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Raman Scattering of Internal Dynamics in Spinel Zn_2TiO_4 Nanostructures

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We present here the results of the Raman study of lattice dynamics and local compositional fluctuations in cubic spinel Zn_2TiO_4 nanostructures. The observed Raman modes of the spinel structure are identified and attributed to local vibrational modes. Additionally, the analysis of the nonpolar $E_2(\text{H})$ ($\sim 437\text{ cm}^{-1}$, 54.2 meV) and A_{1g} ($\sim 716\text{ cm}^{-1}$, 88.7 meV) modes are made and contributed to lattice deformation associated with the distinct coordination preferences of Zn and Ti.

Keywords Thermal oxidation method; Raman scattering; spinel lattice

1. Introduction

Although intensive exploration of nano-ZnO brought significant achievements, the comprehensive studies of their Raman scattering are still a challenge. In particular, Zhang *et al.* found that the Raman frequencies of both the polar $A_1(\text{LO})$ ($\sim 571\text{ cm}^{-1}$, 70.8 meV) and nonpolar $E_2(\text{H})$ ($\sim 438\text{ cm}^{-1}$, 54.3 meV) modes do not shift with varying particle sizes of nearly uniform-sized ZnO nanoparticles [1]. This result indicated that there is no quantum confinement effect on the vibrational modes of both polar and nonpolar optical modes. Obviously, it is interesting that in the same series of the crystalline ZnO nanoparticles, the quantum confinement effect exists in the electronic structure (the photon-electron interaction), but is absent in vibrational modes (the long-range Coulomb (Fröhlich) interaction) [1–2]. As a result, it is very likely that the observed Raman spectra of the ZnO nanoparticles originate from the presence of the long-range (Fröhlich) electron-phonon interaction rather than the quantum confinement effect. Additionally, a complete description of the lattice dynamics of bulk ZnO at low temperature was recently reported via the phonon-dispersion relations by using inelastic neutron scattering with the aid of both *ab initio* calculations and Raman data [3]. It is worth noticing the excellent agreement of phonon frequencies at the Γ point such as the $E_2(\text{H})$ mode at $\sim 439\text{ cm}^{-1}$ (54.4 meV) from inelastic neutron scattering, at $\sim 441\text{ cm}^{-1}$ (54.6 meV) from *ab initio* calculation and at $\sim 438\text{ cm}^{-1}$ (54.3 meV) from Raman scattering. Furthermore, the Raman frequency of this $E_2(\text{H})$ mode in

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bulk ZnO recorded at 7 K was about the same as those of Ref 1 and 4 in nano and bulk ZnO acquired at room temperature, respectively [1, 3, 4].

Typically, as-grown ZnO has *n*-type conductivity; however, doping with other atoms is an important and effective way to improve the properties of metal-oxide semiconductors. Transition metal, such as Ti and/or TiO₂, doped ZnO has become the extensively studied materials because of their wide potential for applications to ultra sensitive gas, dye-sensitized solar cell, DNA detection etc [5–8]. Moreover, understanding the specifics of phonon spectra of these materials can help in their optoelectronic device performance. So far, few reports on the evolution of additional Raman vibrational (phonon) modes within a broader compositional range in the transition metal-doped ZnO have been found, and results are still not fully reconciled. Within the best of our knowledge, detailed measurements of the phonon branch by inelastic neutron scattering are still lacking. In order to elucidate some interesting properties of ZnO-doped Ti and/or TiO₂ systems, it is therefore highly important to carry out Raman scattering studies that are well suited to obtain information about the sample quality as well as to analyze more specific aspects of lattice dynamics properties.

2. Experimental Details

For the synthesis Zn_{1-x}Ti_xO nanostructures, a thermal oxidation method was used, as explained in Ref. [9]. Zn powders were mixed and ground with various mole percentages TiO₂ ($x = 0$ –80%) for 2 h. Then, polyvinyl alcohol was added into the mixed powder forming a paste and the paste was coated onto alumina substrates forming a thick films followed by drying in air for 6 h. The thick films were heated in a tubular furnace at 600°C under normal atmosphere for 24 h. Then, the furnace was cooled down naturally to room temperature. The formation of the Zn_{1-x}Ti_xO obtained sample, as verified by X-Ray diffraction (XRD), energy dispersive spectroscopy (EDS) and Raman spectroscopy (RS), was identified as being in the cubic spinel Zn₂TiO₄ form [9].

Micro-Raman scattering measurements using a triple spectrometer (JY-T64000) were carried out in a 1800 backscattering geometry using a x50 microscope objectives to focus the laser beam on the sample. The line of 514.5 nm (2.41 eV) of an Ar⁺ laser was used for excitation, focused to a spot of 1 μm in diameter. The design of the laser allows a specific laser generation line to be selected. Most of our experiments were done using light of the most powerful line (up to 20 mW). The data were collected in the frequency range up to 1000 cm⁻¹ in air at room temperature.

3. Results and Discussion

The observations of Zn₂TiO₄ sample, again verified by XRD, EDS, and RS, seem to indicate that the formation was still incomplete and free ZnO and TiO₂ were still present in the sample [9]. Figure 1 shows the Raman spectra of the composition-dependent Zn_{1-x}Ti_xO thick films (0–80% TiO₂) prepared at 600°C in comparison to the nominally pure material (TiO₂ prepared at 800°C). The positions of phonon vibrational frequencies and their assignments at Γ point are summarized in Table I for clarity.

Wurtzite ZnO belongs to the C_{6v} or 6 mm symmetry. The zone-center optical phonons can be classified according to the following irreducible representations: $\Gamma_{opt} = A_1 + E_1 + 2E_2 + 2B_1$. The A_1 and E_1 modes are polar modes and, hence exhibit different frequencies for the transverse-optical (TO) and longitudinal-optical (LO) phonons. The A_1 and E_1 modes are both Raman and infrared active (A_1 (TO), A_1 (LO),

Table 1
Frequencies of Raman spectra for ZnO, TiO₂ and Zn₂TiO₄ and their assignments. Presented data are a compilation of the results different studies reported in Ref. [1, 4, 9, 10].

Symmetry	ZnO bulk at RT [4]		Our ZnO data [9]		ZnO NPs at RT [1]	
	(cm ⁻¹)	(meV)	(cm ⁻¹)	(meV)	(cm ⁻¹)	(meV)
A ₁ (TO)	378	46.8	379	47.0	390	48.3
E ₁ (TO)	410	50.8	409	50.7	407	50.4
E ₂ (H)	438	54.3	437	54.2	438	54.3
A ₁ (LO)	574	71.1	—	—	571	70.8
E ₁ (LO)	590	73.1	583	72.2	582	72.1
TiO ₂ bulk at RT [10]						
E _g	144	17.8	143	17.7	143	17.7
E _g	197	24.4	196	24.3	197	24.4
B _{1g}	399	49.4	394	48.8	399	49.4
A _{1g} + B _{1g}	516	63.9	515	63.8	516	63.9
E _g	639	79.2	637	78.9	639	78.2
Zn ₂ TiO ₄ bulk at RT [11]						
F _{2g}	258	32.0	265	32.8	—	—
E _g	310	38.4	307	38.0	—	—
F _{2g}	350	43.3	343	42.5	—	—
F _{2g}	477	59.1	474	58.7	—	—
A _{1g}	722	89.5	716	88.7	—	—
Our Zn ₂ TiO ₄ NPs at RT [9]						
TiO ₂ NPs at RT [10]						

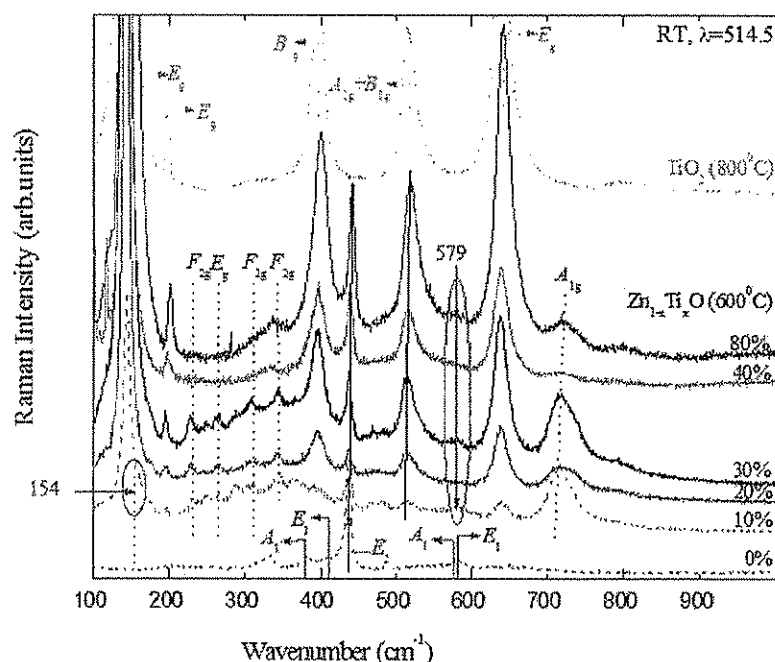


Figure 1. Raman spectra recorded at room temperature for nanostructural $\text{Zn}_{1-x}\text{Ti}_2\text{O}_4$ films (0–80% TiO_2) prepared at 600°C . The standard peak positions for hexagonal wurtzite ZnO phase and tetragonal anatase TiO_2 phase are displayed at the bottom and on the top, respectively.

$E_1(\text{TO})$, and $E_1(\text{LO})$). According to the well-known selection rules we also expect to observe the E_2 modes in unpolarized Raman spectra taken in backscattering geometry. The nonpolar E_2 modes are Raman active only and have two frequencies, $E_2(\text{H})$ associated with oxygen atoms and $E_2(\text{L})$ associated with Zn sublattice. The line-shape asymmetry toward low frequency side observed at $\sim 437\text{ cm}^{-1}$ of $E_2(\text{H})$ mode, involving mainly O motion, is due to its anharmonic phonon-phonon interaction with transverse and longitudinal acoustic modes rather than the lattice disorder [4]. Whereas the B_1 modes are silent modes. The broad peak at about 333 cm^{-1} is attributed to the second-order Raman processes, assigned to overtones and combinations of acoustic and optical phonon branches [4]. The peak at 583 cm^{-1} is positioned between $A_1(\text{LO})^1$ and $E_1(\text{LO})$ related to local vibrational modes associated with intrinsic impurity or defects in the sample [4].

The anatase TiO_2 is characterized by six Raman-active peaks (the top spectrum in Fig. 1) at about 143 cm^{-1} (E_g), 196 cm^{-1} (E_g), 394 cm^{-1} (B_{1g}), 515 cm^{-1} ($A_{1g} + B_{1g}$), and 637 cm^{-1} (E_g). The low wavenumber of E_g mode at about 143 cm^{-1} is very intense and sharp. The anatase E_g mode at 143 cm^{-1} shifts to a higher position with the decrease of particle size [10]. Furthermore, the assignment of the B_{1g} mode at 143 cm^{-1} in Rutile is sharp but weak [12]. Besides the E_g mode at 143 cm^{-1} the two peaks at 196 and 637 cm^{-1} are also assigned as E_g mode in anatase phase. The Raman peak occurring around 515 cm^{-1} at room temperature is split into two peaks at 513 cm^{-1} (A_{1g}) and 519 cm^{-1} (B_{1g}) at 73 K [4, 10].

¹In the bulk ZnO spectrum, a 574-cm^{-1} peak corresponds to $A_1(\text{LO})$ phonon mode while the other peaks are just higher-order peaks of LO phonons.

The $A_{1g}(\nu_3)$, $B_{1g}(\nu_2)$ and $E_g(\nu_1)$ modes are the Ti-O bond stretching type vibrations. The modes of $B_{1g}(\nu_4)$ and $E_g(\nu_5, \nu_6)$ are the O-Ti-O bending type vibrations [13].

The Raman spectra (Fig. 1) revealed vibrational modes at 265, 307, 343, 474 and 716 cm^{-1} in addition to the host phonons of ZnO. The intensity of these additional modes correlates linearly with the TiO_2 concentration and can be used as a quantitative measure of TiO_2 in ZnO. These modes are interpreted as local vibrational modes of cubic spinel Zn_2TiO_4 structure belonging to the space group $O_h^7(Fd3m - 227)$. According to the factor group analysis of the spinel Zn_2TiO_4 , the vibrational modes are

$$\Gamma(k=0) = A_{1g}(R) + E_g(R) + F_{1g} + 3F_{2g}(R) + 2A_{2u} + 2E_u + 4F_{1u}(IR) + 2F_{2u}.$$

There are five Raman active modes and four infrared active modes. However, the Raman observed modes have very high background and broad characteristics, likely implying a large ratio of disorder in the sample [11]. The weak Raman peaks in the spinel Zn_2TiO_4 at about 265, 307, 343, and 474 cm^{-1} are assigned as F_{2g} , E_g , F_{2g} , and F_{2g} symmetric phonon modes, respectively, whereas the strong Raman peak at about 716 cm^{-1} is assigned as A_{1g} mode, in agreement with the assignment in Ref. [11]. The additional vibrational modes located at 154.4 cm^{-1} may be caused by a laser-induced plasma effect [10]. The additional broad peak at 579.1 cm^{-1} is due to the order-disordered effect of Zn and Ti ions over octahedral and tetrahedral site [11]. To study the possible frequency variation from different sample size accurately, it is important to select vibrational modes of high intensity with good signal-to-noise ratio, in addition to have samples with uniform sizes. Here, we shall mainly focus on the local structure of TiO_2 doped Zn, particularly at $E_2(\text{H})$ and A_{1g} modes at about 437 cm^{-1} and 716 cm^{-1} , respectively. In order to obtain information about the position and width of the $E_2(\text{H})$ and A_{1g} modes, the spectra were fitted which was approximated by Lorentzian. Figure 2 shows the profile fittings of both $E_2(\text{H})$ and A_{1g} modes.

As shown in Fig. 2, the two modes ($E_2(\text{H})$ and A_{1g}) of $\text{Zn}_{1-x}\text{Ti}_x\text{O}$ exhibit distinct dependences of phonon energy on the composition. With increasing concentration of TiO_2 , the $E_2(\text{H})$ mode pronounces a redshift, while the A_{1g} mode shows a blueshift. Both two modes exhibit broadening and weakening for the doped ZnO samples, as compared to pure ZnO. For explaining these opposing trends, the vibrational eigenvectors of the wurtzite $E_2(\text{H})$ modes and the spinel A_{1g} mode need to be considered.

The nonpolar $E_2(\text{H})$ mode is a good choice to understand the disorder-induced phenomena in ZnO upon doping. It indicates that the $E_2(\text{H})$ mode of wurtzite ZnO has anharmonic phonon, which is related to lighter components (oxygen) motion in the ab-plane [4, 14, 15]. The existence of the $E_2(\text{H})$ mode in the $\text{Zn}_{1-x}\text{Ti}_x\text{O}$ is adequately attributed to the phonon softening caused by the in-plane lattice expansion. Therefore, the substitution of Ti for Zn (cation, heavier components²) in the $\text{Zn}_{1-x}\text{Ti}_x\text{O}$ should have less influence on the $E_2(\text{H})$ mode energy. The Lorentzian line broadening accompanied by phonon lifetime shortening of $E_2(\text{H})$ mode, in Fig. 2(a), involves lattice imperfections induced by doping. This implies that Ti-substitution increasingly populates the phonon field of $\text{Zn}_{1-x}\text{Ti}_x\text{O}$ and the crystal defects also increase [15].

The A_{1g} mode of Zn_2TiO_4 is determined by the octahedral oxygen motion. As shown in Fig. 2(b), the A_{1g} peak is gradually weakened and shifts to lower frequency with decreasing Ti concentration due to the lower concentration of the octahedral/ Ti^{4+} subunit. The Zn substitution at Ti octahedral sites is expected to induce a significant disorder in the

²The vibration of the cation is associated with the $E_2(\text{L})$ mode.

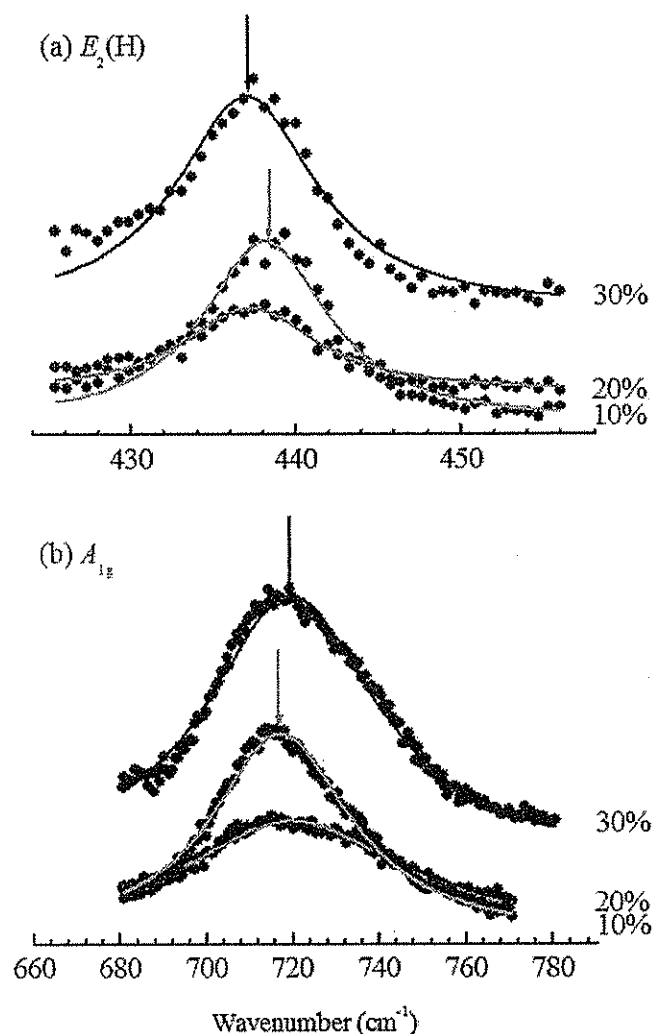


Figure 2. Example of Raman spectra of (a) $E_2(H)$ and (b) A_{1g} modes of TiO_2 (10–30% TiO_2) doped Zn. Solid lines demonstrate quality of the fit.

spinel crystal lattice, resulting in the asymmetry, reduction, and/or split of the A_{1g} mode [16]. The full results are presently being analyzed and will be reported in a subsequent paper.

4. Conclusion

The spinel Zn_2TiO_4 has been clearly detected by the Raman measurements on a series of $\text{Zn}_{1-x}\text{Ti}_x\text{O}$ nanostructures ($x = 0\text{--}80\%$). The structural vibrational modes of $E_2(H)$ and A_{1g} peak at about 437 cm^{-1} and 716 cm^{-1} , respectively, are observed. Results indicate that the peak shapes and line broadenings of the Raman spectra involve the defect and disorder in the spinel crystal lattice.

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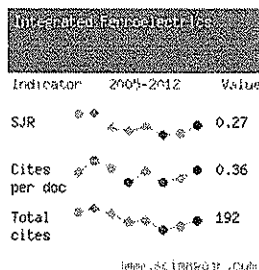
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