2$O$_4$ [7], the T-site Fe$^{3+}$ ions can migrate from T- to O-sites while the same number of Co$^{2+}$ ions move from O- to T-sites, and this inter-site cation migration must break the long-range cation order and introduce disorder at both the T-site and O-site sublattices at the same time. Thus, the result derived from the in situ micro-Raman scattering indicates the existence of local disorder induced by cation migration in spinel CoFe$_2$O$_4$ at elevated temperatures. Taking into account the laser heating effect on the sample surface, the starting temperature $\sim$390 K for cation migration in our experiments agrees well with the previous result ($\sim$450 K) [7]. Furthermore, the high degree of cation migration at $\sim$600 K,
Figure 2. (a) In situ Raman spectra of spinel CoFe$_2$O$_4$ powder between 300 and 870 K, and (b) the FWHM of the Raman modes as a function of temperature. The sharp peaks below 400 cm$^{-1}$ are plasma lines of the argon-ion laser source (in both cases).

consistent with the reported temperature [6], can be of significant assistance in explaining the formation of uniaxial anisotropy in magnetic annealing, where the cobalt–ferrite particles could be aligned by the magnetic field. The broadening of Raman peaks caused by local disorder has been well studied for several materials, e.g. PbBi$_2$Nb$_2$O$_9$ [17], Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$ [11], and NiFe$_2$O$_4$ [18].

Figure 3(a) shows the Raman spectra of CoFe$_2$O$_4$ powder under an external magnetic field (up to 6.0 kOe) at room temperature. The spectra present only slight changes in Raman peak positions. The frequencies of the T-site mode and the O-site mode are obtained by curve fitting and the results are shown in figure 3(b), which shows a monotonic decrease in frequency for both the T-site and O-site modes with increasing magnetic field strength. As reported in the previous work [19], this softening of Raman modes is strongly related to the magnetic ordering induced by an external magnetic field. The results shown in figure 3(a) serve as supporting evidence for magnetism–lattice coupling in spinel CoFe$_2$O$_4$. Further experimental and theoretical work is needed to fully understand the Raman scattering of spinel CoFe$_2$O$_4$.

In conclusion, spinel CoFe$_2$O$_4$ powder has been investigated using in situ high-temperature and magnetic micro-Raman scattering. The inter-site cation migration was successfully
Figure 3. (a) Raman spectra of spinel CoFe$_2$O$_4$ powder under an external magnetic field and (b) the frequency of the Raman modes as a function of magnetic field.

demonstrated by the increase in linewidth of the Raman modes at elevated temperature. Upon applying a relatively weak external magnetic field at room temperature, the frequencies of Raman modes decreased due to the magnetic-field-induced magnetic ordering. Considering both the cation migration at elevated temperature and the magnetic ordering under an external magnetic field, this work is helpful in the understanding of the mechanism underlying the formation of uniaxial anisotropy by magnetic annealing. The results of this work may be extended to other inverse spinels. These results also show that Raman spectroscopy can be a useful probe for optical diagnostics of ferromagnetic oxides.

References