Raman Scattering Study of $Y_{1-x}Ca_xTiO_3$ Single Crystals

Takao Tsurui [a,1], Norio Ogita [b], Masayuki Udagawa [b], Masami Tsubota [c], Kazuyuki Uchihira [c], Fumitoshi Iga [c]

[a] *Venture Business Laboratory, Hiroshima University, Higashi-Hiroshima, 739-8527, Japan*
[b] *Faculty of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima, 739-8521, Japan*
[c] *ADSM, Hiroshima University, Higashi-Hiroshima, 739-8530, Japan*

Abstract

Raman scattering spectra of $Y_{1-x}Ca_xTiO_3$ (x=0, 0.1, 0.3, 0.37, 0.38) have been systematically studied in the temperature region from 298K to 8K. The observed peaks below 600cm^{-1} have been assigned as phonons, and the observed number satisfies the symmetry of *Pbnm* at room temperature. However, the additional phonons appear below 200K. This result shows that the structural phase transition from orthorhombic to monoclinic ones universally occurs for $x \leq$0.38 at round 200K. In $Y_{0.62}Ca_{0.38}TiO_3$, other new peaks, related to the metal-insulator transition, have been observed below 100K.

Key words: $Y_{1-x}Ca_xTiO_3$; metal-insulator transition; Raman scattering

1. Introduction

$YTiO_3$ is well known as a Mott-Hubbard insulator with $3d^1$ (Ti) configuration and has a $GdFeO_3$-type structure with the *Pbnm* symmetry. In $Y_{1-x}Ca_xTiO_3$, the metal-insulator (M-I) transition has been observed at around x=0.40 [1]. Recent X-ray diffraction experiments at around x=0.40 have reported that the structural phase transition from orthorhombic (*Pbnm*) to monoclinic ($P2_1/n$) at around 230K and also the phase separation between the low-temperature orthorhombic and monoclinic ones below the M-I transition temperature ($T_{M\text{-}I}$) [2]. Raman scattering spectra of polycrystalline $Y_{1-x}Ca_xTiO_3$ at 50K were reported by Katsufuji and Tokura [3], but they did not discuss about the structural phase transition.

In this paper, we have systematically studied the polarization and temperature dependence of Raman-scattering spectra using the single crystalline $Y_{1-x}Ca_xTiO_3$, in order to clarify the origin of the M-I transition.

[1] Corresponding author. E-mail: tsurui@vbl.hiroshima-u.ac.jp

2. Experimental

The single crystals of $Y_{1-x}Ca_xTiO_3$ were synthesized by a floating-zone method. In this experiments, the specimens with x=0, 0.1, 0.3, 0.37, and 0.38 were used.

In the Raman scattering measurements, an Ar^+ laser light with a wavelength of 514.5nm was employed as the incident beam. The scattered light was analyzed by a triple monochromator (JASCO, NR-1800), and the analyzed light was detected by a CCD multi-channel detector (Princeton Instruments).

In the orthorhombic structure of *Pbnm*, the number of the Raman active phonons (Γ_O) is given as Γ_O=$7A_g$+$7B_{1g}$+$5B_{2g}$+$5B_{3g}$ [4]. Phonons with total symmetric Raman active modes, A_g, appear in the polarization geometries of (a,a), (b,b) and (c,c), while B_{1g}, B_{2g} and B_{3g} appear in (a,b), (a,c) and (b,c), respectively, where a, b, and c corresponds to the [1,0,0], [0,1,0], and [0,0,1] axes. The symbol of (p_i,p_s) denotes the polarization geometry and p_i or p_s is the polarization direction of the incident or scattered light, respectively.

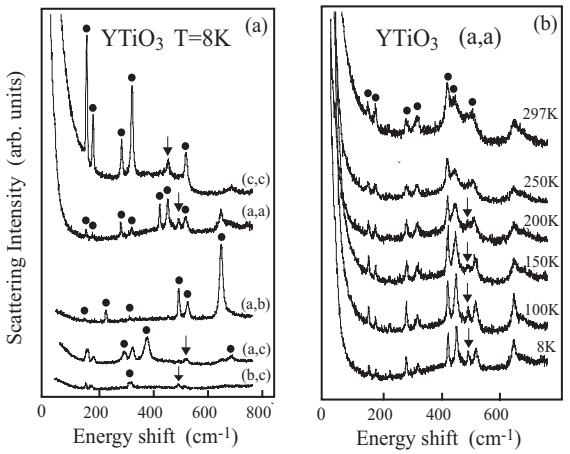

Fig. 1. (a) Polarization dependence at 8K and (b) temperature dependence of the (a, a) spectra for $YTiO_3$. Closed circles denote the assigned phonon by $Pbnm$ and the arrows are the additional phonons observed below 200K.

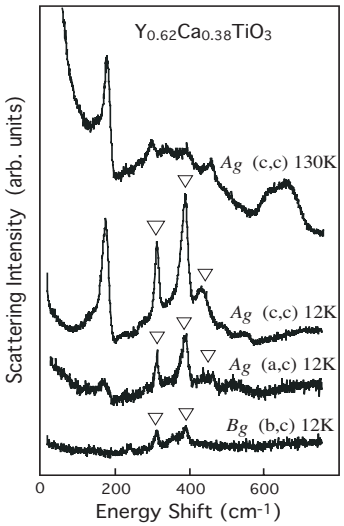

Fig. 2. Polarization dependence of Raman spectra of $Y_{0.62}Ca_{0.38}TiO_3$. For (c, c), the spectra at 130K and 12 K are presented, and those at 12K for (a, c) and (b, c). Note that $T_{M\text{-}I}$ of this sample is $\sim$120K. Open triangles show the new peaks observed below $T_{M\text{-}I}$.

3. Results and discussion

Polarization dependence at 8K and the temperature dependence of (a, a) for $YTiO_3$ are shown in Fig.1(a) and (b), respectively. The peaks below 600cm^{-1} have been assigned as phonons. The assigned phonons by the symmetry of $Pbnm$ are marked by closed circles in the figure, and their observed number satisfies this symmetry. However, new additional phonons, depicted by arrows in the figure, have been observed below 200K. The additional phonons appear in (a, a), (c, c), (a, c), and (b, c). The crystal symmetry is not orthorhombic below 200K, since the observed number of A_g at 8K exceeds the estimated number for $Pbnm$.

For the monoclinic symmetry of $P2_1/n$, the number of the Raman active phonons ($\Gamma_{\rm m}$) is estimated as $\Gamma_{\rm m}$=$12A_g$+$12B_g$, where the A_g modes appear in the polarization geometries of (a, a), (b, b), (c, c) and (a, c), and B_g in (a, b) and (b, c). The results at 8K satisfy the case of $P2_1/n$. Thus, this result shows that the structural phase transition from orthorhombic to monoclinic one occurs at about 200K in $YTiO_3$. Furthermore, this structural phase transition universally occurs in $x \leq 0.38$, since the similar additional phonons have been also observed in this x region.

Figure 2 shows the polarization dependence of the (c, c), (a, c) and (b, c) spectra of $Y_{0.62}Ca_{0.38}TiO_3$ at the representative temperatures. As shown in Fig.2, completely different peaks, depicted by open triangles in the figure, have been found below 100K. These are the similar peaks observed by Katsufuji and Tokura [3]. We can point out two origins for these peaks, because the observed temperature region corresponds to both the phase-separation and metallic one. In Fig.2, we also present the irreducible representations for the monoclinic phase. Since the observed number of the new peaks are three for A_g and two for B_g, the spectra are related to the monoclinic symmetry, not the orthorhombic one. This result excludes the possibility of the phase separation mechanism, where the orthorhombic symmetry becomes important. Therefore, the new peaks below 100K are related to the metallic state, however, the microscopic origin of these excitations is not clear at this stage. To reach the final conclusion, we need the experiments using the different x samples.

Acknowledgements

This work is supported in part by a Grant-in-Aid for COE Research (No.13CE2002) of the Ministry of Education, Culture, Sports, Science and Technology of Japan. The Raman scattering experiment was also supported by the cryogenic center of Hiroshima University.

References

[1] Y. Taguchi et al., Phys. Rev. B**48** (1993) 511.

[2] K. Kato et al., cond-mat/0204227.

[3] T. Katsufuji and Y. Tokura, Phys. Rev. B**50** (1995) 2704.

[4] M. Udagawa et al. Solid State Commun. **16** (1975) 779.