Artificial Second-Order Nonlinear Optics in a Centrosymmetric Optical Material BiVO₄: Breaking the Prerequisite for Nonlinear Optical Materials

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ABSTRACT: Second-order nonlinear optics (NLO) is the foundation of frequency conversion for the generation of coherent light at frequencies where lasers have no emissions or operate poorly. The prerequisite for NLO materials is noncentrosymmetric symmetry that can generate an effectively non-counterbalanced spontaneous electronic polarization. Here, we propose that this material restriction can be broadened by controlling the electron distribution with a local internal electrostatic field (IEF), and we demonstrate artificially created and manipulated second harmonic generation (SHG) in a centrosymmetric optical material, a superimposed Co²⁺- and Mo⁶⁺-doped BiVO₄ thin film with 2/m point group symmetry, where a homojunction producing tunable effective polarization is formed. The SHG was characterized and tuned by IEF. This work breaks the structural symmetry constraint on NLO materials. Besides, the phase-matching-like condition was realized for the further improvement of the efficient frequency conversion. Because polarization is also a prerequisite for many other functions besides SHG, we believe that this work should provide some inspiration for the further development of optoelectronic, photonic, and electronic materials.

1. INTRODUCTION

Since the discovery of second harmonic generation (SHG) in 1961 in an α-SiO₂ crystal, second-order nonlinear optics (NLO) has been considered to be a fundamental process in classical and quantum optics for optical frequency conversion, which allows the emission of coherent light in the wavelength range from soft X-ray to terahertz radiation¹⁻⁷ that are unavailable or suffer from poor operation by direct lasing⁸⁻¹⁰. In the microscopic view, the intensity of the second-order NLO emission is determined by the second power of induced polarization (which generally depends on spontaneous polarization) of component groups in NLO materials¹¹⁻¹⁴ whereas in the macroscopic view, the second-order nonlinear coefficients for evaluating the NLO effect form third-order tensors, which should obey the structural symmetry of the noncentrosymmetric optical material, on the basis of the Neumann principle.¹⁵,¹⁶ No matter which view, a second-order NLO material should have noncentrosymmetric (NCS) symmetry, in which the contribution of the total spontaneous polarization is not eliminated, and the third-order tensors are nonzero. Therefore, an NCS structure, either intrinsic or artificial, is a prerequisite for the selection of second-order NLO materials. Restricted by this prerequisite, many relevant second-order NLO techniques have been realized and developed in the NCS materials system, including bulk crystals [e.g., KBBF (KBe₂BO₃F), KTP (KTiOPO₄), KDP (KH₂PO₄), ZGP...
(ZnGeP₂), and AGS (AgGaS₂), boundaries (e.g., silicon and domain walls), and low-dimensional materials (e.g., asymmetric quantum wells, asymmetric waveguides, and even atomic layer materials). Meanwhile, some theoretical methods, such as anionic group theory, the anharmonic motion model, and first-principles simulations, have been proposed to guide the design of NLO materials and to calculate the SHG coefficients. In fact, light frequencies near the visible region are on the order of hundreds of terahertz, and the second-order NLO processes can be considered to be a perturbation to the electronic polarization. This implies that a second-order NLO process is independent of the material symmetry if the electrons can be successfully manipulated by an applied electric field. Note that the applied electric field must be very large because the atomic field that binds electrons to ions is extremely strong (∼10⁸ V/cm). To satisfy this condition, one possibility is to apply a giant external electric field directly to the material, as proposed in 1962. The polarization required for NLO effects can be generated by the giant external electric field based on the analysis of the Curie principle, which concerns the symmetrical relationship between applied external fields and physical properties, as demonstrated in some gas and organic materials. Three kinds of doped BiVO₄ thin films, namely, Co:BiVO₄, Mo:BiVO₄, and superimposed Mo:BiVO₄/Co:BiVO₄ samples, were prepared with a simple spin-coating method following a subsequent annealing process. In a typical run, the precursor solutions were initially coated on precleaned fluorine-doped tin oxide (FTO) substrates using a spin coater at a spin rate of 1000 rpm for 6 s. Then, a superimposed doped layer was added for coupling to the doped sample. The doping concentrations of Mo⁶⁺ and Co²⁺ are 3 and 6 at. %, respectively, because an optimal Mo concentration at about 3% has been broadly proofed. More detailed information on sample synthesis is given in the Supporting Information. The Fermi energy levels of Co:BiVO₄ and Mo:BiVO₄ are different.

Figure 1. (a) 3% Mo:BiVO₄, (b) 6% Co:BiVO₄, and (c) 3% Mo:BiVO₄/6% Co:BiVO₄ thin films characterized by SEM. (d) Cross-sectional SEM image of typical 3% Mo:BiVO₄/6% Co:BiVO₄ sample.
which builds an IEF by equilibrating the Fermi energy levels when the homojunctions are formed.

The morphology of the thin films was characterized by scanning electron microscopy (SEM, Hitachi S-4800). As shown in the SEM image, porous structures consisting of quite uniform particles with a size of about 100 nm were observed on the surface of the Mo⁶⁺-doped BiVO₄ films (Figure 1a). The particle size was inhomogeneous at about 50−200 nm in Co²⁺-doped BiVO₄ films (Figure 1b). The Mo:BiVO₄/Co:BiVO₄ film shows porous structures with nonuniform particles (Figure 1c). The cross-sectional SEM image (Figure 1d) of a typical Mo:BiVO₄/Co:BiVO₄ sample shows that the thickness of the Mo:BiVO₄/Co:BiVO₄ layer is about 400 nm.

The structure of the thin films was studied by X-ray diffraction (XRD) with an X-ray diffractometer using Cu Kα irradiation (λ = 1.54 Å). The results are shown in Figure 2a. In this figure, all the samples show (101) and (004) peaks that are clearly observed with diffraction peaks at 19.1 and 29.2°, and the predominant orientation is (004) (crystallographic c-direction). The powder XRD patterns (Figure S1) of either Co:BiVO₄ or Mo:BiVO₄ are also consistent with that of pure BiVO₄, indicating that the doping of Co³⁺ or Mo⁶⁺ does not change the centrosymmetric crystal structure of BiVO₄. Singly doped BiVO₄ and coupling doped BiVO₄ were compared to determine the amount of template matching. These peaks are consistent with the standard diffraction database indexed to monoclinic phase BiVO₄.

2.2. SHG Effects of Co:BiVO₄/Mo:BiVO₄ Thin Films. We first investigated SHG at different excitation wavelengths at room temperature with a high-sensitivity fluorescence spectrometer, and the results are shown in Figure S2. Under excitation at 800, 1064, 1301, and 1502 nm, significant SHG peaks at 400, 532, 651, and 751 nm are clearly observed in the Co:BiVO₄/Mo:BiVO₄ sample. Such broad SHG signals exclude the possibility of SHG by interband or intraband transitions, which was previously observed in quantum wells. It should be emphasized that there are no SHG signals observed for the Co:BiVO₄ or Mo:BiVO₄ samples. This result rules out a surface effect formed between the Co:BiVO₄ or the Mo:BiVO₄ layers and the atmosphere as the mechanism for SHG production. Namely, the SHG signal comes directly from the Co:BiVO₄/Mo:BiVO₄ interface because the BiVO₄ structure is centrosymmetric.

To further study the SHG effects in Co:BiVO₄/Mo:BiVO₄ thin films, a nanosecond pulse laser was used at a center wavelength of 1064 nm with a repetition rate of 20 Hz and a pulse width of 20 ns. The excitation beam was linearly polarized, and the initial polarization orientation was perpendicular to the Mo:BiVO₄/Co:BiVO₄ thin film (θ = 0°) and parallel to the IEF formed by the homojunction. As illustrated in Figure S3, a half-wave plate was placed beyond the exciting laser, and a polarization analyzer was arranged to control the change of θ from 0 to 180° with steps of 20°. During the experiments, we rotated the half-wave plate, which is equivalent to rotating the sample polarization orientation. The relative intensity of the SHG peak as a function of θ is depicted in Figure 2b, with an excitation energy (J) of 0.5 mJ. Meanwhile, we found that only the superimposed Co³⁺- and Mo⁶⁺-doped BiVO₄ thin films possess high SHG relative intensity, and there is no signal for Co:BiVO₄ and Mo:BiVO₄ thin films. This result indicates that an IEF is only produced by the homojunction formed between Mo:BiVO₄ and Co:BiVO₄ and thus manipulates the electrons to generate the polarization required for SHG. For reference, the noise signals with Co:BiVO₄ and Mo:BiVO₄ thin films are also presented in Figure 2b.

Although the ionic positions in the Mo:BiVO₄/Co:BiVO₄ homojunction almost obey the symmetry of point group 2/m,
the electrons are polarized along the $z$-axis by the internal electric field that is intrinsically present at the interface, thus breaking centrosymmetry. By analyzing the homojunctions, we conclude that the symmetry of the homojunction should have only a twofold axis perpendicular to the thin film. On the basis of the theoretical analysis of the relationship between the nonlinear polarization and the applied IEF, it can be concluded that the nonlinear polarization is in phase with the electric field and that the second-order polarization intensity is proportional to the second-order nonlinear susceptibility tensor coefficient $\chi_{\text{in}}$ as in

$$
\begin{bmatrix}
 P_1 \\
 P_2 \\
 P_3
\end{bmatrix} =
\begin{bmatrix}
 0 & 0 & \chi_{14} & 0 & \chi_{16} \\
 \chi_{16} & \chi_{22} & \chi_{33} & 0 & \chi_{44} \\
 0 & 0 & \chi_{44} & 0 & \chi_{14}
\end{bmatrix}
\begin{bmatrix}
 E_1^2 \\
 E_2^2 \\
 E_3^2 \\
 2E_1E_3 \\
 2E_2E_3
\end{bmatrix}
$$

where $1 = x$, $2 = y$, $3 = z$, $4 = yz = zy$, $S = xz = zx$, and $6 = xy = yx$. For thin films, $\chi_{14} = \chi_{33} = E_3 = 0$, so

$$
P_1 = \varepsilon_0\chi_{22}E_1E_2,
$$

$$
P_2 = \varepsilon_0(\chi_{16}E_1^2 + \chi_{33}E_2^2).
$$

Thus, the generated SHG signal $I$ is proportional to the effective second-order nonlinear susceptibility tensor coefficient $\chi_{\text{in}}$ as:

$$
I \propto (2\chi_{16}\cos \theta \sin \theta)^2 + (\chi_{16}\cos \theta^2 + \chi_{22}\sin \theta^2)^2.
$$

With the above equation, the SHG peak intensities at different polarization orientations can be deduced, and the red line in Figure 2c is the fit to the experimental data with a relative value of $\chi_{16}/\chi_{22} = 1.88$ using this equation. With the goal of estimating the second-order nonlinear susceptibility of the Mo:BiVO$_4$/Co:BiVO$_4$ thin film, the SHG of KDP crystal powder was also performed for comparison under the same experimental conditions ($f = 0.5$ mJ). The comparison is shown in Figure 2d. From this figure, one finds that the SHG signal of the Mo:BiVO$_4$/Co:BiVO$_4$ thin film at $\theta = 0$ is about 1.1 times that of KDP powder, which has a nonlinear coefficient $\chi_{36}$(KDP) = 0.39 pm/V. Therefore, we estimate the nonlinear coefficients of the Mo:BiVO$_4$/Co:BiVO$_4$ thin film to be $\chi_{16} = 1.05\chi_{36}$(KDP) and $\chi_{22} = 0.56\chi_{36}$(KDP). In addition, we investigated the dependence of SHG intensity on fundamental radiation energy at 1064 nm (Figure 3a). Clearly, the SHG signal increases quadratically with excitation energy, in agreement with the SHG theory. It is proof that the SHG originates from electron polarization in the Mo:BiVO$_4$/Co:BiVO$_4$ homojunction.

2.3. Calculation of the IEF and Spontaneous Polarization Intensity. With the doping strategy employed, the doped Mo$^{6+}$ into the V$^{5+}$ site of BiVO$_4$ strengthens the n-type characteristics by supplying additional free electrons, resulting in an increase in the electric conductivity of BiVO$_4$. Acting as a hole donor, doping of Co$^{2+}$ (substitution on Bi$^{3+}$ site) strengthens the p-type characteristics in the BiVO$_4$ lattice and reduces the carrier concentration. Therefore, a homojunction was formed between Mo:BiVO$_4$ and Co:BiVO$_4$ films, which gave rise to the distortion of Fermi level toward the conduction band minimum and valence band maximum. As a consequence, an IEF would be formed. To explore the IEF and electron activity in the homojunction area, a photoelectrochemical measurement was performed to determine the doped densities ($N_d$) of the Co$^{2+}$- and Mo$^{6+}$-doped BiVO$_4$ thin film. The measurements were performed in a 0.1 M potassium phosphate electrolyte (pH = 7) using a three-electrode electrochemical cell configuration, using the prepared sample as the working electrode, a Pt sheet as the counter electrode, and a saturated calomel electrode as the reference.
For the spontaneous potential produced, equation (4) was used to estimate a value of $P_s = 1.81 \, \mu \text{C/cm}^2$, which is comparable with that of KDP in the ferroelectric phase ($2-5 \, \mu \text{C/cm}^2$), and approximately one order of magnitude smaller than those of KTP ($20 \, \mu \text{C/cm}^2$) and BaTiO$_3$ ($25 \, \mu \text{C/cm}^2$), which are well-studied commercial nonlinear optical crystals.

2.4. First-Principles Calculations and Characterizations of the IEF. To further confirm the existence of the IEF, first-principles calculations on the Mo:BiVO$_4$ and Co:BiVO$_4$ systems were performed. For the simulation models, the doping concentration of Co was set at 6.25%, which is comparable with the experimental concentration of $\sim$6%. The optimized geometries show that Mo$^{6+}$ and Co$^{2+}$ atoms substitute into the V$^{5+}$ and Bi$^{3+}$ sites in BiVO$_4$, respectively, and keep the coordination environment unchanged. The electronic structures of Mo:BiVO$_4$ and Co:BiVO$_4$ exhibit acceptor-type and donor-type semiconductor characteristics, respectively (Figure S4). As the Mo- and Co-doped films are joined together to form a homojunction (Figure 4a), the Fermi level decreases in the former and increases in the latter because of the Fermi level equilibration at a middle value. The amount of band bending is given by the following equation:

$$\Delta E_F = E_{F, Co:BiVO_4} - E_{F, Mo:BiVO_4} = kT \ln \left( \frac{N_d(Co)}{N_d(Mo)} \right)$$

where $\Delta E_F$, Co:BiVO$_4$, and $\Delta E_F$, Mo:BiVO$_4$ are the Fermi energy of Co-doped and Mo-doped BiVO$_4$, respectively, $k$ is the Boltzmann’s constant, and $T$ is the absolute temperature. On the basis of the donor density calculated above, the difference in Fermi levels leads to a total potential drop of 48 mV. In addition, when Mo-doped and Co-doped BiVO$_4$ layers come into contact, a space charge region (SCR) is simultaneously formed, and the width can be estimated using the following equation:

$$W = \sqrt{\frac{2e_0 \Delta E_F}{\varepsilon_0 \left( \frac{N_d(Co)}{N_d(Mo)} + \frac{N_d(Mo)}{N_d(Co)N_d(Mo)} \right)}}$$

Using this relation, the width of the SCR was calculated to be 3.18 nm. The maximum value of the IEF ($E_{\text{max}}$) is found to be 301 kV/cm from $\Delta E_F = \frac{1}{2} E_{\text{max}} W$. For the spontaneous polarization intensity ($P_s$) caused by the IEF, $P_s = \varepsilon_0 E_{\text{max}}$ was used to estimate a value of $P_s = 1.81 \, \mu \text{C/cm}^2$, which is comparable with that of KDP in the ferroelectric phase ($2-5 \, \mu \text{C/cm}^2$), and approximately one order of magnitude smaller than those of KTP ($20 \, \mu \text{C/cm}^2$) and BaTiO$_3$ ($25 \, \mu \text{C/cm}^2$), which are well-studied commercial nonlinear optical crystals.

To further investigate the influence of the electric field on atomic positions, we studied the lattice of Co:BiVO$_4$/Mo:BiVO$_4$ interfaces with a spherical aberration corrected scanning transmission electron microscope (STEM, FEI Titan G2 80-200 ChemiSTEM). By scanning the Mo:BiVO$_4$/Co:BiVO$_4$ interface, we found that the lattice remained...
Figure 5. (a) Tunable SHG signal comparisons among different superimposed thin films with Co-doped concentration of 4, 6, and 8% BiVO₄ and Mo-doped concentration of 3% BiVO₄. (b) Relative SHG intensity fitted with quadratic equation under different numbers of interface n.

periodic and was not obviously disrupted by the IEF. The typical images are shown in Figure S8. The X-ray photoelectron spectroscopy (XPS) (Figure S9) was further performed to investigate the chemical states of Mo:BiVO₄, Co:BiVO₄, and Mo:BiVO₄/Co:BiVO₄. All the Bi 4f and V 2p XPS peaks can be clearly observed without any shift on binding energies, which further confirms that the doping of Mo⁶⁺ and Co²⁺ does not change the lattice structure and coordination environment of BiVO₄.

2.5. Tuning of SHG Intensity. Because the SHG effect is dependent on the IEF, which is tunable by controlling the doping concentrations, we fabricated 4% Co:BiVO₄/3% Mo:BiVO₄ and 8% Co:BiVO₄/3% Mo:BiVO₄ thin film samples. On the basis of the Mott–Schottky measurement (Figure S10) and using eqs 1 and 2, we calculated the width of the SCR in 4% Co:BiVO₄/3% Mo:BiVO₄ and 8% Co:BiVO₄/3% Mo:BiVO₄ thin films to be 4.81 and 1.06 nm, respectively. These values correspond to maximum IEFs of 263 and 264 kV/cm, respectively, which induce respective polarization of 1.57 and 1.59 μC/cm². The SHG signals generated under the same conditions are shown in Figure 5a, which indicates that for 4% Co:BiVO₄/3% Mo:BiVO₄, 6% Co:BiVO₄/3% Mo:BiVO₄, and 8% Co:BiVO₄/3% Mo:BiVO₄ thin films, the ratio of SHG intensity is 0.86:1:0.88 and the ratio of the nonlinear coefficients is 0.7:1:0.8. The results in Figure 5a indicate that the nonlinear coefficients can be tuned by artificial polarization fields created by the IEF, by considering the maximum value and width of SCR in the homojunctions.

On the basis of previous results and condition of the polarization direction formed by the local IEF along the c-direction (004) (Supporting Information), we fabricated the superimposed Co²⁺- and Mo⁶⁺-doped BiVO₄ thin films with periods ranging from 1 to 9 shown in the schematic diagram in Figure S11. The relative frequency doubled light intensity (I) with number of interfaces n ranging from 1 to 17 are presented in Figure 5b. By fitting the theoretical quadratic relationship between the relative frequency doubled light intensity I and the effective length l to I ∝ lⁿ, we find that the theoretical and experimental results agree well with each other, indicating that the frequency doubling process can be phase-matched. Here, p is the width of the SCR, 3.18 nm. It should be noted that the good fit of the SHG signals from all the samples also demonstrates that the SHG signal is generated by the local IEF, because the sample with only one period has a different thickness from the others and the IEF has no influence on the structure of BiVO₄ systems. It is proposed that an analogous process as shown above may be realized at other fundamental wavelengths by suitably controlling the orientation of the thin film.

3. CONCLUSIONS

This discovery not only promises to be a good method for extending the range of alternative materials but also reflects a breakthrough in second-order NLO and nanometer optics, especially for efficient SHG by the phase-matching-like condition. Because the polarization is directly related to many nonlinear properties, such as piezoelectricity, ferroelectricity, and pyroelectricity, and so forth, the spontaneous polarization caused by an IEF provides a novel approach to the development of NLO in the future.

In summary, with the creation of an IEF in a homojunction, SHG was achieved in a Co:BiVO₄/Mo:BiVO₄ thin film, a centrosymmetric optical material. Broadband SHG was produced with fundamental wavelengths ranging from 800 to 1501 nm. The symmetry of the SHG effect was analyzed and found to possess a twofold axis. The nonlinear second-order susceptibility tensor coefficients were tuned and measured and are comparable with the nonlinear coefficients of KDP. By producing an IEF at the interfaces, phase-matching for efficient SHG was demonstrated. We believe that this work will open the door for artificially created NLO based on the IEF and should present inspiration for further development of piezoelectricity, ferroelectricity, and pyroelectricity, in which polarization is also a primary factor.

4. MATERIALS AND METHODS

4.1. Syntheses. Commercial FTO-coated glass with about 50 nm thick FTO layer (Pilkington Co.) was employed as the substrate with a thickness of 3 mm and a diameter of 1.5 cm. It was ultrasonically cleaned in ethanol (99.0%, Aldrich) for 10 min, rinsed with distilled water, and dried before the BiVO₄ deposition process. Precursor mixing solutions of 0.2 M Bi(NO₃)₃·5H₂O in glacial acetic acid (0.2 M, 0.9 mL) and vanadyl acetylacetonate (C₁₀H₁₄O₄V, 0.03 M, 5.82 mL) in acetylacetone with a Bi⁵⁺ and V⁵⁺ stoichiometric ratio of 1:1 were obtained by ultrasonication (power, 1.4 kW) for 20 min at room temperature. For the Mo⁶⁺- or Co²⁺-doped BiVO₄, molybdhenyl acetylacetonate (C₁₀H₁₆MoO₆) and cobalt acetylacetonate (C₁₀H₁₄CoO₄) were dissolved in acetylacetone (C₆H₁₂O₂) separately and then interfused with the precursor solutions containing Bi⁵⁺ and V⁵⁺. A spin coater coated the mixtures on reserved FTO substrates for four layers at a spin rate of 1000 rpm for 6 s. To ensure uniformity and stability of
the doped BiVO₄ thin films, they were then dried in air at 150 °C for 10 min and calcined at 470 °C for 30 min per layer. For the superimposed doped BiVO₄, the Mo:BiVO₄ mixed solution (380 µl) was first coated on an FTO substrate using the aforementioned procedure, and then, the Co-BiVO₄ mixed solution was spin-coated over the Mo:BiVO₄ layer. For the superimposed Co⁷⁺ and Mo⁶⁺-doped BiVO₄ thin films with various numbers of interfaces, one Mo:BiVO₄ layer was coated on the FTO substrate, and then, the Co:BiVO₄ mixed solution was spin-coated over the Mo:BiVO₄ layer to form one period. Subsequent periods were fabricated using the same spin coating procedure.

4.2. First-Principles Calculations. To simulate the doped BiVO₄ films and homojunction structures, a large supercell (BiVO₄)₁₆ of dimensions 5.096 × 5.097 × 42.661 Å was built. A vacuum thickness of 15 Å was added to avoid interaction between the film and its image produced by the periodicity. According to symmetry analysis, this model belongs to the P2 space group, so it possesses a twofold rotation axis along the z-direction, which is consistent with experimental measurements. Geometry optimizations were performed by the CASTEP package⁵⁰ with ultrasoft pseudopotentials⁵¹ and GGA-PBE functionals.⁵²,⁵³ A plane wave basis with an energy cutoff of 600 eV was used in our calculations. The convergence thresholds between optimization cycles for energy change and maximum force were set to 5.0 × 10⁻⁶ eV per atom and 0.03 eV/Å, respectively. Monkhorst-Pack grids of 2 × 1 × 1 k-points were used for the (001) surface of BiVO₄.⁵⁴ On the basis of the optimized structures, the Fermi energy, electron potential, and electron density of BiVO₄, Mo-doped BiVO₄, Co-doped BiVO₄, and Mo:BiVO₄/Co:BiVO₄ were calculated. The doping concentrations of Mo and Co were set at 1/16 concentrations (6%).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomeg.a8b02453.

The polarization direction judgment, XRD patterns of samples, characterizations of SHG effects, SHG experimental setup, electronic structures of Mo:BiVO₄, and Co:BiVO₄ Fermi levels calculations of perfect/Mo-/Co-doped BiVO₄ STEM spectrum of doped interfaces, XPS spectrum of samples, Mott–Schottky plots of Co:BiVO₄, and schematic diagram with various periods (PDF)

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Notes

The authors declare no competing financial interest.

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H.Y. conceived the idea. B.Z. and Z.W. worked on the sample fabrication. Y.X. built the optical setup. Y.X. and F.L. performed the measurements and analyzed the data. Y.X. and F.L. wrote the manuscript, assisted by Z.W., H.Y., Z.L., B.G., H.Z., B.H., and J.W. All authors discussed the results and commented on the manuscript. The authors wish to thank Professor R. I. Boughton, Department of Physics and Astronomy of Bowling Green State University, for the discussion and linguistic advice.

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