Optical Studies on the Phase Transitions in YBaMn$_2$O$_6$ Single Crystals

Rea Divina Mero, Kirari Ogawa, Shigeki Yamada, and Hsiang-Lin Liu*

Cite This: ACS Omega 2021, 6, 22137–22150

ABSTRACT: The double perovskite YBaMn$_2$O$_6$ exhibited complex structural, magnetic, and charge/orbital ordering phase transitions. In this paper, we investigated the correlation between the temperature-dependent optical response and complex phase transitions of YBaMn$_2$O$_6$ single crystals through spectroscopic ellipsometry and Raman scattering spectroscopy. The room temperature optical absorption spectrum of YBaMn$_2$O$_6$ revealed three bands of approximately 1.50, 4.05, and 5.49 eV. The lowest optical absorption band was assigned to on-site d–d transitions in Mn ions, whereas the other two optical features were assigned to charge-transfer transitions between the 2p states of O and 3d states of Mn. The room temperature Raman scattering spectrum revealed 25 phonon modes. Notably, the MnO$_6$ octahedral tilting and bending modes between 360 and 440 cm$^{-1}$ increased in intensity at temperatures <200 K. Furthermore, several new phonon peaks appeared at temperatures <200 K, which were associated with charge ordering. Additionally, the magnetic order-induced changes were observed in the breathing modes, with reduced intensity of the 620 cm$^{-1}$ phonon peaks. The Jahn–Teller mode at approximately 496 cm$^{-1}$ exhibited strong hardening at temperatures <200 K, which indicated a linear correlation with the square of the magnetic susceptibility and thus revealed the occurrence of spin–phonon coupling. Anomalies in the phonon frequency, line width, and intensity observed near the phase transition temperatures highlighted the importance of lattice–charge–spin interactions in YBaMn$_2$O$_6$.

1. INTRODUCTION

The A-site-ordered double perovskites with a general formula of RBA$_{2}$Mn$_2$O$_6$, consist of alternately stacked layers of RO, MnO$_2$, and BaO along the c-axis. This creates a MnO$_6$ square sublattice sandwiched between two types of rock-salt layers (RO and BaO) with substantially different sizes depending on the R atom. When the temperature changes, complex regions of the charge/orbital ordered phase, ferromagnetic/antiferromagnetic phase, and metal/insulator phase are formed. The reduced disorder introduced by the mismatch of the R and Ba atoms results in random electronic potential. This is crucial for colossal magnetoresistance (CMR) and the phase competition between the ferromagnetic metallic phase and the charge/orbital ordered insulating phase. The CMR property is promising for next-generation memory devices. Moreover, double perovskites can also be utilized in novel devices with combined functionalities of their magnetoelectronic, optical, thermal, and thermoelectric properties.

Early reports on RBA$_{2}$Mn$_2$O$_6$ compounds indicated that as the ionic radius R increases, the ground-state property shifts from a charge/orbital ordered insulator (first and second group) to an A-type antiferromagnetic metal with a competing ferromagnetic metal phase (third group). The first group, consisting of R = Ho, Y, Dy, and Tb, has the smallest radius and exhibits a structural phase transition at high temperatures and a CE-type antiferromagnetic insulating phase transition at low temperatures. The second group, consisting of R = Eu, Sm, and Gd, exhibits similar phase transitions with the first group except for the structural transition at high temperatures. Notably, the charge/orbital ordering temperature of the first and second groups decreases as the ionic radius R is increased. However, the Néel temperature ($T_N$) does not significantly change upon R substitution.

We recently reported the optical and vibrational properties of the double perovskite NdBaMn$_2$O$_6$, which belongs to the third group. NdBaMn$_2$O$_6$ exhibits no tilting of the MnO$_6$ octahedra due to Nd ions’ relatively large size. YBaMn$_2$O$_6$, unlike NdBaMn$_2$O$_6$, has heavily tilted and distorted MnO$_6$ octahedra. This is due to the large mismatch between the ionic radii of Y and Ba atoms. Previous results of the X-ray powder
diffraction of the polycrystalline samples by Nakajima et al.\textsuperscript{14} revealed that YBaMn$_2$O$_6$ crystallizes at room temperature in a monoclinic structure. The lattice parameters are as follows: $a = 3.901(9)$ Å, $b = 3.898(1)$ Å, $c = 7.602(2)$ Å, $\beta = 90.2(1)^\circ$, and $V = 115.5(9)$ Å$^3$.\textsuperscript{14} This is described as a pseudotetragonal structure because $a \approx b$ and $\beta \approx 90^\circ$. A structural transition is observed at a high temperature of approximately 520 K. The crystal still assumes a monoclinic form, but it has a pseudo-orthorhombic structure wherein $a > b$ and $\beta \approx 90^\circ$.\textsuperscript{14} A structural transition occurred, and an orthorhombic Cmmm symmetry was assumed. The space group was indicated from the Rietveld refinement of the neutron diffraction by Nakajima et al.\textsuperscript{15} The orthorhombic structure wherein $a > b$ and $\beta \approx 90^\circ$.\textsuperscript{14} This structure persisted up to 473 K. At 498 K, the structure was no longer triclinic, R as evidenced by the absence of (220) peak splitting and the presence of the (202) peak split, which characterizes a monoclinic structure. The space group was fitted to a monoclinic C2/m. Between 673 and 723 K, another structural transition occurred, and an orthorhombic Cmmm symmetry was observed.

Temperature-dependent magnetic susceptibility and resistivity measurements of the polycrystalline YBaMn$_2$O$_6$ samples by Nakajima et al.\textsuperscript{14,15} clearly revealed three successive transitions at 520, 480, and 200 K. At temperatures higher than 520 K, YBaMn$_2$O$_6$ was paramagnetic with the metallic property. It transitioned from a paramagnetic metal into a paramagnetic insulator.\textsuperscript{14} A structural transition at 350 K, the structure assumes a triclinic $\tilde{P}$1 symmetry. Williams et al.\textsuperscript{16,17} also conducted a Rietveld refinement on the neutron diffraction data of the polycrystalline YBaMn$_2$O$_6$ samples. Their structure and phase transition assignments differed from those of Nakajima et al.\textsuperscript{15} They assigned the ground-state structure at 300 K to a triclinic $\tilde{P}$1, which persisted up to 473 K. At 498 K, the structure was no longer triclinic, as evidenced by the absence of (220) peak splitting and the presence of the (202) peak split, which characterizes a monoclinic structure. The space group was fitted to a monoclinic C2/m. Between 673 and 723 K, another structural transition occurred, and an orthorhombic Cmmm symmetry was observed.

To date, no optical and vibrational properties have been reported for YBaMn$_2$O$_6$ single crystals. To fill this gap, we performed spectroscopic ellipsometry and Raman scattering measurements. Comparing the results of YBaMn$_2$O$_6$ with those of other RBaMn$_2$O$_6$ double perovskites, particularly NdBaMn$_2$O$_6$, can clarify the effects of MnO$_6$ octahedral tilting and A-site cation substitution. Furthermore, the result can help establish agreement on the layout of the complex physics of these materials and elucidate the effects of strong correlations between lattice, charge, and spin degrees of freedom in YBaMn$_2$O$_6$.

2. RESULTS AND DISCUSSION

2.1. Electronic Excitations. Figure 2 indicates the room temperature absorption spectrum of YBaMn$_2$O$_6$ obtained through spectroscopic ellipsometry analysis.\textsuperscript{13} We observed peaks centered at 1.50, 4.05, and 5.49 eV, which were fitted with Lorentz oscillators.\textsuperscript{20} The high energy peaks at 4.05 and 5.49 eV originated from the charge-transfer transitions from O 2p to Mn 3d orbitals. The origin of these high energy peaks is clearly established in the literature.\textsuperscript{4,21,22} The peak at 1.50 eV can be attributed to Mn d−d transitions.\textsuperscript{22} The absorption spectrum of NdBaMn$_2$O$_6$ is also illustrated in Figure 2. We noticed that the peak intensity of YBaMn$_2$O$_6$ was relative higher than that of NdBaMn$_2$O$_6$. The d−d excitation peak was also more pronounced in YBaMn$_2$O$_6$ but suppressed in NdBaMn$_2$O$_6$. This enhanced d−d excitation peak explains the insulating behavior of YBaMn$_2$O$_6$ whereas the suppressed peak in NdBaMn$_2$O$_6$ contributes to its metallic ground state. In the MnO$_6$ compounds,\textsuperscript{23} a similar decrease was noted in the spectral weight in the low-energy absorption region (<3 eV) as the Mn ion radii increased. This phenomenon correlated with the systematic increase of the Néel temperature ($T_N$) as the Mn ion radii increased. Coincidentally, the same behavior was exhibited by RBaMn$_2$O$_6$ when the $T_N$ of NdBaMn$_2$O$_6$ (235 K) was higher than that of YBaMn$_2$O$_6$ (200 K). Furthermore, the increase in spectral weight also correlated with an increase in
the charge and orbital ordering temperature of RBaMn2O6. These phenomena imply that the tilting disorder induced by the smaller R radii favors the charge/orbital ordering as well as the spin ordering due to the enhanced Jahn–Teller distortions. Next, as we examined the d–d peak center position of RBAaMn2O6 with R = Y, Sm, and Nd, we observed a notable R site ion dependence. The d–d peak energy is summarized in the inset of Figure 2. The SmBaMn2O6 d–d peak was reported by Akahoshi et al. in their optical conductivity data, and it had a photon energy of approximately 1.1 eV. As the size of the R cation increased from Y to Nd, the d–d excitation peaks were shifted to lower energies. This shift was also related to the modification of Jahn–Teller distortions.

2.2. Vibrational Properties. Figure 3 illustrates the room temperature polarized Raman scattering spectra of YBaMn2O6.

We performed the factor group analysis on the crystal structures of polycrystalline YBaMn2O6 as proposed in the literature. The details of the factor group analysis are provided in Tables 1–4. Nakajima et al. proposed a monoclinic structure with the P2 space group at room temperature. This structure contains 20 atoms in the unit cell with Z = 2 and allows for 60 degrees of freedom. The P2 structure tabulated in Table 1 results in 25A + 32B vibrational modes, which are both Raman and infrared active. Only the

Table 2. Factor Group Analysis of YBaMn2O6 for Nakajima et al.'s Triclinic Structure with P1 Space Group Assignment

| triclinic P1 YBaMn2O6 | atom | Wyckoff notation | site symmetry | irreducible representation |
|------------------------|------|------------------|---------------|---------------------------|
| Y (1)                  | 1a   | C2               | Γγ = 3A       |
| Y (2)                  | 1a   | C2               | Γγ = 3A       |
| Ba (1)                 | 1a   | C2               | Γγ = 3A       |
| Ba (2)                 | 1a   | C2               | Γγ = 3A       |
| Mn (1)                 | 1a   | C2               | Γγ = 3A       |
| Mn (2)                 | 1a   | C2               | Γγ = 3A       |
| Mn (3)                 | 1a   | C2               | Γγ = 3A       |
| Mn (4)                 | 1a   | C2               | Γγ = 3A       |
| O (1)                  | 1a   | C2               | Γγ = 3A       |
| O (2)                  | 1a   | C2               | Γγ = 3A       |
| O (3)                  | 1a   | C2               | Γγ = 3A       |
| O (4)                  | 1a   | C2               | Γγ = 3A       |
| O (5)                  | 1a   | C2               | Γγ = 3A       |
| O (6)                  | 1a   | C2               | Γγ = 3A       |
| O (7)                  | 1a   | C2               | Γγ = 3A       |
| O (8)                  | 1a   | C2               | Γγ = 3A       |
| O (9)                  | 1a   | C2               | Γγ = 3A       |
| O (10)                 | 1a   | C2               | Γγ = 3A       |
| O (11)                 | 1a   | C2               | Γγ = 3A       |
| O (12)                 | 1a   | C2               | Γγ = 3A       |

Γcryst = 60A; Γacoustic = 3A; Γinh = 57A. A is Raman and infrared active.

Table 3. Factor Group Analysis of YBaMn2O6 for Williams et al.'s Triclinic Structure with P1 Space Group Assignment

| triclinic P1 YBaMn2O6 | atom | Wyckoff notation | site symmetry | irreducible representation |
|------------------------|------|------------------|---------------|---------------------------|
| Y (1)                  | 1a   | C2               | Γγ = 3A       |
| Y (2)                  | 1a   | C2               | Γγ = 3A       |
| Ba (1)                 | 1a   | C2               | Γγ = 3A       |
| Ba (2)                 | 1a   | C2               | Γγ = 3A       |
| Mn (1)                 | 1a   | C2               | Γγ = 3A       |
| Mn (2)                 | 1a   | C2               | Γγ = 3A       |
| Mn (3)                 | 1a   | C2               | Γγ = 3A       |
| Mn (4)                 | 1a   | C2               | Γγ = 3A       |
| O (1)                  | 1a   | C2               | Γγ = 3A       |
| O (2)                  | 1a   | C2               | Γγ = 3A       |
| O (3)                  | 1a   | C2               | Γγ = 3A       |
| O (4)                  | 1a   | C2               | Γγ = 3A       |
| O (5)                  | 1a   | C2               | Γγ = 3A       |
| O (6)                  | 1a   | C2               | Γγ = 3A       |
| O (7)                  | 1a   | C2               | Γγ = 3A       |
| O (8)                  | 1a   | C2               | Γγ = 3A       |
| O (9)                  | 1a   | C2               | Γγ = 3A       |
| O (10)                 | 1a   | C2               | Γγ = 3A       |
| O (11)                 | 1a   | C2               | Γγ = 3A       |
| O (12)                 | 1a   | C2               | Γγ = 3A       |

Γcryst = 30Aγ + 30Aδ; Γacoustic = 3Aγ; Γinh = 30Aγ + 27Aω. A is Raman active and Aω is infrared active.

Table 4. Factor Group Analysis of YBaMn2O6 for Williams et al.'s Monoclinic Structure with C2/m Space Group Assignment

| monoclinic C2/m YBaMn2O6 | atom | Wyckoff notation | site symmetry | irreducible representation |
|---------------------------|------|------------------|---------------|---------------------------|
| Y (1)                     | 4i   | C2               | Γγ = 2A + Aδ + Bδ + 2Bω |
| Ba (1)                    | 4i   | C2               | Γγ = 2A + Aδ + Bδ + 2Bω |
| Mn (1)                    | 8j   | C2               | Γγ = 2A + Aδ + Bδ + 2Bω |
| O (1)                     | 4h   | C2               | Γγ = 2A + Aδ + Bδ + 2Bω |
| O (2)                     | 8g   | C2               | Γγ = 2A + Aδ + Bδ + 2Bω |
| O (3)                     | 4i   | C2               | Γγ = 2A + Aδ + Bδ + 2Bω |
| O (4)                     | 4i   | C2               | Γγ = 2A + Aδ + Bδ + 2Bω |
| O (5)                     | 8j   | C2               | Γγ = 2A + Aδ + Bδ + 2Bω |

Γcryst = 16Aγ + 12Aδ + 14Bω + 18Aδ; Γacoustic = 3Aγ; Γinh = 16Aγ + 11Aδ + 4Bω + 14Bδ + 16Bω. Aγ and Bω are Raman active and Aω and Bω are infrared active.

25A modes were expected in our selected configuration. Williams et al. resolved the structure into a triclinic P1 shown in Table 3 that yields 30Aγ + 27Aω vibrational modes,
with the \( A_g \) mode being Raman active and \( A_u \) mode being infrared active. We identified 25 Raman active phonon modes at room temperature (see Table 5) and fitted them with Lorentz oscillators.\(^{20}\) This satisfies the monoclinic structure with the \( P_2 \) space group assigned by Nakajima et al.\(^{14,15}\) Figure 3 displays the presence of all phonon peaks in the \( Z(YY)\bar{Z} \) scattering configuration, while they are suppressed in the \( Z(XY)\bar{Z} \) scattering configuration. We deduced from the polarization data that the phonon modes were of \( A \) symmetric character.

The temperature-dependent unpolarized Raman scattering spectra are illustrated in Figure 4. The temperature-dependent Raman scattering spectra generally exhibited a softening of the phonon frequencies as the temperature increased, which was accompanied by a broadening of the line width and a decrease in intensity. We stopped monitoring a phonon peak when its intensity dipped to <50 units following the subtraction of a constant background. Based on this condition, only 16 phonon modes tabulated in Table 6 remained at high temperatures (480 K).

At high temperatures (>498 K), a monoclinic structure with the \( C2/m \) space group was indexed by William et al.\(^{16,17}\) This yields the vibrational modes of 16\( A_g \) + 11\( A_u \) + 14\( B_g \) + 16\( B_u \). The \( A_g \) and \( B_g \) modes are Raman active, while the \( A_u \) and \( B_u \) modes are infrared active (see Table 4). Meanwhile, at temperatures >520 K, a triclinic structure was assigned by Nakajima et al.\(^{14,15}\) The factor group analysis of the \( P1 \) structure detailed in Table 2 results in 57\( A \) modes, which are both Raman and infrared active. Table 6 summarizes the phonon modes identified at 540 K, which are noticeably less than the phonon modes expected in this structure. The discrepancy in the number of the phonon modes with the \( P1 \) structure is due to a lot of factors. Primarily, the high-temperature anharmonic effects are dominant and together with the structural phase transition greatly broaden the peak line width. Also, the phonon modes become too weak to be visible, and the strong modes tend to overlap the weak modes.

The low-temperature Raman scattering spectra from 6 to 160 K were consistently fitted with 35 Lorentz peaks,\(^{20}\) as illustrated in the inset of Figure 4. The mode frequencies at 6 K and atomic motion assignments are summarized in Table 7. The number of phonon modes observed at 6 K is more than that of the expected ones in YBaMn\(_2\)O\(_6\) for a monoclinic structure with the \( P2 \) space group (see Table 1). This emphasizes the capability of Raman scattering spectroscopy to probe local lattice distortions induced by charge rearrangement and octahedral tilting that cannot be easily identified in the overall average structure.

The vibrational mode assignments of YBaMn\(_2\)O\(_6\) were parallel to NdBaMn\(_2\)O\(_6\) \(^{13}\) at 20 K and other perovskite manganites\(^{2,26–30}\) (see Table 7). The phonon frequencies of

### Table 5. Raman Phonon Modes of YBaMn\(_2\)O\(_6\) at 210 and 300 K

| phonon mode | frequency (cm\(^{-1}\)) | symmetry |
|-------------|------------------------|----------|
| \( \omega_2 \) | 105 \( 107 \) | \( A \) |
| \( \omega_3 \) | 122 \( 121 \) | \( A \) |
| \( \omega_4 \) | 136 \( 135 \) | \( A \) |
| \( \omega_5 \) | 146 \( 145 \) | \( A \) |
| \( \omega_6 \) | 163 \( 160 \) | \( A \) |
| \( \omega_7 \) | 185 \( 180 \) | \( A \) |
| \( \omega_{11} \) | 202 \( 201 \) | \( A \) |
| \( \omega_{12} \) | 215 \( 214 \) | \( A \) |
| \( \omega_{13} \) | 253 \( 250 \) | \( A \) |
| \( \omega_{16} \) | 267 \( 266 \) | \( A \) |
| \( \omega_{19} \) | 302 \( 298 \) | \( A \) |
| \( \omega_{20} \) | 315 \( 313 \) | \( A \) |
| \( \omega_{21} \) | 334 \( 334 \) | \( A \) |
| \( \omega_{22} \) | 346 \( 345 \) | \( A \) |
| \( \omega_{23} \) | 373 \( 376 \) | \( A \) |
| \( \omega_{34} \) | 388 \( 387 \) | \( A \) |
| \( \omega_{26} \) | 417 \( 418 \) | \( A \) |
| \( \omega_{27} \) | 442 \( 436 \) | \( A \) |
| \( \omega_{28} \) | 475 \( 472 \) | \( A \) |
| \( \omega_{30} \) | 497 \( 496 \) | \( A \) |
| \( \omega_{31} \) | 513 \( 512 \) | \( A \) |
| \( \omega_{32} \) | 547 \( 544 \) | \( A \) |
| \( \omega_{33} \) | 574 \( 572 \) | \( A \) |
| \( \omega_{34} \) | 623 \( 620 \) | \( A \) |
| \( \omega_{35} \) | 646 \( 642 \) | \( A \) |

### Table 6. Raman Phonon Modes of YBaMn\(_2\)O\(_6\) Identified at 480 and 540 K

| phonon mode | frequency (cm\(^{-1}\)) | symmetry |
|-------------|------------------------|----------|
| \( \omega_2 \) | 105 \( 105 \) | \( A \) |
| \( \omega_3 \) | 115 \( 115 \) | \( A \) |
| \( \omega_4 \) | 124 \( A \) | \( A \) |
| \( \omega_5 \) | 140 \( A \) | \( A \) |
| \( \omega_{12} \) | 149 \( 146 \) | \( A \) |
| \( \omega_{15} \) | 201 \( 202 \) | \( A \) |
| \( \omega_{16} \) | 242 \( A \) | \( A \) |
| \( \omega_{19} \) | 266 \( A \) | \( A \) |
| \( \omega_{20} \) | 285 \( 275 \) | \( A \) |
| \( \omega_{21} \) | 335 \( 315 \) | \( A \) |
| \( \omega_{22} \) | 376 \( A \) | \( A \) |
| \( \omega_{23} \) | 380 \( A \) | \( A \) |
| \( \omega_{26} \) | 406 \( A \) | \( A \) |
| \( \omega_{28} \) | 454 \( A \) | \( A \) |
| \( \omega_{30} \) | 492 \( 468 \) | \( A \) |
| \( \omega_{34} \) | 620 \( A \) | \( A \) |

---

**Figure 4.** Temperature dependence of the unpolarized Raman scattering spectra of YBaMn\(_2\)O\(_6\). The inset illustrates the results of fitting the spectrum obtained at 6 K by using the Lorentzian model.
YBaMn$_2$O$_6$ were divided into four regions. The first region had frequencies <200 cm$^{-1}$ and mainly involved vibrations from Y and Ba atoms (Figures 5 and 6). The second region had modes between 200 and 400 cm$^{-1}$ and was due to MnO$_6$ octahedral distortions from either an out-of-phase rotation or octahedral tilting and bending (Figures 7 and 8). The third region had frequencies between 400 and 600 cm$^{-1}$ primarily due to Jahn–Teller stretching (Figures 9 and 10). Finally, the fourth region had frequencies >600 cm$^{-1}$ and contained the oxygen cage breathing modes (Figure 10).

The detailed temperature-dependent evolution of the phonon frequency, line width, and normalized intensity of the peaks in each region are illustrated in Figures 5–10. Notably, the intensities were normalized at 200 K. The phonon peaks that can be monitored from 6 to 600 K were fitted with the anharmonic model. The frequency above the magnetic ordering (>200 K) and below the structural phase transition temperature (<520 K) was used to obtain the best fit line of the anharmonic model, expressed as follows: \[ \omega(T) = \omega_0 + a \left( 1 + \frac{2}{\exp{(\frac{\Theta}{T})}} - 1 \right) \] (1)

In this model, \( \omega_0 \) is the intrinsic frequency of the optical phonon mode, \( \Theta \) is the Debye temperature, and \( A \) is the anharmonic coefficient. The following values were obtained by fitting parameters for the Jahn–Teller mode at 496 cm$^{-1}$ (Figure 10a): \( \omega_0 \approx 522 \text{ cm}^{-1} \), \( A \approx -23 \text{ cm}^{-1} \), and \( \Theta \approx 1000 \text{ K} \). The negative value of the anharmonic coefficient \( A \) corresponds to the increase in the thermal motion as the temperature increases, which results in a phonon frequency decrease. The thin solid line in Figures 5c,d, 6c, 7c, 8a, and 10b represents the theoretical predictions based on eq 1.

Notable features and discontinuities were observed at the phase transition temperatures of approximately 520, 480, and 200 K deviating from the anharmonic model predictions. At the structural phase transition temperature of approximately 520 K, the phonon intensities of the remaining modes were further reduced by over half at 480 K. The breathing and Jahn–Teller modes became indistinguishable at high temperatures. Large broadening in line width, which began at approximately 480 K, was also noted. The disappearance of these phonon modes indicated the metallic behavior of the material. The phonon modes exhibited a dramatic increase in intensity at approximately 200 K. This particularly applies to those phonon peaks between 360 and 440 cm$^{-1}$, mainly involving MnO$_6$ octahedra tilting and bending motions. This phenomenon marks the onset of charge and orbital ordering. At temperatures <200 K, the phonon modes \( \omega_{10}, \omega_{13}, \omega_{15}, \omega_{16}, \omega_{18}, \omega_{20}, \omega_{23}, \omega_{24}, \omega_{25}, \omega_{26}, \omega_{34} \), and \( \omega_{34} \) appeared at approximately 103, 123, 148, 179, 187, 195, 205, 227, 234, 289, 298, 397, 408, 552, 572, and 608 cm$^{-1}$, respectively. The activation of these phonon peaks supports the formation of superstructures due to charge and orbital ordering. \[ \text{12} \]

In the following section, we detail the anomalies in the phonon frequencies at the phase transition temperatures, starting with the peaks involved with Y and Ba motions, which are displayed in Figures 5 and 6. We observed an approximately 4 cm$^{-1}$ splitting of 105 cm$^{-1}$ into \( \omega_{1} \approx 103 \text{ cm}^{-1} \) and \( \omega_{2} \approx 107 \text{ cm}^{-1} \) at temperatures <200 K shown in Figure 5b. Similarly, the phonon peak centered at 163 cm$^{-1}$ at approximately 200 K appeared as two intense peaks at \( \omega_{6} \approx 161 \text{ cm}^{-1} \) and \( \omega_{7} \approx 168 \text{ cm}^{-1} \), as shown in Figure 6c. Moreover, the magnetic phase transition at 200 K was also marked by a dramatic increase in the intensity of phonon peaks, \( \omega_{10}, \omega_{12}, \omega_{13}, \omega_{15}, \omega_{16}, \omega_{23}, \omega_{24}, \omega_{25}, \omega_{34} \), and \( \omega_{34} \) appeared at approximately 123, 148, 179, 187, 195, 205, 227, 234, 289, 298, 397, 408, 552, 572, and 608 cm$^{-1}$, respectively (see Figure 6). Figure 5d displays the temperature dependences of the phonon frequency, line width, and normalized intensity of \( \omega_{10} \) peak at approximately 138 cm$^{-1}$. A discontinuity in intensity was apparent across the phase transition temperatures (200 and 520 K). Discontinuities in the line width were noted at approximately 200 and 480 K, and a large broadening was observed at 480 K. Deviations from the anharmonic behavior were observed for the phonon frequency at 200 and 480 K.

---

Table 7. Phonon Frequencies of YBaMn$_2$O$_6$ at 6 K and Phonon Frequencies of NdBaMn$_2$O$_6$ at 20 K with their Main Atomic Motion Assignments$^a$

| phonon mode | frequency (cm$^{-1}$) | YBaMn$_2$O$_6$ | NdBaMn$_2$O$_6$ | atomic motions |
|-------------|----------------------|---------------|-----------------|----------------|
| \( \omega_1 \) | 103 | | | mixed vibrations from Y and Ba atoms |
| \( \omega_2 \) | 107 | | | |
| \( \omega_3 \) | 123 | 117 | | |
| \( \omega_4 \) | 138 | | | |
| \( \omega_5 \) | 148 | | | |
| \( \omega_6 \) | 161 | | | |
| \( \omega_7 \) | 168 | 177 | | |
| \( \omega_8 \) | 179 | | | |
| \( \omega_9 \) | 187 | | | |
| \( \omega_{10} \) | 195 | | | |
| \( \omega_{11} \) | 205 | | | |
| \( \omega_{12} \) | 214 | | | octahedral distortions (tilting and bending) |
| \( \omega_{13} \) | 227 | | | |
| \( \omega_{14} \) | 234 | | | |
| \( \omega_{15} \) | 255 | | | |
| \( \omega_{16} \) | 267 | | | |
| \( \omega_{17} \) | 289 | | | |
| \( \omega_{18} \) | 298 | | | |
| \( \omega_{19} \) | 307 | 296 | | |
| \( \omega_{20} \) | 312 | | | |
| \( \omega_{21} \) | 324 | 332 | | |
| \( \omega_{22} \) | 370 | | | |
| \( \omega_{23} \) | 378 | | | |
| \( \omega_{24} \) | 397 | | | |
| \( \omega_{25} \) | 408 | | | |
| \( \omega_{26} \) | 418 | | | |
| \( \omega_{27} \) | 452 | | | Jahn–Teller distortions |
| \( \omega_{28} \) | 477 | 442 | | |
| \( \omega_{29} \) | 491 | | | |
| \( \omega_{30} \) | 507 | 489 | | |
| \( \omega_{31} \) | 514 | | | |
| \( \omega_{32} \) | 552 | | | |
| \( \omega_{33} \) | 572 | | | |
| \( \omega_{34} \) | 608 | 600 | | breathing vibrations |
| \( \omega_{35} \) | 659 | 653 | | |

$^a$The data for NdBaMn$_2$O$_6$ is adapted from ref 13. No subject to Copyright.
Figures 7 and 8 present the temperature dependences of phonon peaks of the MnO$_6$ octahedra bending and tilting at frequencies between 210 and 360 cm$^{-1}$. We highlight the anomalies in phonon frequency, line width, and normalized intensity of $\omega_{17-20}$ phonon peaks in Figure 8b. At room temperature, the Raman scattering spectrum was fitted with a main Lorentz peak at approximately 298 cm$^{-1}$ and a side peak centered near 312 cm$^{-1}$. At temperatures <200 K, four phonon peaks were distinctly observed at approximately 289, 298, 307, and 312 cm$^{-1}$ (see Figure 8a). Similar peak frequency behaviors were noted for phonon modes $\omega_{11-14}$ (see Figure 7b). The phonon mode $\omega_{21}$, as presented in Figure 8c, appears as a double peak centered at approximately 334 and 345 cm$^{-1}$ at room temperature. It becomes a single peak centered at approximately 342 cm$^{-1}$ at temperatures <200 K, which contrasts with the split exhibited by $\omega_{17-20}$. Moreover, at high temperatures, the $\omega_{21}$ phonon peak appeared as a single peak near the structural phase transition at 520 K. A reduction of the phonon intensities by more than half across the phase transitions was also observed in addition to the anomalous broadening at high temperatures. These anomalies involving phonon modes associated with MnO$_6$ octahedra tilting and
bending modes indicate the sensitivity of these atomic motions during the phase transitions. The atomic motions also indicate the charge rearrangement at 200 K.

Figures 9a and 10a display the temperature-dependent Jahn–Teller modes. Figure 10b describes the frequency, line width, and normalized intensity of (b) $\omega_5$, (c) $\omega_{6-7}$, and (d) $\omega_{8-10}$ modes. The vertical dashed lines denote the phase transition temperatures at 200, 480, and 520 K. The thin solid line is the fitting results obtained with the anharmonic model.

The temperature-dependent breathing modes $\omega_{34-35}$ are displayed in Figure 10a,c. The breathing mode appears as a broad peak at room temperature, which was resolved into two peaks at approximately 620 and 642 cm$^{-1}$. A third breathing mode positioned at approximately 608 cm$^{-1}$ was also identified at room temperature, which was very weak and fell short of our

---

**Figure 6.** (a) Temperature dependence of the unpolarized Raman scattering spectra of YBaMn$_2$O$_6$ for frequencies between 140 and 200 cm$^{-1}$. The temperature dependence of frequency, line width, and normalized intensity of (b) $\omega_5$, (c) $\omega_{6-7}$, and (d) $\omega_{8-10}$ modes. The vertical dashed lines denote the phase transition temperatures at 200, 480, and 520 K. The thin solid line is the fitting results obtained with the anharmonic model.
cutoff intensity. The 608 cm$^{-1}$ peak gradually increased in intensity at temperatures <200 K, and a triplet peak was observed at 170 down to 140 K. Notably, the 620 cm$^{-1}$ breathing mode appeared split into two centered at approximately 608 and 659 cm$^{-1}$ at temperatures <140 K, reflecting the charge and orbital orderings. Near the structural phase transition temperature, the breathing modes greatly reduced in intensity and could no longer be distinguished (inset of Figure 10a).

Next, we discuss the large deviation from the anharmonic model at temperatures under the charge/orbital ordering and magnetic ordering temperatures noted for the Jahn–Teller mode shown in Figure 10b, wherein $\omega_{30}$ positioned at approximately 496 cm$^{-1}$. This mode mainly contained Mn–O stretching vibrations along the c-axis. Deviations from the anharmonic model have been noted for materials with strong lattice, charge, and spin correlations. We ruled out the contributions of thermal lattice expansion because anharmonic effects generally have negligible contributions at low temperatures.31 A hardening of more than 10 cm$^{-1}$ was exhibited by this mode. We attribute this to the renormalization of the phonon frequency that was caused by magnetic ordering and is

Figure 7. (a) Temperature dependence of the unpolarized Raman scattering spectra of YBaMn$_2$O$_6$ for frequencies between 180 and 280 cm$^{-1}$. The temperature dependence of frequency, line width, and normalized intensity of (b) $\omega_{11}$, (c) $\omega_{15}$, and (d) $\omega_{16}$ modes. The vertical dashed lines denote the phase transition temperatures at 200, 480, and 520 K. The thin solid line is the fitting results obtained with the anharmonic model.
a signature of spin–phonon coupling. This shift in phonon frequency due to spin–phonon coupling can be described as follows:

$$\Delta \omega(T) \approx \lambda \langle S_i S_j \rangle \approx 6 \lambda \left( \frac{M(T)}{M_s} \right)^2$$  \hspace{1cm} (2)

In this model, the spin–phonon coupling factor, \( \lambda \), is multiplied by the nearest neighbor spin correlation, given by \( \langle S_i S_j \rangle \), to obtain the renormalization of the phonon frequency, \( \Delta \omega(T) \). Here, \( \langle S_i S_j \rangle \) was estimated from the square of \( \frac{M(T)}{M_s} \), where \( M(T) \) is the sublattice magnetization per magnetic ion and \( M_s \) is the saturation magnetization. The factor of six gives the number of nearest neighbors. To illustrate that the observed hardening is a consequence of the magnetic ordering, we plotted the magnetic susceptibility contribution with the phonon renormalization. The described magnetic susceptibility is a sum of the parallel and perpendicular contributions, expressed as \( \chi = \chi_{||} + \chi_{\perp} \), which is appropriate for an ab twin structure. Figure 11 displays a linear relationship between the square of the magnetic susceptibility and the phonon renormalization that confirms the spin–phonon coupling in...
the present study. Moreover, linear dependence was observed at temperatures \(< T_N = 200 \text{ K} \), whereas a departure from this linear relationship was observed at low temperatures \(< 20 \text{ K} \). This behavior agrees with those observed in the stretching mode of multiferroics such as Cu$_2$OCl$_2$, BiFeO$_3$, and NiO, which exhibited spin-phonon coupling.

3. CONCLUSIONS

Spectroscopic ellipsometry and Raman scattering spectroscopy were used to determine the correlation between the temperature-dependent optical response and complex phase transitions of YBaMn$_2$O$_6$ single crystals. The room-temperature optical absorption spectrum of YBaMn$_2$O$_6$ manifested the d–d
on-site transitions in Mn at approximately 1.50 eV. The spectrum also revealed charge-transfer transitions between the 2p states of O and 3d states of Mn at approximately 4.05 and 5.49 eV. The d−d transition peak for RBaMn₂O₆ compounds was observed to increase as R radii were decreased. The enhancement of the intensity of MnO₆ octahedral bending modes between 360 and 440 cm⁻¹ marked the onset of charge and orbital ordering. This was accompanied by the activation of phonon modes at temperatures <200 K. The Jahn–Teller mode at approximately 496 cm⁻¹ along with the breathing...
mode at approximately 620 and 644 cm$^{-1}$ exhibited sensitivities to the structural phase transition at 520 K, metal–insulator transition at 480 K, and the antiferromagnetic ordering transition at 200 K. The temperature dependence of the Jahn–Teller mode exhibited an anomalous hardening of approximately 10 cm$^{-1}$ at temperatures <200 K. A linear dependence between the phonon renormalization and the square of the magnetic susceptibility of YBaMn$_2$O$_6$ was exhibited at temperatures <200 K, thus indicating the establishment of spin–phonon coupling. These phenomena confirm the existence of a strong correlation between the lattice, charge, and spin degrees of freedom in YBaMn$_2$O$_6$.

### 4. EXPERIMENTAL SECTION

YBaMn$_2$O$_6$ single crystals were prepared through a floating zone method. The preparation method is similar to those for SmBaMn$_2$O$_6$ and NdBaMn$_2$O$_6$ and entails the use of the precursor powders of Y$_2$O$_3$, MnO$_2$, and BaCO$_3$. The crystals with the (001) surface used in the present study had approximate dimensions of 2 × 1.5 × 0.5 mm$^3$. Magnetic susceptibility measurements of YBaMn$_2$O$_6$ single crystals shown in Figure 12 revealed an antiferromagnetic phase transition at $T_N = 200$ K. Spectroscopic ellipsometry measurements were performed at angles of incidence between 60° and 75° using a J. A. Woollam Co. M-2000U ellipsometer over a spectral range of 0.73–6.42 eV.\textsuperscript{13} The micro-Raman scattering spectra were measured in a backscattering configuration using a laser with an excitation wavelength of 532 nm and a SENTERRA spectrometer with a 1024 pixel wide charge-coupled detector. The spectral resolution using this spectrometer was typically lower than 0.5 cm$^{-1}$, and the laser power was kept lower than 2.0 mW to avoid thermal damage due to heating effects.\textsuperscript{13} The polarized Raman scattering spectra were also obtained in $Z(YY)Z$ and $Z(XY)Z$ scattering configurations. In this Porto notation, the first letter and the last letter represent the propagation directions of the incident and the scattered light, whereas the letters in parentheses indicate the electric field polarizations of the incident and scattered light, respectively. X, Y, and Z were parallel to the monoclinic [100], [010], and [001] crystal directions, respectively. The temperature-dependent Raman scattering measurements were performed under a continuous-flow helium cryostat for the temperature range of 6–300 K, whereas a LINKAM heating stage was used for the temperature range of 300–600 K. No substantial differences were observed in the spectra obtained at 300 K between the low- and high-temperature setups apart from marginal intensity changes.

### AUTHOR INFORMATION

Corresponding Author

Hsiang-Lin Liu — Department of Physics, National Taiwan Normal University, Taipei 11677, Taiwan; orcid.org/0000-0003-1960-2776; Email: hliu@ntnu.edu.tw

Authors

Rea Divina Mero — Department of Physics, National Taiwan Normal University, Taipei 11677, Taiwan

Kirari Ogawa — Department of Material System Science, Yokohama City University, Yokohama 236-0027, Japan

Shigeki Yamada — Department of Material System Science, Yokohama City University, Yokohama 236-0027, Japan

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c02763

Author Contributions

H.L.L. and S.Y. conceived the research idea and were responsible for the experimental design. R.D.M. conducted the experiments. K.O. and S.Y. were responsible for the sample preparation. R.D.M. and H.L.L. drafted the paper. All of the authors have discussed the results and provided comments regarding the manuscript.

Notes

The authors declare no competing financial interest.

The data that support the findings of this study are available from the corresponding author upon reasonable request.
ACKNOWLEDGMENTS

H.L.L. thanks the Ministry of Science and Technology of the Republic of China for its financial support under Grant no. MOST 110-2112-M-003-017. S.Y. thanks the Grant-in-Aid for Scientific Research (no. 24540380) of the Japan Society for the Promotion of Science and Strategic Research Promotion (no. G2503) of Yokohama City University for their financial support.

REFERENCES

(1) Akahoshi, D.; Uchida, M.; Tomioka, Y.; Arima, T.; Matsu, Y.; Tokura, Y. Random potential effect near the bccritical region in perovskite manganites as revealed by comparison with the ordered perovskite analogs. Phys. Rev. Lett. 2003, 90, No. 177203.

(2) Akahoshi, D.; Okimoto, Y.; Kubota, M.; Kumai, R.; Arima, T.; Tomioka, Y.; Tokura, Y. Charge-orbital ordering near the multicritical point in A-site ordered perovskites SmBaMnO$_3$ and NdBaMnO$_3$. Phys. Rev. B: Condens. Matter Mater. Phys. 2004, 70, No. 064418.

(3) Ueda, Y.; Nakajima, T. The A-site ordered manganese perovskite and its colossal magnetoresistance. Prog. Solid State Chem. 2007, 35, 397–406.

(4) Loktev, V. M.; Pogorelov, Y. G. Peculiar physical properties and the colossal magnetoresistance of manganites (Review). Low Temp. Phys. 2000, 26, 171–193.

(5) Kézsmárki, I.; Tomioka, Y.; Miyasaka, S.; Demkó, L.; Okimoto, Y.; Tokura, Y. Optical phase diagram of perovskite colossal magnetoresistance manganites near half doping. Phys. Rev. B: Condens. Matter Mater. Phys. 2008, 77, No. 075117.

(6) Moritomo, Y.; Asamitsu, A.; Kuwahara, H.; Tokura, Y. Giant magnetoresistance of manganese oxides with a layered perovskite structure. Nature 1996, 380, 141–144.

(7) Tabi, M.; Gupta, D. C. Study of the magneto-electronic, optical, thermal and thermoelectric applications of double perovskites Ba$_3$MTaO$_6$ (M = Er, Tm). RSC Adv. 2019, 9, 15852–15861.

(8) Mir, S. A.; Gupta, D. C. Systematic investigation of the magneto-electronic structure and optical properties of new halide double perovskites Cs$_2$NaMCl$_6$ (M = Mn, Co and Ni) by spin polarized calculations. RSC Adv. 2020, 10, 26277–26287.

(9) Mir, S. A.; Gupta, D. C. Scrutinizing the stability and exploring the dependence of thermoelectric properties on band structure of 3d metal-based double perovskites Ba$_2$FeNiO$_6$ and Ba$_2$CoNiO$_6$. Sci. Rep. 2021, 11, No. 10506.

(10) Nakajima, T.; Kageyama, H.; Yoshizawa, H.; Ueda, Y. Structures and electromagnetic properties of new metal-ordered manganites: RBaMnO$_3$ (R = Y and rare-earth elements). J. Phys. Soc. Jpn. 2002, 71, 2843–2846.

(11) Nakajima, T.; Kageyama, H.; Yoshizawa, H.; Ohoyama, K.; Ueda, Y. Ground state properties of the A-site ordered manganites, RBaMnO$_3$ (R = La, Pr and Nd). J. Phys. Soc. Jpn. 2003, 72, 3237–3242.

(12) Kageyama, H.; Nakajima, T.; Ichihara, M.; Ueda, Y.; Yoshizawa, H.; Ohoyama, K. New stacking variations of the charge and orbital ordering in the metal-ordered manganese YBaMn$_2$O$_5$. J. Phys. Soc. Jpn. 2003, 72, 241–244.

(13) Mero, R. D.; Ogawa, K.; Yamada, S.; Liu, H.-L. Optical study of the electronic structure and lattice dynamics of Nd$_3$Ba$_2$Mn$_2$O$_9$ single crystals. Sci. Rep. 2019, 9, No. 18164.

(14) Nakajima, T.; Kageyama, H.; Ueda, Y. Successive phase transitions in a metal-ordered manganese perovskite YBaMnO$_3$. J. Phys. Chem. Solids 2002, 63, 913–916.

(15) Kageyama, T.; Kageyama, H.; Ichihara, M.; Ohoyama, K.; Yoshizawa, H.; Ueda, Y. Anomalous octahedral distortion and multiple phase transitions in the metal-ordered manganese YBaMn$_2$O$_5$. J. Solid State Chem. 2004, 177, 987–999.

(16) Williams, A. J.; Attfield, J. P. Ferro-orbital order in the charge and cation-ordered manganese YBaMn$_2$O$_5$. Phys. Rev. B - Condens. Matter Mater. Phys. 2005, 72, No. 024436.
multiferroic BiFeO$_3$ through Raman spectroscopy. *J. Mol. Struct.* 2020, 1222, No. 128884.

(37) Aytan, E.; Debnath, B.; Kargar, F.; Barlas, Y.; Lacerda, M. M.; Li, J. X.; Lake, R. K.; Shi, J.; Balandin, A. A. Spin-phonon coupling in antiferromagnetic nickel oxide. *Appl. Phys. Lett.* 2017, 111, No. 252402.

(38) Yamada, S.; Maeda, Y.; Arima, T. Successive electronic transitions and anisotropic properties in a double-perovskite SmBaMn$_2$O$_6$ single crystal. *J. Phys. Soc. Jpn.* 2012, 81, No. 113711.

(39) Yamada, S.; Sagayama, H.; Higuchi, K.; Sasaki, T.; Sugimoto, K.; Arima, T. Physical properties and crystal structure analysis of double-perovskite NdBaMn$_2$O$_6$ by using single crystals. *Phys. Rev. B* 2017, 95, No. 035101.