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2011 J. Phys.: Condens. Matter 23 225901

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The dielectric properties of La(Mg$_{0.5}$Ti$_{0.5}$)O$_3$ ceramics studied by Raman-scattering, infrared reflectivity spectroscopy, and first-principles calculations

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Received 21 December 2010, in final form 5 April 2011
Published 17 May 2011
Online at stacks.iop.org/JPhysCM/23/225901

Abstract

La(Mg$_{0.5}$Ti$_{0.5}$)O$_3$ (LMT) ceramics were prepared by either the solid-state reaction (LMT)$_{SS}$ or the citric-acid chemical method (LMT)$_{CA}$. A combination of Raman scattering, infrared reflectivity, and first-principles calculations was carried out to elucidate the correlation between lattice dynamics and the dielectric properties of these materials. Twelve Raman-active phonons are observed in both samples, displaying similar frequency positions. Interestingly, the Ag phonon ($g_{11}$ mode) of (LMT)$_{SS}$ at about 717 cm$^{-1}$ involving the oxygen octahedron breathing vibrations demonstrates a narrower linewidth, suggesting its better crystallinity. Furthermore, an infrared-active $u_2$ phonon band due to the vibrations of OI and OII layers, which possesses the largest oscillator strength, exhibits stronger intensity for (LMT)$_{SS}$, as compared with those for (LMT)$_{CA}$. Additionally, the $Q \times f$ values (the product of dielectric $Q$ values and measurement frequency) of (LMT)$_{SS}$ estimated from either microwave cavity or infrared spectroscopic measurements are larger than those of (LMT)$_{CA}$. These results indicate that the better coherence of lattice vibrations in (LMT)$_{SS}$ leads to its higher $Q \times f$ value, providing evidence for a strong connection between optical spectroscopic behavior and microwave dielectric characteristics in these materials.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Ceramic dielectrics with high quality factor ($Q$), high dielectric constant ($\varepsilon_1$), and near zero temperature coefficient of resonant frequency ($\tau_f$) are extensively used in microwave communication systems. Generally, the dielectric losses in microwave dielectrics could be induced either intrinsically or extrinsically. The intrinsic losses are related to the material compositions and crystal structures, which are less process dependent, whereas the extrinsic losses are associated with the defects (vacancies, impurities), structural disorders, porosities, or second phases, which vary with the processing parameters markedly. According to Tamura [1], intrinsic dielectric loss is mainly due to the contribution of anharmonic terms in the crystal potential energy. The anharmonicity is increased by lattice defects such as disordered charge distribution. Petzelt et al [2] concluded that anharmonicity increases with the increase in permittivity and thereby an increase in dielectric loss. Investigations of the dielectric properties at microwave frequencies are sometimes controversial, which
is primarily due to the interference of extrinsic factors with the measured dielectric characteristics. The most promising approach to understanding the intrinsic microwave dielectric properties of materials is to investigate their high-frequency dielectric response, including that in the submillimeter and infrared regimes, since the intrinsic losses are overwhelmingly stronger than the extrinsic ones in the far-infrared region and beyond [3–6].

Recently there has been a growing interest on rare earth based 1:1 B-site ordered complex perovskites with the chemical formula Ln(B'B'')x5O3 (where Ln = La and Nd; B' = Mg, Co, and Zn; and B'' = Ti and Sn) for the production of microwave resonators [7–11]. These materials crystallize with a monoclinic P21/n space group due to a' a'' c* tilting and B-site ordering, exhibiting large values of negative temperature coefficient, a high quality factor, and a moderate dielectric constant. Spectroscopic measurements of La(Mg0.5Ti0.5−xSnx)O3 and (1 − x)La(MgSn)x0.5O3−xNd(MgSn)x0.5O3 ceramics have been performed in an attempt to understand the nature of these low-loss dielectric materials in terms of the lattice vibrational modes in the infrared region of the spectra [12, 13]. Moreover, the Raman-scattering spectrum provides valuable insight into order–disorder phenomena [12, 13]. Raman scattering, in particular, is very sensitive to sample composition and structural variations, making it suitable for studying the effects of atomic substitution on both the Raman phonon position as well as linewidth. In this way correlations between phonon vibrations and the microwave properties can be addressed.

In this paper, we present the Raman-scattering and infrared reflectivity measurements of La(Mg0.5Ti0.5)O3 (LMT) ceramics prepared by either the solid-state reaction or the citric-acid chemical method. The Raman and infrared phonon lines are assigned to definite atomic motions by comparison with predictions of first-principles calculations. Dielectric parameters obtained by extrapolating infrared fitting values to the microwave frequency regime are compared with microwave data, and the correlation of phonon modes with the dielectric properties is discussed. Moreover, we emphasize how the processing method influences the spectroscopic behavior and the microwave dielectric properties of these materials.

2. Experiment

To study the effect of processing methods on the intrinsic microwave dielectric properties of the materials, La(Mg0.5Ti0.5)O3 powders were prepared either by the solid-state reaction or the citric-acid chemical method. In the solid-state reaction method, the high-purity oxides La2O3, MgO, and TiO2 with stoichiometric proportion were mixed homogeneously and were calcined at 1400 °C for 5 h. The calcined powders were then pelletized and sintered at 1600 °C for 6 h. The thus obtained samples were designated as (LMT)SS. In the citric-acid chemical method, the La(NO3)3 and Mg(NO3)2 were first mixed in stoichiometric proportion with a solution containing tetraethyl-titanium (TEOT) in nitric acid. The citric acid was then added dropwise in the cationic solution to precipitate out the cations, followed by calcination at 1250 °C for 5 h, pelletization, and sintering at 1350 °C for 6 h. The thus obtained samples were designated as (LMT)CA. It should be noted that the cations were mixed more homogeneously in citric-acid processed materials and the derived powders are more active, such that the (LMT)CA materials can be calcined and sintered at lower temperature than those required for preparing the (LMT)SS materials.

The crystal structures of the samples were checked by x-ray powder diffraction (Rigaku/MiniFlex II). Data were analyzed using the program GSAS [14]. For refinements the space group P21/n was used. The morphology and microstructure of the samples were examined using scanning electron microscopy (SEM, JEOL 6700F) and transmission electron microscopy (TEM, JEOL 2100). The microwave dielectric constant and the quality factor of the samples were measured using a cavity method at 6 GHz.

The samples were polished with 0.05 μm grain size Al2O3 powders until an optically reflecting surface was achieved. The room-temperature Raman spectra were then measured in backscattering geometry using a Renishaw inVia 1000 single monochromator equipped with a notch filter, a Leica microscope, and a Peltier cooled charge-coupled detector. The linearly polarized laser light of an Ar+ ion laser (wavelength 514.5 nm) was focused on the sample through a 100× optical microscope objective (0.95 NA) with a spatial resolution of <1 μm. The laser power used was less than 1.5 mW. The scattered light without polarization analysis was collected. The spectral resolution of these instruments was typically less than 1 cm−1. All Raman spectra were corrected for the frequency-dependent response of the system, and for the optical response of the materials.

Near-normal infrared and optical reflectance measurements were carried out at room temperature. A Bruker IFS 66v Fourier transform infrared spectrometer was used in the far-infrared and mid-infrared regions (30–6000 cm−1), while the near-infrared to near-ultraviolet regions (4000–55000 cm−1) were covered using a Perkin-Elmer Lambda-900 spectrometer. The modulated light beam from the spectrometer was focused onto either the sample or an Au (Al) reference mirror, and the reflected beam was directed onto a detector appropriate for the frequency range studied. The different sources and detectors used in these studies provided substantial spectral overlap, and the reflectance mismatch between adjacent spectral ranges was less than 1%. Spectral resolution was 2 cm−1. The optical properties (i.e. the complex conductivity σ(ω) = σ1(ω) + iσ2(ω) or dielectric constant ε(ω) = 1 + 4πiσ(ω)/ω) were calculated from a Kramers–Kronig analysis of the reflectance data [19]. To perform these transformations one needs to extrapolate the reflectance at both low and high frequencies. At low frequencies the extension was done by modeling the reflectance using the Lorentz model and using the fitted results to extend the reflectance below the lowest frequency measured in the experiment. The high-frequency extrapolations were done by using a weak power law dependence, R ≈ ωs with s ≈ 1–2.
3. Theoretical detail

To illustrate how the lattice vibrational modes are correlated to the microwave dielectric properties of the materials, we performed first-principles calculations for LMT since its structural parameters have been sufficiently studied for the theoretical calculations. The ground-state electronic structure and lattice dynamics of LMT were investigated by means of first-principles plane-wave pseudopotential density functional perturbation theory (DFPT) calculations as implemented in ABINIT [15]. The local density approximation (LDA) is employed to describe the electronic exchange-correlation interactions. Electronic configurations of La(5s$^2$, 5p$^2$, 5d$^1$, 6s$^2$), Mg(3s$^2$), Ti(3d$^2$, 4s$^2$), and O(2s$^2$, 2p$^4$) are treated as valence states respectively to generate pseudopotentials in the Kleinman–Bylander form [16] for all calculations. A cutoff energy up to 100 Ryd for the plane-wave basis set expansion is needed for fully converged results.

To model LMT, a ABO$_3$ perovskite supercell with 20 atoms (4 La, 2 Mg, 2 Ti, and 12 O atoms, respectively) is constructed in our calculations. Atomic positions within the fixed experimental lattice constants of the supercell ($a = 6.203$ Å, $b = 5.57$ Å, $c = 7.862$ Å, $\alpha = \gamma = 90^\circ$, and $\beta = 90.06^\circ$) are optimized under the influence of Hellmann–Feynman forces. The Brillouin zone (BZ) integrals for total energy and phonon calculations of the 20-atom supercell are approximated by $8 \times 8 \times 4$ and $4 \times 4 \times 3$ Monkhorst–Pack k-grid sampling [17], respectively. Furthermore, within the linear response framework, the lattice dynamical matrix, Born effective charges, dielectric properties, and phonon frequencies can be obtained from ground-state properties under a perturbation of small atomic displacement [18].

4. Results and discussion

The SEM and TEM micrographs of the (LMT)$_{SS}$ and (LMT)$_{CA}$ samples are shown in figure 1, revealing that the microstructures and the crystals of two materials are essentially the same. Both materials contain uniform grains with plate-like geometry. Figure 2 displays the x-ray diffraction (XRD) profiles of the (LMT)$_{SS}$ and (LMT)$_{CA}$ samples at room temperature. All the reflections can be indexed and no impurity phases are apparent above the background level. Rietveld refinement results of (LMT)$_{SS}$ and (LMT)$_{CA}$ listed in table 1 reveal that the lattice parameters of two samples are very much alike. The typical dielectric resonance curves measured using a cavity method for these materials are shown in figure 3. The $Q \times f$ values of (LMT)$_{SS}$ and (LMT)$_{CA}$ are around 38.561 GHz and 24.777 GHz, respectively. These values are smaller than those of LMT ceramics previously also prepared by the solid-state method [12], and are apparently due to large porosity contained in our samples. It should be noted that the materials characteristics (SEM and TEM morphologies and XRD crystallinity) of our two samples are similar, implying that the difference in $Q \times f$ properties of (LMT)$_{SS}$ and (LMT)$_{CA}$ is primarily due to intrinsic factors. The lattice dynamics of the two samples are thus investigated in detail.
to understand the intrinsic mechanism that influences their microwave dielectric behavior.

Figure 4 shows the Raman-scattering spectra of (LMT)$_{ss}$ and (LMT)$_{CA}$. Both spectra are composed of several phonon modes. We fit the phonon peaks using a standard Lorentzian profile (not shown). The frequencies and linewidths of the phonon modes shown in figure 4 are listed in table 2. The results of our samples are compared to those (g mode) derived by first-principles calculations later. Notably, (LMT)$_{ss}$ possess smaller resonance linewidths than (LMT)$_{CA}$. For example, the linewidth of the Raman phonon mode at about 717 cm$^{-1}$ (corresponding to the $g_{11}$ mode: the breathing vibrations of oxygen octahedra) is about 10 cm$^{-1}$ for (LMT)$_{ss}$ and about 12 cm$^{-1}$ for (LMT)$_{CA}$, respectively. This suggests that in (LMT)$_{ss}$, the displacement of lattice vibrations is more coherent, leading to its higher quality factor.

Although the Raman-scattering response is very sensitive to the coherence of the vibrations of the lattices, it cannot...
be directly correlated with the microwave properties of the materials. To gain insight into this correlation, we examined the infrared properties of (LMT)_{SS} and (LMT)_{CA}. Figure 5 displays the measured infrared reflectance spectra of (LMT)_{SS} and (LMT)_{CA}. In all cases, the spectra of the samples reveal the characteristics of an insulator at low frequencies. A number of phonon features are observed in the far-infrared region, which needs the first-principles calculation to unambiguously identify each resonance mode. The reflectance is modeled using Lorentzian oscillators [19]\(^4\)

\[
\epsilon(\omega) = \sum_{j=1}^{N} \frac{\omega_{pj}^2}{\omega_{pj}^2 - \omega^2 - i\gamma_j} + \epsilon_\infty, \tag{1}
\]

where \(\omega_{pj}\), \(\gamma_j\), and \(\omega_{pj}\) are the frequency, damping, and oscillator strength of the \(j\)th Lorentzian contribution; and \(\epsilon_\infty\) is the high-frequency limit of \(\epsilon(\omega)\) which includes interband transitions at frequencies above the measured range. At normal incidence, \(\epsilon(\omega)\) is related to the reflectance via

\[
R(\omega) = \left| \frac{\sqrt{\epsilon(\omega) - 1}}{\sqrt{\epsilon(\omega) + 1}} \right|^2. \tag{2}
\]

Using equations (1) and (2), the reflectance spectrum is well reproduced by considering ten Lorentzian oscillators representing the phonon peaks and two representing the electronic interband transitions. A list of fitting parameters is given in table 3.

<table>
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<th>(\omega_j) (cm(^{-1}))</th>
<th>(\gamma_j) (cm(^{-1}))</th>
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<th>(\omega_j) (cm(^{-1}))</th>
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<td>22 233</td>
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<td>103 021</td>
<td>68 568</td>
<td>49 189</td>
<td>105 472</td>
<td>65 462</td>
</tr>
</tbody>
</table>

\(\epsilon_\infty = 1.3\) \(\epsilon_\infty = 1.2\)

Figure 5. Room-temperature infrared reflectance spectra (solid lines) of the LMT materials prepared by either (a) solid-state or (b) citric-acid chemical methods. The dashed lines are the best fit using the Lorentzian model.

The real and imaginary parts of the dielectric constant, calculated by a Kramers–Kronig analysis of the reflectance curves, are presented in figures 6(a) and (b). The infrared vibrational excitations result in a negative real dielectric function between the transverse (\(\omega_{TO}\)) and the optical (\(\omega_{LO}\)) frequency of each mode. By extrapolating the low-frequency far-infrared data to zero frequency, we estimate the static dielectric constant for (LMT)_{SS} and (LMT)_{CA} samples to be \(\epsilon(\omega) = 24.5\) and 23.6. In the mid-infrared region, a flat \(\epsilon(\omega)\) can be seen and gives \(\epsilon_1 \approx 4.0\) to 3.0. The quality factor data \(Q = 1/\tan \delta = \epsilon_1/\epsilon_2\) in the 1.0–2.0 THz frequency regime evaluated from figures 6(a) and (b), are plotted in figure 7. This shows that the \(Q \times f\) values of (LMT)_{SS} are larger than those of (LMT)_{CA} in the terahertz frequency region. Moreover, for both samples, the \((Q \times f)_1\) and \((Q \times f)_2\) values
Figure 6. (a) The real part and (b) imaginary part of the dielectric constant (from a Kramers–Kronig transformation) for the \((LMT)_{SS}\) and \((LMT)_{CA}\) compounds from 30 to 800 cm\(^{-1}\).

Figure 7. The frequency dependence of the quality factor of the \((LMT)_{SS}\) and \((LMT)_{CA}\) compounds in 1.0–2.0 THz.

determined at 1.5 THz are larger than those determined at 1.0 THz, the \((Q \times f)_{1.0\;\text{THz}}\)-values, which is presumably due to the occurrence of a vibrational resonance mode near 100 cm\(^{-1}\).

A comparison between the calculated and the experimental Raman- and infrared-mode frequencies is shown in table 4. Generally, aside from some \(g\) and \(u\) modes which are too weak to be detected in the Raman and infrared spectra, the frequencies of Raman and infrared phonon peaks for the LMT materials agree well with those of the lattice vibration modes predicted by first-principles calculations. The calculated atomic displacements for the certain phonon modes are depicted in figures 8 and 9. First-principles calculations indicate that the major Raman resonance peaks in figure 4 correspond to the vibrational modes of the oxygen octahedra \((O_{\text{oct}})\), \((\text{TiO}_6)^{-\text{I}}\), or \((\text{MgO}_6)^{-\text{I}}\). For example, the calculated \(g_8\) mode at about 446 cm\(^{-1}\) is related to an asymmetric breathing vibration of Ti–O bonds in a TiO\(_6\) octahedron (figure 8(a)), the \(g_9\) mode at about 493 cm\(^{-1}\) is connected with a slightly distorted bond stretching of Ti–O bonds (figure 8(b)), and the \(g_{11}\) mode at about 713 cm\(^{-1}\) involves a symmetric breathing motion of the O\(_{\text{oct}}\) (figure 8(c)). It should be noted that, in \(g_9\) mode, the top and bottom oxygen ions of the octahedron are almost stationary and only those in the waist of octahedra are vibrating. In contrast, in \(g_8\) and \(g_{11}\) modes, all the oxygen ions of the octahedra are oscillating simultaneously and correspond to \(B_g\) and \(A_g\) symmetries, respectively.

According to first-principles calculations, the infrared resonance modes listed in table 4 can be grouped into five fractions: (i) low-frequency vibration dominated by a rigid shift of La-cation layers, \(u_1\) mode; (ii) \(O_1\)- and \(O_2\)-layers coherent vibration, \(u_2\) mode (figure 9(a)); (iii) \(O_2\)-layer vibration opposing Mg-cation motion, \(u_6\) mode (figure 9(b)); (iv) cations Mg and Ti vibrate in opposite directions, \(u_7\) and \(u_8\) modes; and (v) asymmetric vibration of the \(O_2\) layer in MgO\(_6\) octahedron, with the \(O_1\) layer stationary, \(u_{10}\) mode (figure 9(c)). We notice that the \(O_1\) layer is the layer containing oxygen and lanthanum ions, whereas the \(O_2\) layer corresponds to that containing oxygen and magnesium (or titanium) ions. In general, the vibrational modes in which the ions vibrate coherently in the same direction with respect to the inversion center exhibit stronger intensity whereas those in which the ions have incoherent vibration display weaker intensity of spectra. Specifically, the lattice vibrations of \(u_2\), \(u_6\), and \(u_{10}\) modes that have eigenvectors nearly parallel to one another contribute prominently, whereas the other modes that have eigenvectors oriented in different directions, such as \(u_1\), \(u_7\), and \(u_8\) modes, contribute insignificantly to the dielectric properties for the LMT materials. Moreover, both \(u_6\) and \(u_{10}\) modes are mainly attributed to the motion of oxygen. The difference in these modes is that, in the \(u_6\) mode, the oxygen ions in the \(O_1\) layer vibrate along the direction of the crystallographic lattice

Table 4. The normal modes of the LMT materials obtained from first-principles calculations (\(g\) and \(u\) modes) and experimental values. All units are in cm\(^{-1}\).

<table>
<thead>
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Figure 8. Normal-mode eigenvectors of (a) asymmetric breathing vibration of Ti–O bonds in a TiO$_6$ octahedron, $g_4$ mode, (b) distorted stretching of Ti–O bonds, $g_5$ mode, and (c) symmetric breathing of oxygen octahedra, $g_{11}$ mode, of the Raman-active modes of the LMT materials. The symbols are as follows: O—small red spheres; La—large gray spheres; Ti—medium yellow spheres; Mg—medium green spheres.

axis $a$, whereas, in the $u_{10}$ mode, the ions in the O$_{II}$ layer vibrate along the Mg–O–Ti bonding direction.

We now address the implications of the above analysis of Raman-scattering and infrared response of the LMT materials.

Figure 9. Normal-mode eigenvectors of (a) coherent motion of O$_I$ and O$_{II}$ oxygen layers, $u_2$ mode, (b) O-layer vibration opposing Mg-cation motion, $u_6$ mode, and (c) O$_{II}$-layer asymmetric vibration with O$_I$ layer stationary, $u_{10}$ mode, of the infrared-active modes of the LMT materials. The symbols are as follows: O—small red spheres; La—large gray spheres; Ti—medium yellow spheres; Mg—medium green spheres.

(LMT)$_{SS}$ exhibits a higher $Q \times f$ value than (LMT)$_{CA}$. The smaller linewidth of the high-frequency Raman phonon mode at about 717 cm$^{-1}$ ($g_{11}$ mode) in (LMT)$_{SS}$ indicates that the coherence of O$_{oct}$ vibration is high. This result implies that the linewidth of the O$_{oct}$ phonon in (LMT)$_{SS}$ exactly reflects the quality of the oxygen octahedron structure, which is strongly correlated with the $Q \times f$ value. Furthermore, the relative peak intensity of the two most prominent infrared phonon modes...
at about 171 (u_2 mode) and 353 cm^{-1} (u_6 mode) is larger in (LMT)_{SS}. That is, the larger intensity of the u_2 vibrational mode leads to a better quality factor for the LMT materials. As pointed out above, in the u_2 mode, all the oxygen ions vibrate in the same direction (the cations are essentially not contributing the vibration mode at such frequencies). In contrast, in the u_6 mode, the oxygen in the O_II layer is almost stationary and only the oxygen ions in the O_I layer and Mg cations contribute to this lattice vibration and are moving in opposite directions. The coherence of the vibration in the u_2 mode is evidently better than that in the u_6 mode. Finally, the dielectric constant (\epsilon = \frac{1}{\Omega} \text{Tr}(\epsilon_{\alpha\beta})) at low frequency (~35 cm^{-1}) was estimated using the effective charge in u modes derived by first-principles calculations, using the formula [21, 22]

\[ \epsilon_{\alpha\beta} = (\epsilon_{\infty})_{\alpha\beta} + \sum_{\mu,\nu} \frac{Z_{\mu\alpha}^* Z_{\nu\beta}}{m_\mu e_0 \Omega(2\pi \nu_u)^2}, \]  

where \nu_u is the frequency of the u-mode phonon, (\epsilon_{\infty})_{\alpha\beta} is the \alpha\beta component of the electronic dielectric tensor, e_0 is the permittivity of free space, \Omega is the volume per unit cell, and Z_{\mu\alpha} and Z_{\nu\beta} are effective charges of the u mode in Cartesian directions \alpha and \beta, respectively. The calculated dielectric constant (\epsilon)_{\gamma\delta} was about 23.80, which agrees well with the infrared measurements.

5. Summary

We investigated the dielectric properties of the LMT materials prepared by either the solid-state reaction or the citric-acid chemical method using Raman-scattering and infrared reflectivity spectroscopy and compared our results with the predictions of first-principles calculations. The Q \times f values estimated from the infrared measurements in (LMT)_{SS} are larger than those in (LMT)_{CA}, which is in accord with the microwave dielectric characteristics evaluated by the conventional cavity method. The high-frequency Raman-active A_g phonons (g_11 mode) corresponding to oxygen octahedron breathing vibrations exhibit smaller linewidth for (LMT)_{SS}, indicating that better coherence in lattice vibration leads to higher Q \times f values. Moreover, the analysis of infrared spectra shows that the most dominant phonon peak (u_2 mode) influencing the microwave quality factor of the LMT materials is the coherent vibration of the oxygen layer. The larger that the intensity of this vibrational mode is, the better the quality factor for the materials. All of these observables provide valuable information about the strong correlation between lattice dynamics and dielectric properties of the LMT materials.

Acknowledgments

We would like to gratefully acknowledge financial support from the National Science Council of the Republic of China under grant Nos. NSC 98-2112-M-003-004-MY3 (H-L Liu) and NSC-99-2112-M-032-007 (H-C Hsueh) and from NCTS of the Republic of China. H-C Hsueh also thanks NCHC of the Republic of China for CPU time.

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