Spin–phonon coupling in multiferroic YbMnO$_3$ studied by Raman scattering

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Abstract

Hexagonal YbMnO$_3$ bulk polycrystals were prepared and studied by Raman scattering in the temperature range of 15–300 K. A total of 15 phonon modes of A$_1$, E$_1$ and E$_2$ type were identified. Some E$_2$ phonon modes showed anomalous temperature variations in frequency at $T_N \sim 80$ K, suggesting a coupling between the spin and phonon systems below T_N. As another evidence of spin–phonon coupling, softening of an A$_1$-phonon mode for the O–Mn vibration was observed at $\sim T_N$. Substitution of Mn by Al suggests this view.

1. Introduction

Rare-earth and yttrium manganites, RMnO$_3$, crystallize in hexagonal structures for R with smaller ionic radius (R = Ho, Er, Tm, Yb, Lu, Y) or in orthorhombic structures for larger ionic radius (R = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy) [1–3]. The hexagonal compounds show ferroelectricity and magnetic ordering simultaneously in the ordered phase, leading to a coupling effect called the magnetoelectric effect: the onset of magnetic ordering can be controlled by electric field and vice versa. Such materials, called multiferroics, have a high potential in opening a new field of innovative devices.

A hexagonal ferroelectric compound, YbMnO$_3$, shows complicated magnetic orderings below $T_N \sim 80$ K; Mn spins order antiferromagnetically in the c plane, while Yb spins show ferromagnetic ordering along the c axis, and these spin systems are mutually correlated [4]. In investigating the mechanism, characterization of lattice properties coupled with the magnetic orderings brings us rich information. Raman scattering is one of the powerful methods: lattice vibrations of Mn^{3+} in the c plane coupled with magnetic ordering have been observed in HoMnO$_3$ single crystals and YMnO$_3$ bulk polycrystals [5, 6]. More recently, similar behavior was observed in YbMnO$_3$ epitaxial films for the first time [7]. However, the reported phonon modes were limited to those observable by back scattering from the c plane and, furthermore, they were all relatively broad, making detailed frequency analysis difficult.

In order to investigate the effect of spin–phonon coupling more precisely, we observed here the temperature variation of
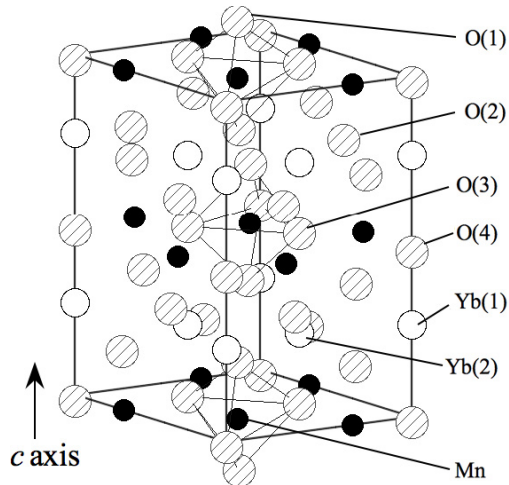

Figure 1. Crystal structure of hexagonal YbMnO$_3$.

the Raman spectra in YbMnO$_3$ bulk polycrystals. As a result, a greater number of sharp phonon peaks have been clearly observed than in previous film samples [7], and a more detailed phonon-mode assignment has been presented. At T_N, an anomalous frequency variation of some E$_2$-phonon modes due to spin–phonon coupling has been observed more clearly than in the film samples. Furthermore, we have observed softening of an A$_1$-phonon mode with decreasing temperature at $\sim T_N$. In RMnO$_3$ systems, to date, softening of phonon modes has
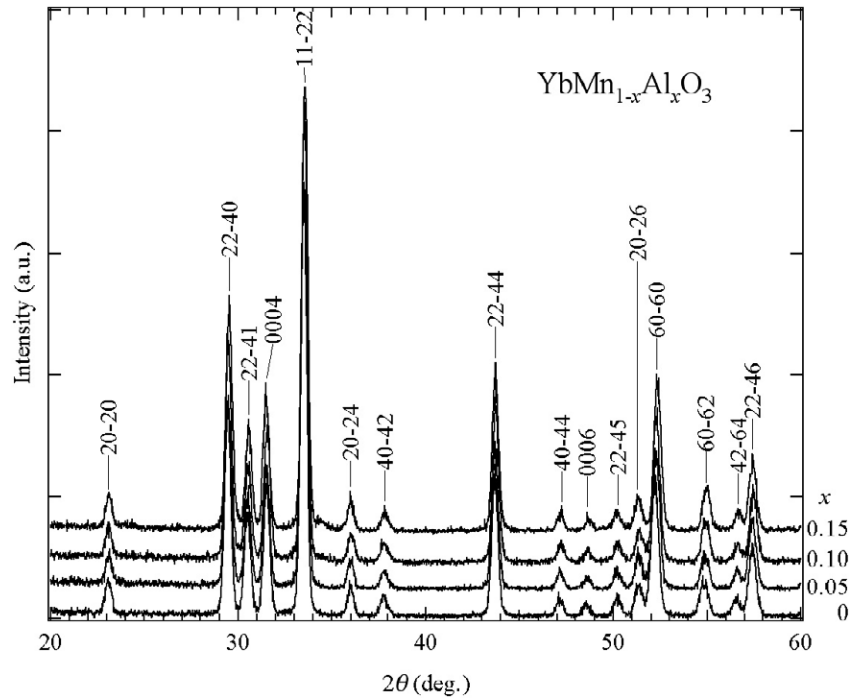
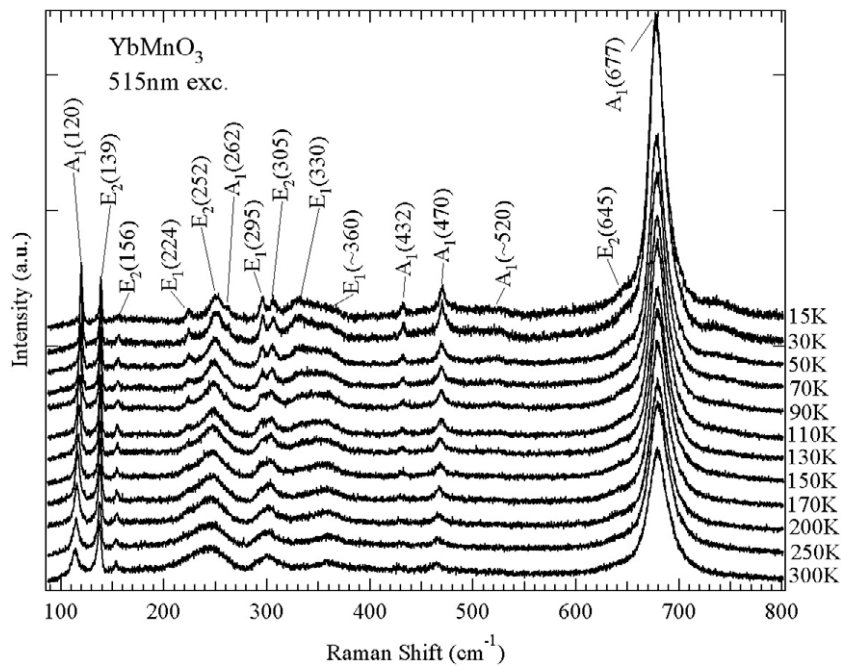**Figure 2.** XRD patterns of YbMn$_{1-x}$Al$_x$O$_3$ samples.

Figure 3. Raman spectra of YbMnO$_3$ at 15–300 K.

been observed only in orthorhombic systems and attributed to spin–phonon coupling due to phonon modulation of the superexchange integral of Mn^{3+} ions in the xz plane [8–11]. We expected a similar coupling mechanism in the present hexagonal YbMnO$_3$ system. To further investigate this point, we prepared YbMn$_{1-x}$Al$_x$O$_3$ bulk polycrystals, where Mn^{3+} ions in YbMnO$_3$ are partially substituted by a non-magnetic element Al, and observed the softening as a function of the Al content.

2. Experiment

Figure 1 shows the unit cell structure of hexagonal YbMnO$_3$ in the ferroelectric phase. This structure, which is a noncentrosymmetric system, belongs to the space group $P6_3cm$ (C$_{6v}^3$). The structure contains layers of corner-sharing MnO$_5$ bipyramids with a triangular base with nonequivalent O(3) and O(4) ions, whereas the O(1) and O(2) ions occupy the apical sites. The Mn–O(1) and Mn–O(2) bonds are slightly

tilted against the *c* axis. The Yb (1) and Yb(2) ions are located between the bipyramidal layers [12]. The elementary cell contains six formula units. There are 38 Raman-active phonon modes ($9A_1 + 14E_1 + 15E_2$) in the ferroelectric phase with possible TO–LO splitting for the A_1 and E_1 modes because of the induced dipole moment.

We prepared $YbMn_{1-x}Al_xO_3$ bulk polycrystals with $x = 0$, 0.05, 0.10 and 0.15 by a conventional ceramic process [13]: Yb_2O_3, Mn_2O_3 and Al_2O_3 powders were mixed and calcined at 1473 K. Then, the powders were smashed with a ball mill. The fine powders were pressed by one axis pressing and cold isotropic press methods. The ceramic compact was sintered at 1623 K. Figure 2 shows typical x-ray diffraction (XRD) patterns of $YbMn_{1-x}Al_xO_3$ samples observed at room temperature. It shows only the sharp peaks of $YbMnO_3$, indicating that the samples have high crystalline quality and no secondary phases. Each peak shows a systematic shift in the diffraction angle from $x = 0$ to 0.15, suggesting systematic substitution of Al, possibly, for the Mn site. The [0004] and [60$\bar{6}$0] diffraction peaks show that the *a* axis length decreases and the *c* axis length increases with increasing Al concentration.

For the Raman scattering measurement at 15–300 K, the samples were fixed to a cold finger of a closed-cycle He-gas cryostat. An Ar^+ gas laser was used at wavelength 514.5 nm for excitation. The laser beam was focused by a lens at the sample surface, and the scattered light was collected in a quasi-back-scattering geometry to a double monochromator of focal length 85 cm (SPEX 1403). The Raman spectra were detected by a liquid-nitrogen-cooled charge-coupled-device (CCD) camera. Since there are no mechanical movements of the monochromator during the observation of temperature variation of phonon spectra, we can make a precise comparison between the spectra for the spectral peak positions to within ~ 0.1 cm^{-1}. The calibration of Raman frequency was conducted by a standard Ne lamp with known line-spectral peak frequencies.

3. Results and discussion

Figure 3 shows the Raman spectra of a $YbMnO_3$ bulk polycrystal observed at 15–300 K. With the decrease of temperature from bottom to top, all the peaks become sharp and shift to higher frequencies. A total of 15 phonon peaks were clearly observed at low temperature, and classified to A_1, E_1 and E_2 modes with reference to the previous result for epitaxial films [7]. Four E_1 phonon modes were newly observed in this study. However, recalling that there are 38 Raman-active phonon modes ($9A_1 + 14E_1 + 15E_2$) in the ferroelectric phase, many phonon modes, mainly the E_1 and E_2 modes, are still left undiscovered. It is a remaining issue to complete the listing of the phonon frequencies.

By careful observation of figure 3, we find a peculiar temperature variation in some phonon peak frequencies. The E_2 mode at 252 cm^{-1} (at 15 K) is a representative case: figure 4(a) shows the variation in detail. As plotted in figure 4(b), the peak frequency shows an abrupt change of slope at around 80 K. Here, the dashed curves show theoretical
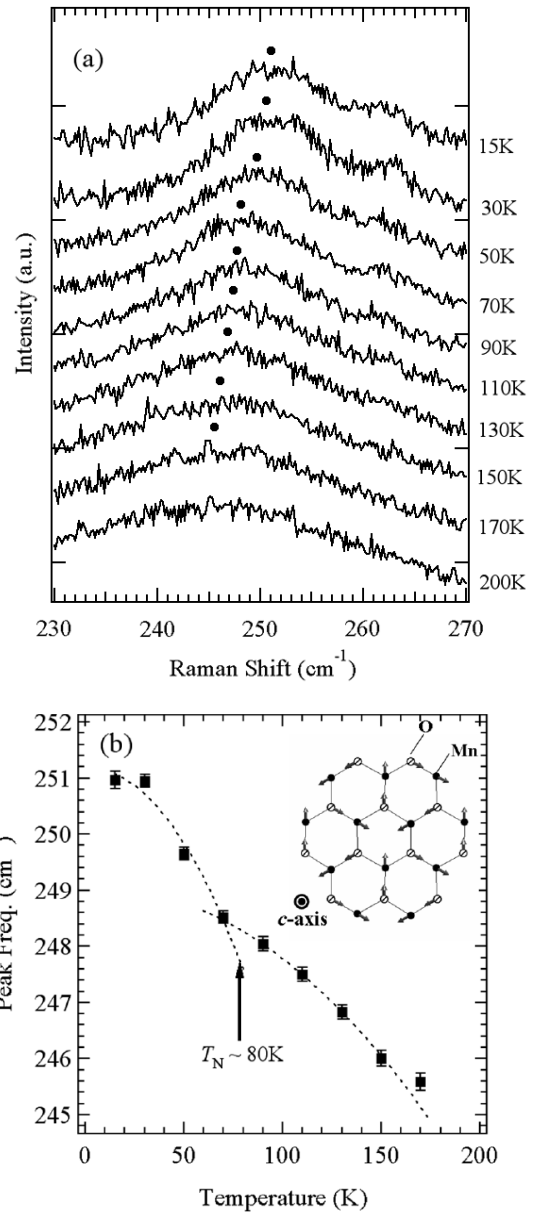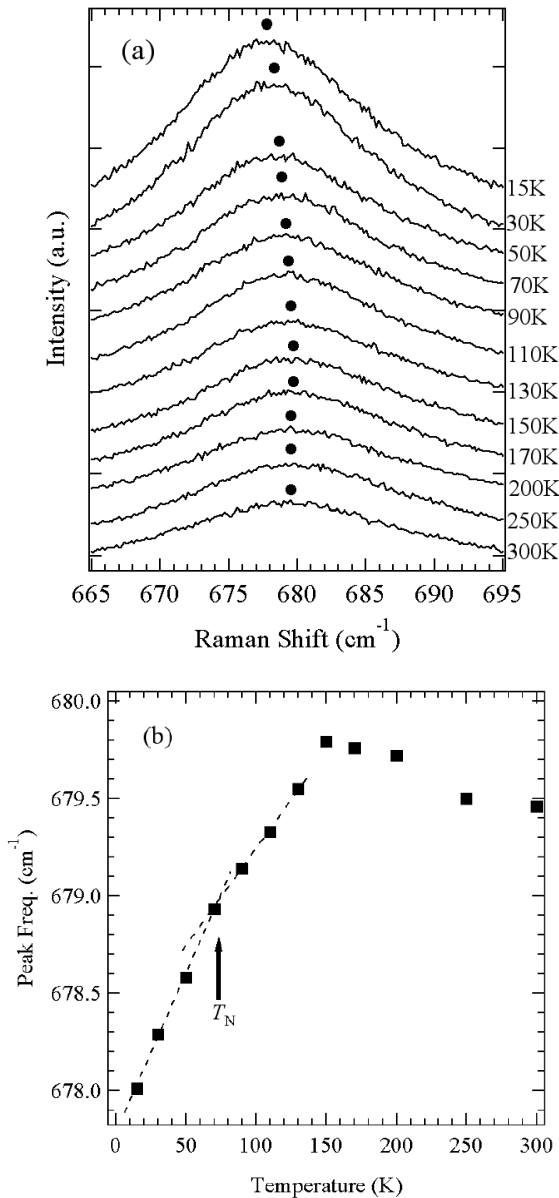

Figure 4. Temperature variation of the E_2 phonon at ~ 252 cm^{-1} in the $YbMnO_3$ sample. The dots in the raw spectra (a) show peak positions determined by curve fitting. Dashed curves in the peak-frequency plot (b) show theoretical fits to the data by considering anharmonic coupling effects up to four phonons. The inset shows ion displacements for the E_2 phonon mode [5].

fits to the phonon-frequency variation using a conventional formula considering anharmonic phonon coupling terms with up to four phonons [14],
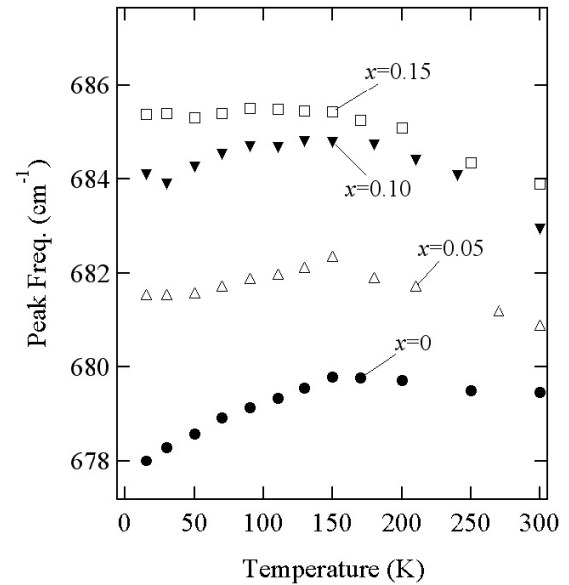
$$\omega(T) = \omega_0 + A\left[1 + \frac{2}{e^x - 1}\right] + B\left[1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2}\right] \quad (1)$$

where, $x = \hbar\omega_0/2kT$, $y = \hbar\omega_0/3kT$ with kT being the thermal energy, and A, B and ω_0 are fitting parameters. The observed anomalous variation at ~ 80 K cannot be described by a single theoretical curve. Similar anomalies have been observed in the isomorphic compounds, $HoMnO_3$ and $YMnO_3$ [5, 6]. The E_2 mode of $YbMnO_3$ at 252 cm^{-1}

Figure 6. Temperature variation of the frequency for the A_1 phonon at ~677 cm^{-1} in YbMn$_{1-x}$Al$_x$O$_3$ samples.

Figure 5. Temperature variation of the A_1 phonon at ~677 cm^{-1} in the YbMnO$_3$ sample. The dots in the raw spectra (a) show peak positions determined by curve fitting. Dashed curves in the peak-frequency plot (b) are guides to the eyes.

corresponds to a displacement of Mn and O ions in the c plane (see the inset of figure 4(b)) [5]. This mode effectively modulates the Mn–O–Mn bond angles and, hence, the Mn–Mn exchange interaction. Therefore, this anomalous behavior at ~80 K suggests an onset of spin–phonon coupling in the magnetically ordered phase. Compared to the YbMnO$_3$ epitaxial films [7], the anomalous behavior appears more clearly in bulk polycrystals. Furthermore, the E_2 mode at 305 cm^{-1} in figure 3, which is probably related to a displacement of O(1) and O(2) ions along the c axis and O(4) in the c plane [5], also shows an anomalous frequency variation at $T_N \sim 80$ K (not shown here). This is an indication of either a more complex mechanism of spin–phonon coupling or strong mixing of phonon modes as suggested by Iliev *et al* [15] in an orthorhombic ferromagnetic system.

The strong A_1 mode at 677 cm^{-1} in figure 3 shows a different kind of anomalous temperature variation as redrawn in figure 5(a) on an expanded frequency scale: on decreasing the temperature from 300 to 150 K, the mode frequency rises, as usually expected for phonons, as shown in figure 5(b). However, below ~150 K, a softening of the phonon mode occurs, and this feature becomes more pronounced below $T_N \sim$ 80 K. This feature is very similar to the results of orthorhombic RMnO$_3$ systems (R = La, Pr, Nd and Sm) [8–11]. For example, in PrMnO$_3$, the softening started at ~150 K, which is much higher than its T_N = 97 K, and the feature became more pronounced below T_N [11]. These orthorhombic compounds belong to the A-type antiferromagnets, where the Mn^{3+} spins are ferromagnetically ordered in the xz planes and antiferromagnetically coupled along the y direction. Granado *et al* explained the softening in terms of spin–phonon coupling by phonon modulation of the exchange integral [10]. Although the lattice and magnetic structures of hexagonal YbMnO$_3$ are very different from those of the orthorhombic RMnO$_3$ systems, we may expect a similar softening mechanism: the phonon frequency is effectively modulated by exchange interactions between Mn ions in the magnetically ordered phase.

To further investigate this point, we observed the softening behavior by substituting the Mn ions by a non-magnetic element of Al. Figure 6 shows the temperature variation of the peak frequencies in the A_1 modes for the series of YbMn$_{1-x}$Al$_x$O$_3$ bulk polycrystals. At 300 K, the peak frequencies rise with increasing Al content, supporting the systematic substitution of Al to the Mn sites. Although the softening is observed in all samples below ~150 K, the effect is clearly reduced with increasing Al content. It suggests that the softening is closely correlated to the magnetic ordering between Mn spins. The A_1 mode at 677 cm^{-1} includes a displacement of apical O ions along the c axis [5]. Therefore, our result suggests that the magnetic ordering

between Mn spins may cause lattice distortion of MnO_5 bipyramids and affects the apical O–Mn bond length. Further studies on this softening mechanism are expected.

4. Conclusion

Hexagonal $YbMnO_3$ bulk polycrystals were studied by Raman scattering in the temperature range of 15–300 K. A total of 15 phonon modes were observed and classified to A_1, E_1 and E_2 modes. Four E_1 phonon modes were newly observed in this study. Some E_2 phonon modes clearly showed an anomalous temperature variation in frequency at $T_N \sim 80$ K, suggesting a coupling between the spin and phonon systems below T_N. Furthermore, an A_1-phonon mode for apical O–Mn vibrations in the MnO_5 bipyramid structure showed softening at $\sim T_N$. This is further evidence of spin–phonon coupling in $YbMnO_3$. This view is supported by replacing Mn by Al ($YbMn_{1-x}Al_xO_3$), which weakened the softening.

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