Alkaline-Earth Metals-Doped Pyrochlore Gd$_2$Zr$_2$O$_7$ as Oxygen Conductors for Improved NO$_2$ Sensing Performance

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This work proposed a novel strategy to fabricate highly-stable NO$_2$ sensor based on a pyrochlore-phase Gd$_2$Zr$_2$O$_7$ oxygen conductor. The incorporation of alkaline-earth metals distinctly enhances the sensing performance of the Gd$_2$Zr$_2$O$_7$ based sensors. The excellent sensor based on Gd$_{1.95}$Ca$_{0.05}$Zr$_2$O$_{7+\delta}$ exhibits rapid response-recovery characteristics with the maximum response current value ($\Delta I = 6.4\,\mu A$), extremely short 90% response (3 s) and 90% recovery (35 s) time towards 500 ppm NO$_2$ at 500 °C, which is better than that of commercial YSZ under the same condition. The $\Delta I$ value towards NO$_2$ is much higher than those towards other gases (CH$_4$, C$_3$H$_6$, C$_3$H$_8$, CO, NO, SO$_2$, C$_2$H$_4$, CO$_2$ and C$_2$H$_6$), exhibiting excellent selectivity for detecting NO$_2$. The response signal basically maintains a stable value of 6.4 $\mu A$ after the sensors was stored for half a month and a month. The outstanding selectivity and highly stability of the NO$_2$ sensors based on Gd$_{2-x}$M$_x$Zr$_2$O$_{7+\delta}$ are expected to a promising application in automotive vehicles.

Nitrogen oxides (NOx, NO and NO$_2$), which are mainly released from automotive engines, are harmful to humans and the environment$^{1-3}$. To monitor NO$_2$ emission, great efforts are devoted to develop high performance and compact solid electrolyte type NO$_2$ sensor with a sensitive, stable, selective and quick response$^{4-11}$. As to NO$_2$ sensors, the solid electrolytes play a very important role in the sensing performances. To further improve the properties of the NO$_2$ sensors, great efforts have been devoted to improve the ionic conductivity of solid electrolytes and develop novel oxygen conductors$^{12-14}$. YSZ possesses exceedingly high ionic conductivity only when the temperature exceeds 1073 K, whereas the high operating temperature inevitably not only limits the selection of compatible electrode and interconnect materials, but shortens the service life of the sensor$^{12-14}$. Perovskite-phase (ABO$_3$) solid electrolytes have been recently indicated to be quite optimal materials for NO$_2$ sensors. One of the most promising materials is doped LaGaO$_3$,$^{15}$ such as (La, Nd)$_{0.96}$Sr$_{0.04}$Ga$_{0.8}$Mg$_{0.2}$O$_{2.9}$,$^{16,17}$, the conductivity of which is comparable to YSZ. Unfortunately, Gallium has a volatility, which greatly restricts the application of such sensor in NO$_2$ detection too. Inspired by the studies on doped LaGaO$_3$ above, we have recently reported the NO$_2$ sensors based on perovskite-phase GdAlO$_3$ substrates, in where Ca was arranged at A-sites$^{18}$. However, the response and recovery time is very long in excess of 119 and 92 s, respectively. The most key reason leading to the long response and recovery time can be related to the oxygen transport capacity of the solid electrolyte and the ability to capture NO$_2$ of the sensor$^{19}$. Therefore, it stimulates us to seek a novel solid electrolyte material, expecting to further enhance oxygen vacancies and NO$_2$ adsorption capacity to improve the electrochemical catalytic performance.

For the general amperometric NO$_2$ sensor, NO$_2$ gas is first absorbed on the porous surface of the sensing electrode (SE), which makes NO$_2$ gas many contacts with the surface of the SE grains that is high catalytic activity, making NO$_2$ gas decompose into NO and NO further decompose into N$_2$ with Eqs 1 and 2 in the vicinity of the electrode, respectively$^{20,21}$. The decomposition substance will diffuse through the bulk electrode which makes the target gas NO$_2$ hardly reach the electrode/electrolyte interface, causing a low sensitivity towards NO$_2$. The higher
catalytic activity of NO2 gas decomposition into NO or N2 gives the lower sensitivity towards NO2. Therefore, the sensitivity of the sensor strongly depends on the catalytic activity of the oxide electrode. Recently, p-type semiconducting metal-oxides have drawn a lot of attention as sensing electrode, such as NiO, TeO2, Co3O4 and CuO. Among these oxides, NiO is widely used as sensing electrode of NO2 sensor due to its non-poisonous and large NO2 adsorption capacity. To improve the sensitivity of NiO-based sensor, conventional tactics is to reduce the catalytic activity of the oxide electrode via adding the corresponding electrolyte material such as YSZ to NiO in order to extend the length of three phase boundary (TPB), which will necessarily influence the adsorption capacity of NO2. As it is well-known, the larger the capacity of NO2 adsorption is, the faster the catalytic reaction rate of Eq. 3 is as well as the higher the sensitivity of the sensor is. A fraction of NO generated by Eq. 3 would be further reduced to N2 by gaining electrons (Eq. 4) due to the high catalytic activity of SE, which in turn promotes the generation rate of O2− on SE. The O2− generated by the cathodic reaction is quickly transported along the direction of the electrolyte grains to the reference electrode (RE), where the anodic reaction (Eq. 5) takes place. In whole of the electrochemical reaction cycle, the rate-determining step is strongly dependent on the oxygen ion carriers to modulate the oxygen transport capacity of the solid electrolyte, the adsorption−desorption behavior of NO2 at the electrolyte/electrode interface. How to restrain NO2 gas catalytic decomposition on SE and enhance the pyrochlore-phase structure due to the existence of the superstructure peaks. However, the pyrochlore superelectrolyte, consequently active for NO2 sensing. And then we fabricated several amperometric-type NO2 sensors

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\text{Decomposition reaction: } \text{NO}_2 \rightarrow \text{NO} + 1/2\text{O}_2
\]  

(1)

\[
\text{NO} \rightarrow 1/2\text{N}_2 + 1/2\text{O}_2
\]  

(2)

\[
\text{Cathodic reaction: } \text{NO}_2 + 2e^- \rightarrow \text{NO} + \text{O}_2^-
\]  

(3)

\[
\text{NO} + 2e^- \rightarrow 1/2\text{N}_2 + \text{O}_2^-
\]  

(4)

\[
\text{Anodic reaction: } \text{O}_2^+ \rightarrow 1/2\text{O}_2 + 2e^-
\]  

(5)

Generally, the function of the solid electrolyte with high conductivity used for the sensor is to only transport oxygen ion as the medium. Expectedly, there exists in a solid electrolyte with high concentration of oxygen vacancies that can not only carry the oxygen ion but simultaneously modulate NO2 transport capacity at mild-temperature. Compared to the perovskite-phase binary oxides (ABO3), pyrochlore-phase oxides with the general formula of A2B2O7□, where six oxygen sites are always fully occupied while the seventh can be arranged in an additional oxygen non-stoichiometry □, exhibit very high intrinsic concentration of oxygen vacancies with the minimal number of 12.5%. Interestingly, introducing disordered extra vacancies can further enhance the conductivity of materials. For example, Ca-doped Gd2Ti2O7 (Gd0.55Ca0.45Ti2O7-xOy), the ion conductivity is as high as 0.05 S cm−1 at 800 °C over a large pO2 range (10−1 to 10−20 atm). Another advantage of the pyrochlore-phase oxides (A2B2O7□) can provide both A sites for doping cations with larger ionic radius and B sites with smaller ionic radius to adjust the range of 1.46 ≤ r (A3+) ≤ r (B4+) ≤ 1.78 that is the prerequisite to form stable pyrochlore structure18, making them promise hosts for solid electrolytes for NO2 sensor in the intermediate-temperature.

In the family of pyrochlore-phase compounds, it was reported that Gd2Zr2O7 exhibited the highest ionic conductivity (1 × 10−3 S cm−1) at the intermediate temperature of 1000 K. Several studies demonstrated that the incorporation of Ti cations at B sites and Nd cations at A sites resulted in the enhanced conductivity of pyrochlore-phase Gd2Zr2O7 in the temperature range of 773–973 K. In this work, we studied firstly the incorporation of alkaline earth metals (Ca, Sr, and Ba) in pyrochlore-phase Gd2Zr2O7 based on the following two core considerations: (1) Incorporation of alkaline earth metals creates more amounts of oxygen vacancy into the solid electrolyte and increases oxygen migration to facilitate the anodic reaction; (2) Alkaline earth metals serve as a dopant in view of its strong NO2 storage capacity required for the electrochemical catalytic performance at low temperatures.

Results and Discussion

XRD patterns of Gdx−yCa0.55Zr0.45Ti2O7−x samples calcined at 1500 °C for 4 h in air are presented in Fig. 1. It is observed that pure Gd2Zr2O7 exhibits an ordered pyrochlore-phase structure, which is characterized by the presence of the typical superstructure diffraction peaks at 2θ ≈ 14° (111), 28° (311), 37° (331) and 45° (511)11−13. As seen from Fig. 1, with the substitution of Gd3+ cations by Ca2+ cations, Gdx−yCa0.55Zr0.45Ti2O7−x (0 < x < 0.2) can maintain the pyrochlore-phase structure due to the existence of the superstructure peaks. However, the pyrochlore superstructure reflections lost and the samples display a defective fluorite-phase structure with x ≥ 0.2. This means that the phase transition from pyrochlore to defective fluorite happens when the doping content x is beyond 0.2. Interestingly, perovskite structure CaZrO3 will not produce until x > 0.2. Among these oxides, NiO is widely used as sensing electrode of NO2 sensor due to its non-poisonous and large NO2 adsorption capacity. To improve the sensitivity of NiO-based sensor, conventional tactics is to reduce the catalytic activity of the oxide electrode via adding the corresponding electrolyte material such as YSZ to NiO in order to extend the length of three phase boundary (TPB), which will necessarily influence the adsorption capacity of NO2. As it is well-known, the larger the capacity of NO2 adsorption is, the faster the catalytic reaction rate of Eq. 3 is as well as the higher the sensitivity of the sensor is. A fraction of NO generated by Eq. 3 would be further reduced to N2 by gaining electrons (Eq. 4) due to the high catalytic activity of SE, which in turn promotes the generation rate of O2− on SE. The O2− generated by the cathodic reaction is quickly transported along the direction of the electrolyte grains to the reference electrode (RE), where the anodic reaction (Eq. 5) takes place. In whole of the electrochemical reaction cycle, the rate-determining step is strongly dependent on the oxygen ion carriers to modulate the oxygen transport capacity of the solid electrolyte, the adsorption−desorption behavior of NO2 at the electrolyte/electrode interface. How to restrain NO2 gas catalytic decomposition on SE and enhance the pyrochlore-phase structure due to the existence of the superstructure peaks. However, the pyrochlore superstructure reflections lost and the samples display a defective fluorite-phase structure with x ≥ 0.2. This means that the phase transition from pyrochlore to defective fluorite happens when the doping content x is beyond 0.2. Interestingly, perovskite structure CaZrO3 will not produce until x ≥ 0.1. Figure S1 represents the XRD patterns of Gdx−ySr0.55Zr0.45Ti2O7−x and Gdx−yBa0.55Zr0.45Ti2O7−x for the compositions corresponding to x = 0−0.2, whereas they exhibit...
the onsets of phase separation to pyrochlore [ICDD PDF 16–0799], perovskite structure SrZrO$_3$ [ICDD PDF 74–2231], and BaZrO$_3$ [ICDD PDF 89–2486] (marked by asterisks) even when the doping concentration is very low such as $x = 0.02$. This is attributed to the great difference of the ionic radius of Gd$^{3+}$ and Sr$^{2+}$ (Ba$^{2+}$), resulting in the difficult substitution of small Gd$^{3+}$ by large Sr$^{2+}$ or Ba$^{2+}$ cations. In whole of doping concentration, Gd$_{2-x}$Sr$_x$Zr$_2$O$_7$ and Gd$_{2-x}$Ba$_x$Zr$_2$O$_7$ retain the pyrochlore-phase structure.

It is noted from Fig. 2A that the peak of (311) $F/(622)_{Py}$ for Gd$_{2-x}$Ca$_x$Zr$_2$O$_7$-$\delta$ distinctly shifts towards lower angle for $x \leq 0.05$, and then tardily shifts towards higher angle for $x \geq 0.1$, predicating the lattice expansion as Ca$^{2+}$ is introduced, which probably induces variation in oxygen vacancies. The cell parameters of all the compositions of Gd$_{2-x}$Ca$_x$Zr$_2$O$_7$-$\delta$ samples were calculated using MDI Jade program, and the results were depicted in Fig. 2B. Clearly, the cubic lattice parameters with pyrochlore-phase structure display a rapid increase for $x \leq 0.05$, and then gradual decrease for $x \geq 0.1$, whereas the lattice parameters of the samples with defect fluorite structure are nearly half of the corresponding pyrochlore value. Since Ca$^{2+}$ possesses similar ionic radius to Gd$^{3+}$ other than Zr$^{4+}$, the excess Ca$^{2+}$ tends to be arranged in A-site. The substitution of Gd$^{3+}$ by a fraction of Ca$^{2+}$ is favorable to the pyrochlore-phase structure as the ionic radius of Ca$^{2+}$ is slightly larger than that of Gd$^{3+}$, which makes the ionic radius ratio of $r$(Gd$^{3+}$-Ca$^{2+}$)$_{\text{average}}$/r(Zr$^{4+}$) larger than 1.46 and inevitably creates larger A-site volume. Too much Ca can combine with Zr at B-site to form perovskite structure CaZrO$_3$, resulting in the phase transition from pyrochlore to defect fluorite structure. The split and shift of the peak of (311) $F/(622)_{Py}$ towards higher angle for Gd$_{2-x}$Ca$_x$Zr$_2$O$_7$-$\delta$ ($x \geq 0.1$) in Fig. 2A are attributed to the lattice disordering and the phase change of the formation of a new matter CaZrO$_3$ due to the dissociation of doped Ca ions from the Gd,Zr,O$_3$ lattice structure.

To further confirm the structure, Raman spectroscopic investigations were carried out on all these samples at ambient conditions in the range 200–1000 cm$^{-1}$, as shown in Fig. 3. Group theoretic analysis for the defect pyrochlore-phase compounds with space group Fd3m predicts six-Raman active modes, which are $A_{1g} + E_g + 4F_{2g}$.

The spectrum of the Gd$_2$Zr$_2$O$_7$ pyrochlore only shows four distinct bands due to the disorder, which is in quite good agreement with the literature. A very obvious band at ~300 cm$^{-1}$ that is identified as the $E_g$ mode has been observed, whereas the other two vibrational frequencies at 412 and 608 cm$^{-1}$ may be assigned to two of the four $F_{2g}$ modes. The Raman-active band at 518 cm$^{-1}$ has been assigned as the $A_{1g}$ mode. As seen
from Fig. 3A, the Raman spectra of Gd$_{2-x}$Ca$_x$Zr$_2$O$_{7+\delta}$ $(0.2 < x \leq 0.3)$ is reduced to a broad continuum of density of states. It has been reported that the Raman spectra of the defect fluorites (A$_{0.5}$B$_{0.5}$O$_{1.75}$) has a single broad band as the seven oxygen ions in the fluorite structure are randomly distributed over the eight anion sites. This implies that the phase transition from pyrochlore to defect fluorite has happened for Gd$_{2-x}$Ca$_x$Zr$_2$O$_{7+\delta}$ $(0.2 < x \leq 0.3)$ samples, which is agreement with the XRD result above. In addition, a new band is observed at around 720 cm$^{-1}$ when M is introduced at the A site of the lattice. This new vibrational mode is assigned to the M–O symmetrical stretch vibration. These results further confirm that M is introduced to the A site of the lattice.

The microstructures of Gd$_{2-x}$M$_x$Zr$_2$O$_{7+\delta}$ pellets sintered at 1500 °C for 4 h are given in Fig. 4. As shown, Gd$_{2-x}$M$_x$Zr$_2$O$_{7+\delta}$ substrates prepared by hydrothermal method present the dense pores with a clear boundary during the grains. Pores are seldom found in the grain boundaries. The surface morphology of Gd$_2$Zr$_2$O$_7$ exhibited non-uniform grain structure, high density and homogeneous surface with the grain size in the range of 0.2–1.2 μm. With M$^{2+}$ dopped, the average grain size of the pellets begins to decrease. The average grain size of Gd$_{1.95}$M$_{0.05}$Zr$_2$O$_{7+\delta}$ (M = Ca, Sr, Ba) pellets is in the range of 0.2–1 μm, 0.1–0.8 μm, and 0.05–0.6 μm, respectively. It should be noted that the Gd$_{1.95}$Ca$_{0.05}$Zr$_2$O$_{7+\delta}$ pellet exhibits relatively fine grains of 0.2–1 μm in size as shown in Fig. 4B, as compared with other ones of Gd$_{1.95}$Sr$_{0.05}$Zr$_2$O$_{7+\delta}$ and Gd$_{1.95}$Ba$_{0.05}$Zr$_2$O$_{7+\delta}$ of which secondary perovskite phase (SrZrO$_3$ and BaZrO$_3$) seems to appear. To confirm the form of perovskite structure, the BSE image of Gd$_{1.95}$Sr$_{0.05}$Zr$_2$O$_{7+\delta}$ with higher doped concentration for better observation as a good case is shown in Fig. 5. SEM photomicrograph of Gd$_{1.8}$Sr$_{0.2}$Zr$_2$O$_{7+\delta}$ is shown in Fig. 5A. The micrograph manifests heterogeneous grain structures, which could be second phase SrZrO$_3$. The BSE image of the same location (Fig. 5B) exhibits high contrast, corresponding to the heterogeneous grain regions of the SE image. To confirm the heterogeneous grain, X-ray mapping was carried out, as shown in Fig. 5C, D, E and F. The heterogeneous grain in the BSE image is found to be rich in gadolinium, zirconium, strontium, and oxygen. The element analysis displays that the atomic ratio of the second phase for Sr: Zr: O is close to 1: 1: 3, suggesting that the second phase could be perovskite SrZrO$_3$, which is in agreement with the result of XRD. We speculate that the form of perovskite structure CaZrO$_3$, SrZrO$_3$ and BaZrO$_3$ can influence the sensing performance of the sensors based on Gd$_{1.95}$M$_{0.05}$Zr$_2$O$_{7+\delta}$ substrates. Figure 4C and D shows the SEM photographs of NiO sensitive electrode calcined at 1400 °C for 2 h and the cross-section for porous layer in view of the sensor based on Gd$_{1.95}$Ca$_{0.05}$Zr$_2$O$_{7+\delta}$ substrates, respectively. It is observed that the surface of NiO SE shows a porous and three-dimensional network structure, which is in favor of prolonging the
and basically ignore. It was reported that CaZrO₃, SrZrO₃ and BaZrO₃ belong to proton conductivities, which rapidly increase upon injecting the NO₂ gas and sharply recover to an original level after removal of the NO₂ gas. To better distinguish the response curve, the base current levels have been shifted. Clearly, the response signals exposed to 500 ppm NO₂ with a polarized potential of −300 mV at 500 °C are shown in Fig. 6A, where in order to better distinguish the response curve, the base current levels have been shifted. The response signal rapidly increase upon injecting the NO₂ gas and sharply recover to an original level after removal of the NO₂ gas. In our study, the response current value was defined as the difference of current value between the sample gas and base gas (ΔI = Igas − Ibase), where Igas and Ibase referred to the response current values in the targeted concentration and 0 ppm NO₂ gas. As seen from Fig. 6C, the ΔI value of the undoped Gd₂O₃ is relatively small (2.42 μA) at 500 °C. After introducing Ca ions, ΔI reaches the maximum 6.40 μA for x = 0.05 at 500 °C as compared with the sensor based on YSZ (6.20 μA) commercially used. However, ΔI of x = 0.1, 0.15, 0.2 drops to 5.61, 3.46, and 2.07 μA, respectively, suggesting that the calcium doping concentrations have a great effect on the ΔI values of the sensor at 500 °C. It is reasonable that the higher the conductivity is, the better the sensing performance is. However, the sensor based on Gd₁.95Ca₀.05Zr₂O₇ substrates when exposed to 500 ppm NO₂ with a polarized potential of −300 mV at 500 °C are shown in Fig. 6B. Clearly, the ΔI values of the sensors are very low and basically ignore. It was reported that CaZrO₃, SrZrO₃ and BaZrO₃ belong to proton conductivities, which results in not only the loss of oxygen transport function, but the decrease of NO₂ adsorption capacity, which restrains the electrode catalytic reaction of Eq. 3. Consequently, the ΔI values of the NO₂ sensors will be lowered. The response and recovery time shown in Fig. 6D confirms the conclusion. The response time that is commonly

**Figure 5.** (A) SEM photomicrograph of Gd₁.8Sr₀.2Zr₂O₇ (SE image); (B) SEM photomicrograph of Gd₁.8Sr₀.2Zr₂O₇ (BSE image); (C), (D), (E), and (F): X-ray maps for the constituent ions with the image for Gd₁.8Sr₀.2Zr₂O₇ (SE image); (BSE image); (C).
defined as the time that the resistance of the sensor reaches to 90% of the saturation value when the sensor is exposed to NO₂ for x = 0, 0.02, 0.05, 0.1 and 0.2 s is 5, 4, 3, 4, 5 and 6 s, respectively. The recovery time that is in general defined as the time required for recovering the 90% of the original resistance for x = 0, 0.02, 0.05 and 0.1 is 45, 43, 35 and 38 s, respectively, whereas the recovery time is obviously delayed and exceeds 60 s when Ca content is greater than 0.1. This can be ascribed to more CaZrO₃ produced as Ca ions increase, which makes the sensitivity lower. The results in this work indicate that among the sensors based on Gd₂₋ₓCaxZr₂O₇₋₄δ substrates, the sensor based on Gd₁.₉₅Cₐ₀.₀₅Zr₂O₇₋₄δ substrate displays the optimal device with the highest ΔI (6.4 μA), the shortest response (3 s) and recovery time (35 s), which is obviously better than the sensor based on commercial YSZ with ΔI (6.2 μA), the response (7 s) and recovery time (39 s).

For the purpose in comparison of the sensing performances, the effect of different doping element (Ca, Sr and Ba) and doping concentration on the ΔI values in 500 ppm NO₂ at 500 °C is shown in Fig. 7A. Obviously, the ΔI values of the sensors based on Gd₂₋ₓCaxZr₂O₇₋₄δ substrates are higher than those for Gd₂₋ₓSrₓZr₂O₇₋₄δ and Gd₂₋ₓBaₓZr₂O₇₋₄δ substrates. This is mainly because SrZrO₃ and BaZrO₃ are easy to be produced even if the doping content is greater than 0.1. Thus the effect of Sr and Ba doping on the sensing performance is weak. For each doping element, the sensors based on the substrates for x = 0.05 manifest the highest ΔI value. It is concluded that the pyrochlore-phase Gd₁.₉₅Mₐ₀.₀₅Zr₂O₇₋₄δ is a kind of outstanding electrolyte for NO₂ sensor. Therefore, the effect of different operating temperature on the ΔI values of the sensors based on Gd₁.₉₅Mₐ₀.₀₅Zr₂O₇₋₄δ substrates in 500 ppm NO₂ is presented in Fig. 7B. Clearly, when increasing operating temperature at a fixed doping element, the ΔI values of the sensors increase as well. For example, the ΔI value is 0.59 μA for the sensor based on Gd₁.₉₅Cₐ₀.₀₅Zr₂O₇₋₄δ substrate at 400 °C. With increasing temperature such as 500 °C, the ΔI value increases to 6.4 μA. This is mainly attributed to the enhanced conductivity and electrochemical reaction rate when increasing temperature. In addition, over the whole range of temperature, the sensor based on Gd₁.₉₅Cₐ₀.₀₅Zr₂O₇₋₄δ substrate gives the highest ΔI value of 6.4 μA, exhibiting highly sensing performance to NO₂ at the bias potential of −300 mV at 500 °C.

To investigate in depth the sensing performance, the dynamic amperometric response and recovery transients for the sensors based on Gd₁.₉₅Mₐ₀.₀₅Zr₂O₇₋₄δ substrates as a function of the NO₂ concentration at the applied potential of −300 mV at 500 °C are presented in Fig. 7C. The response current value gradually increases when NO₂ concentration ascends to
500 ppm, the response current value raises to 6.40 μA at under the same conditions. Very good linear relationships between the response signal ΔI and NO2 concentrations in the range from 100 to 500 ppm are achieved (Fig. 7D), indicating that the sensors based on Gd_{1.95}Ca_{0.05}Zr_{2}O_{7+δ} substrates have an excellent sensitive performance to NO2 at 500 °C. The sensitivity of the sensor is defined as the slope of response current value ΔI on the target gas concentration at a certain temperature, which can be calculated from the fitting results of ΔI on various NO2 concentrations. And the sensitivities of the Gd_{1.95}Ca_{0.05}Zr_{2}O_{7+δ}, Gd_{1.95}Sr_{0.05}Zr_{2}O_{7+δ}, Gd_{1.95}Ba_{0.05}Zr_{2}O_{7+δ} based on sensor is 9.28, 7.97, and 4.18 nA/ppm at 500 °C, respectively. It is manifested that Gd_{1.95}Ca_{0.05}Zr_{2}O_{7+δ} substrate is most excellent substrate among Gd_{2−x}M_{x}Zr_{2}O_{7+δ} ones of the sensor. Therefore, the dynamic amperometric response and recovery transients to NO2 in concentrations range of 100–500 ppm for the sensor based on Gd_{1.95}Ca_{0.05}Zr_{2}O_{7+δ} substrate with a polarized potential of −300 mV at 400, 450 and 500 °C are investigated and presented in Fig. S3A. The response current value is almost linear to the NO2 concentration from 100 to 500 ppm at 400, 450 and 500 °C (Fig. S3B). It is found that the response signal is very low at 400 °C, whereas increasing operating temperature, the response signal greatly increases at each NO2 concentration. The sensor based on Gd_{1.95}Ca_{0.05}Zr_{2}O_{7+δ} substrate exhibits the highest ΔI value of 6.40 μA with 500 ppm NO2 at 500 °C. For NO2 sensor, the response current depends on the electrochemical catalytic activities of the NiO sensing electrode at TPB. The number of NO2 molecules adsorbed on the sensing electrode increases when NO2 concentration changes from 100 to 500 ppm, implying that more oxygen ions (O2−) would be produced through the cathodic reaction of Eq. (3). As a result, the response current value of the sensor is enhanced. While the electrochemical reaction rate of both Eqs (3) and (5) increases when increasing operating temperature at a fixed NO2 concentration, causing the response current value of the sensor to increase as well. The sensitivities fitted from Fig. S3B are 0.97, 3.59, and 9.28 nA/ppm at 400, 450 and 500 °C, respectively. It is found that the sensitivity greatly increases as increasing operating temperature. In practical automobile exhaust application, the concentration for NO2 gas detection can be very low. Therefore, the response and recovery transients of the Gd_{1.95}Ca_{0.05}Zr_{2}O_{7+δ} based sensor towards 25–500 ppm NO2 with lower NO2 concentration at 500 °C is exhibited in Fig. S3C. Figure S3D depicts the good

Figure 7. (A) The effect of doping concentration for different element on the ΔI value in 500 ppm NO2 at 500 °C: (a) Gd_{2−x}Ca_{x}Zr_{2}O_{7+δ}, (b) Gd_{2−x}Sr_{x}Zr_{2}O_{7+δ}, (c) Gd_{2−x}Ba_{x}Zr_{2}O_{7+δ}; (B) the effect of doping element and temperature on response signal ΔI in 500 ppm NO2 at 500 °C; (C) Amperometric response and recovery transients to various NO2 concentrations of the sensor in the presence of 5 vol. % O2 at 500 °C (applied potential −300 mV, flow rate 200 cm3/min): (a) Gd_{1.95}Ca_{0.05}Zr_{2}O_{7+δ}, (b) Gd_{1.95}Sr_{0.05}Zr_{2}O_{7+δ}, (c) Gd_{1.95}Ba_{0.05}Zr_{2}O_{7+δ}; (D) the relationship between the response current values ΔI and NO2 concentrations at 500 °C: (a) Gd_{1.95}Ca_{0.05}Zr_{2}O_{7+δ}, (b) Gd_{1.95}Sr_{0.05}Zr_{2}O_{7+δ}, (c) Gd_{1.95}Ba_{0.05}Zr_{2}O_{7+δ}.
which only accounts for 0.16 and 0.31% of the original response current value of 6.4 μA. It was observed that the present sensor displayed an excellent sensitivity and selectivity for NO₂ over the other gases tested, while a slight cross sensitivity was detected with compounds such as CO, CH₄, C₃H₈, C₃H₆, NO, SO₂, C₂H₄, CO₂, and C₂H₆. The maximum response current reached 6.4 μA towards 500 ppm NO₂ at 500 °C, outdistancing the other gases. Compared with NO₂ gas, the ΔI value of interference gases such as CO, CH₄, C₃H₈, C₃H₆, NO, SO₂, C₂H₄, CO₂, and C₂H₆ is fairly small and basically ignored in the whole of operating temperatures.

The stability of the sensors based on Gd₁.₉₅Ca₀.₀₅Zr₂O₇₊δ substrates was measured for 3 h upon exposure to 500 ppm NO₂ gas at 500 °C, as shown in Fig. 8B. The ΔI value of the sensor based on Gd₁.₉₅Ca₀.₀₅Zr₂O₇₊δ basically maintains constant and slightly decreases on Gd₁.₉₅Ba₀.₀₅Zr₂O₇₊δ whereas the ΔI value of the sensor based on Gd₁.₉₅Sr₀.₀₅Zr₂O₇₊δ obviously decreases during whole the test, suggesting excellent stability towards Gd₁.₉₅Ca₀.₀₅Zr₂O₇₊δ substrate as compared to Gd₁.₉₅Sr₀.₀₅Zr₂O₇₊δ and Gd₁.₉₅Ba₀.₀₅Zr₂O₇₊δ ones. Meantime, good NO₂ sensors should possess the ability to maintain a reliable stabilized sensing performance after a period of storage. The ΔI values with slight fluctuation decreases by 0.01 and 0.02 μA, which only accounts for 0.16 and 0.31% of the original response current value of 6.4 μA after the sensors based on Gd₁.₉₅Ca₀.₀₅Zr₂O₇₊δ was stored for half a month and a month, respectively, indicating good long-term stability for NO₂ detection.

The coordination between the GMZ electrolyte and the SE can be one of pivotal factors of the NO₂ sensing performance. When the negative electrode is applied on SE, the SE preferentially absorbs NO₂ molecules on the surface other than O₂ or other rest of gas among atmosphere as the electron affinity of NO₂ is about five times higher than that of oxygen. NO₂ gas diffuses through the porous NiO along TPB to GMZ electrolyte due to its large adsorption capacity at mild temperature, which necessarily extends the length of TPB. This makes NO₂ gas fewer contacts with the surface of the NiO grains and reach TPB interface without serious catalytic decomposition of NO₂. The mass spectrum trace signal of off-gas (500 ppm NO₂) was stored for half a month and a month, respectively, indicating low high sensitivity for NO₂ detection.

Conclusions
A highly-stable amperometric-type NO₂ sensor based on pyrochlore-phase Gdₓ₋₂MₓZr₂O₇₊δ solid electrolyte with NiO as the SE and a noble metal Pt as the RE was fabricated and investigated here. The sensor presented excellent sensing performance to NO₂ gas. The response current value at −300 mV was almost linear to NO₂ concentration in the range of 0~500 ppm at 400~500 °C. The optimal sensor based on the Gd₁.₉₅Ca₀.₀₅Zr₂O₇₊δ substrate gave the highest NO₂ sensitivity (9.28 nA/ppm), the maximum response current value (6.4 μA), and the shortest 90% response (3 s) and 90% recovery (35 s) time to 500 ppm NO₂ at 500 °C, which is better than that of commercial YSZ under the same condition. The outstanding selectivity and high stability towards NO₂ sensing of the sensors based on Gdₓ₋₂MₓZr₂O₇₊δ are expected to a promising application in monitoring exhaust emission of motor vehicles.

Methods
Preparation of GMZ electrolyte. The pyrochlore-phase Gdₓ₋₂MₓZr₂O₇₊δ (GMZ, M = Ca, Sr, and Ba, x = 0~0.3) oxides were synthesized through a urea hydrolysis-based hydrothermal method. The stoichiometric
amount of Gd(NO$_3$)$_3$·6H$_2$O (99.99% purity), M(NO$_3$)$_2$ (M = Ca, Sr, and Ba) (AR Grade), and ZrOCl$_2$·8H$_2$O (AR Grade) were first dissolved in deionized water, and the total cation concentration was fixed at 0.25 mol/L. Then urea (AR Grade) as precipitation agent was added to the reaction solutions above with the molar ratio of the total cation: urea = 1: 2.5. Thereafter, 80 mL solution was poured into a Teflon bottle and sintered at 40°C for 2 h to create the sensing electrode. Pt paste was painted on the back-side of the electrolyte, and then two Pt wires (0.2 mm diameter) were wound around the NiO and Pt surfaces to make contact with the sensor, respectively. Then the samples were calcined at 1000°C for 1 h in air to get the (Pt) NiO/GMZ/Pt sensor. Phase analysis was done on a Panalytical XPert Pro diffractometer at 40 kV and 40 mA with a step size of 0.0167° at a scanning rate of 4° min$^{-1}$, using Co K$_\alpha$ radiation and then revised by Cu K$_\alpha$. Scanning electron microscopy (SEM, Hitachi$\times$4800 instrument) was applied for observing the morphology of the samples. The Raman spectra were measured on a multichannel modular triple Raman system (inVia Reflex, Renishaw Corp.) with confocal microscopy at room temperature excited with the 532 nm line of an Ar laser. The complex-impedance measurements of the GMZ electrolytes were carried out in ambient air, and typically in the frequency range of 1 MHz to 0.01 Hz with signal amplitude of 5 mV using the Zahner IM6 electrochemical workstation.

### Sensor fabrication and characterization.

The samples calcined at 600°C above were uniaxially pressed into a pellet (8 mm diameter, 2 mm thickness). Subsequently, the molded pellet was further compacted by cold isostatic pressing at 280 MPa for 5 min. Finally, the compacts were sintered at 1500°C for 4 h in air. The NiO paste was painted on one of the surfaces of GMZ pellet by screen printing technique and then sintered at 1400°C for 2 h to create the sensing electrode. Pt paste was painted on the back-side of the electrolyte, and then two Pt wires (0.2 mm diameter) were wound around the NiO and Pt surfaces to make contact with the sensor, respectively. Then the samples were calcined at 1000°C for 1 h in air to get the (Pt) NiO/GMZ/Pt sensor. Phase analysis was done on a Panalytical XPert Pro diffractometer at 40 kV and 40 mA with a step size of 0.0167° at a scanning rate of 4° min$^{-1}$, using Co K$_\alpha$ radiation and then revised by Cu K$_\alpha$. Scanning electron microscopy (SEM, Hitachi$\times$4800 instrument) was applied for observing the morphology of the samples. The Raman spectra were measured on a multichannel modular triple Raman system (inVia Reflex, Renishaw Corp.) with confocal microscopy at room temperature excited with the 532 nm line of an Ar laser. The complex-impedance measurements of the GMZ electrolytes were carried out in ambient air, and typically in the frequency range of 1 MHz to 0.01 Hz with signal amplitude of 5 mV using the Zahner IM6 electrochemical workstation.

### Evaluation of sensing properties.

NO$_2$ sensing properties were carried out on a fixed bed continuous flow reactor. The fabricated sensors were held in a quartz glass (i. d. 10.0 mm) with heating tube furnace in the temperature range 400–500°C. The gas environment consisted of a changing concentration of NO$_2$ (0–500 ppm) and the flow rate of the sensor placed in testing tube was performed on a mass spectrometry (Dycor Dymaxion, DME200MS) electrochemical work station (Instrument corporation of Shanghai, China, CHI600E). The trace signal of off-gas was monitored with base gases (5 vol. % O$_2$/He+5 vol. % O$_2$/He+He balance) at a total flow rate of 200 mL/min, which was controlled by mass flow meter. The amperometric responses of the sensors were measured by potentiostatic method at −300 mV using the Zahner IM6 electrochemical workstation.

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Author Contributions
Fulan Zhong and Jilin Long conceptualized the idea and device design. Fulan Zhong and Jiuzhou Zhao performed the experiments and the data analysis. Fulan Zhong and Jilin Long wrote the main manuscript text. Lanqian Shi, Yihong Xiao, Guohui Cai, and Yong Zheng involved in correction of the manuscript. All the authors discussed the results and reviewed the manuscript.

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