A New Ceramic Sr₂Fe₈O₁₈: Crystal Structure and Analysis of Application on Solid Electrolytes

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Abstract: All-solid-state batteries have been expected to overcome the safety problem of present lithium-ion batteries including organic liquid electrolytes. The materials with high ionic conductivity are urgently needed. In this paper, we reported a new ionic crystal Sr₂Fe₈O₁₈ which can be applied on solid electrolyte. Sr₂Fe₈O₁₈ is a typical p-type semiconductor and shows a layered monoclinic crystal structure. The resistivities of Sr₂Fe₈O₁₈ in the temperature range of 20–145°C were above 10⁷ Ω·cm. The microstructure of Sr₂Fe₈O₁₈ was flaky, and the size of flaks were 1μm ~ 5μm. The E-P curve suggested that it was a ferroelectric semiconductor and had small ferroelectric effect. The dielectric response study (Cole-Cole plot) showed that Sr₂Fe₈O₁₈ had two separated relaxation time, each of which contained a group of relaxation. The ionic conductivity σ of the sample was calculated to be 0.2196x10⁻⁴ S/cm. The conductive mechanism which confirmed by the results of First principle calculation at 300K is mainly sublattice vacancy cation diffusion with self-diffusion coefficient D of 1.794x10⁻⁵ cm²/s. Fe ion has two dimensional diffusion path (x and y axial), and Sr ion has on dimensional diffusion path (x axial). The crystal structure of Sr₂Fe₈O₁₈ shows tremendous potential application on the solid electrolyte preparation.

Keywords: Oxygen-deficient perovskite; Solid electrolyte; Crystal structure; Ion conductor

Introduction
Current commercial lithium-ion batteries use combustible organic liquid electrolytes and thus suffer from fire risks during overcharge or abused operations, especially in large-scale applications [1-3]. Getting solid is the most important study point in the secondary battery research area. However, the development of solid-state batteries was largely been hindered by the availability of solid electrolytes with fast ion conductivity. Therefore, the materials with high ionic conductivity are urgently needed for the development of solid-state secondary batteries. Up to now, solid electrolytes containing Li ion has attracted extensive research[4-16], while the reports about other solid electrolytes were rare. The Brownmillerite Sr$_2$Fe$_2$O$_5$, which belongs to the oxygen-deficient perovskite family, has earned much attention because it has many interesting physical properties, such as being ion conducting, ferroelectric, ferromagnetic etc. [17-19]. Due to its special crystal structure, there were abundant research about structural characterization of oxygen-deficient perovskites [20-24]. The latest report about Ca$_2$Fe$_{0.5}$Ga$_{1.5}$O$_5$ by Hona et al. [25] pointed out that in oxygen deficient perovskites, the B-site cations usually form BO$_6$, BO$_5$, or BO$_4$ polyhedral depending on the structure, while the A-site cations reside in spaces between the polyhedral. Changes in the A or B-site cations in oxygen-deficient perovskites can change crystal structures and lead to significant differences in electrical properties. This characteristic of oxygen-deficient perovskites indicates enormous potential in applications of sensing, solid-oxide fuel cells, and electrocatalysts.

Among all research of oxygen-deficient perovskites, materials with 1:1 atom proportion of Sr to Fe (or A-site to B-site) significantly outnumbered those with other atom proportions of Sr to Fe, such as that in Sr$_4$Fe$_6$O$_{13}$. We are interested in finding new material based on Brownmillerite and exploring better properties. Therefore, in this paper, we reported a new compound Sr$_2$Fe$_8$O$_{18}$ with high ionic conductivity which have an atom proportion of Sr: Fe= 1:4. The crystal material, electronic structure, and the basic
electrical properties (ferroelectricity, dielectric response, and ionic conductivity) were studied. The analysis of conductive mechanism of Sr$_2$Fe$_8$O$_{18}$ indicated that the crystal structure of Sr$_2$Fe$_8$O$_{18}$ shows tremendous potential application on the solid electrolyte preparation.

**Experimental section**

The Sr$_2$Fe$_8$O$_{18}$ ceramic was synthesized directly by pure SrCO$_3$ (> 99.9%) and Fe$_2$O$_3$ (> 99.9%) powders via solid-state method. The mixed powders were pressed into pellets after 24h ball milling, and sintered at 1220°C for 3h. The phase structure were examined by X-ray diffraction (XRD) in the 2θ range of 20 - 50° with a step size of 0.02° using the Bruker D8 advance at 40kV/40mA with Cu Kα radiation (λ=0.154nm). The polished samples after thermal etching were prepared and observed using a Scanning Electron Microscope (JSM-6510-LV, JEOL, Japan). The ceramic pellets for electrical characterization were polished and coated with silver electrodes. The resistivities were measured using an Keithley digital multimeter (DMM7510 7 1/2, United States) from room temperature to 435°C. The polarization-electric field hysteresis loops were measured with a Precision LC ferroelectric test system (Radiant Technologies, Northford, United States) at room temperature. EIS (Electrochemical Impedance Spectroscopy) was carried out using electrochemical workstation measurement system in the frequency range of 0.1Hz to 100kHz.

**Results and Discussions**

The XRD patterns of the Sr$_2$Fe$_8$O$_{18}$ sample is shown in Fig.1 (a). The sample shows a monoclinic structure (space group: $P_{1}2_{1}1$) with $a=8.4009\,\text{Å}$, $b=8.4623\,\text{Å}$, $c=6.4648\,\text{Å}$, $\beta=111.676$, and $V_{\text{cell}}=427.09\,\text{Å}^3$. The crystal structure was calculated and refined [26] with $R$ factor of $R_p=5.81$, $R_{wp}=7.39$, $R_e=5.42$, $Chi^2=1.86$, and the parameter detail of crystal structure was shown in Table 1. Fig. 1 (b) ~ (e) shows the graphical results of refinement and the detail of crystal structure of Sr$_2$Fe$_8$O$_{18}$. Fig. 1 (b) shows the
graphical results of refinement. Fig. 2 (c)–(e) show the detail of crystal structure of Sr$_2$Fe$_8$O$_{18}$. There were two molecules in one unit cell, in other words, Z=2. The whole structure composed by layered FeO$_6$ and the FeO$_6$ was a distorted oxygen octahedrons. Every four FeO$_6$ was a repetitive unit, where three of them were connected by edge and one by angle. Sr$_2$Fe$_8$O$_{18}$ has excess oxygen ions, therefore, it has many cation vacancy, shows character of p-type semiconductor. Those cation vacancy provides the possibility for sublattice vacancy cation diffusion which shows ionic conduction macroscopically. Furthermore, the geometry of crystal structure had been optimization by First principle calculation. Fig. 2 shows the relative results of First principle calculation [27-30] and the resistivities of Sr$_2$Fe$_8$O$_{18}$ in the temperature range of room temperature to 435°C. Fig. 2 (a) shows the energy optimizing results during the last time of geometry optimization. The geometry optimization was taken twice. The plane wave basis set cut-off of the first time was 340eV with the function of GGA by Perdew, Burke and Ernzerhof [31], and the energy decreased from about -16380eV to -16440eV . The plane wave basis set cut-off of the second time was 340eV with the function of GGA by Perdew-Wang 1991 (PW91) [32], and the energy decreased from about -16440eV to -16470eV . Fig. 2 (b) ~ (e) shows the final crystal structure after geometry optimization. The whole structure is composed by FeO$_4$ which is connected by angle and SrO$_6$ which is connected by edge. Every three FeO$_4$ that are connected by O$_3$ is a repeat unit, and every repeat unit is connected by O$_5$. Fig. 2 (f) shows the resistivity of Sr$_2$Fe$_8$O$_{18}$ in the temperature range of room temperature to 435°C. It was the typical resistivity characteristic of semiconductor, and the relative relationship between resistivity and temperature was:

$$\rho = \rho_0 e^{-\alpha T}$$

where $\rho_0$ is the resistivity in room temperature; $\rho$ is the resistivity; $T$ is the temperature; $\alpha$ is the temperature coefficient of resistivity, the $\alpha$ could be calculated. In this study, the $\alpha$ of Sr$_2$Fe$_8$O$_{18}$ was -
0.02334. The insulating property is important to solid electrolyte. Therefore, the resistivities in the temperature range of 20–145°C are shown in the inset of Fig. 2 (f). The resistivities of Sr₂Fe₈O₁₈ in the temperature range of 20–145°C were from 1.5556 × 10⁸ to 1.1227 × 10⁷ Ω·cm, respectively. Fig. 3 shows the SEM photograph of Sr₂Fe₈O₁₈ sample. In the first sight, the Sr₂Fe₈O₁₈ ceramic composed by granule microstructure. But take a good look at the photograph, every granule was actually layered. Therefore, it also can be seen from the zoom-in picture on the right side, the microstructure of Sr₂Fe₈O₁₈ was flaky, and the size of flaks were 1μm ~ 5μm. In view of this feature, Sr₂Fe₈O₁₈ might have the potential applications in the area of energy storage and conversion [33-36]. Fig. 4 shows the dielectric and ferroelectric properties of Sr₂Fe₈O₁₈ samples. Fig. 4 (a) shows the Polarization Electric field (P-E) hysteresis loops of the Sr₂Fe₈O₁₈ samples tested at room temperature. The largest voltage which Sr₂Fe₈O₁₈ sample (thickness d= 0.75mm) can bear was 2kV. The whole loops show the anomalous hysteresis phenomena. The polarization was keeping increase for a period during the decrease of voltage. J. Wei et al. [37] once reported a model of P-E loop, as shown in the formula below:

\[
\text{from } -V_{\text{max}} \text{ to } V_{\text{max}}, \quad Q_T = cV + \frac{V^2}{2RA} + Q_F \approx cV + \frac{V^2}{2R} \frac{\Delta t}{|\Delta V|} + Q_F
\]

\[
\text{from } V_{\text{max}} \text{ to } -V_{\text{max}}, \quad Q_T = cV + \frac{V_{\text{max}}^2}{2RA} - \frac{V^2}{2RA} + Q_F \approx cV + \left( \frac{V_{\text{max}}^2}{2R} - \frac{V^2}{2RA} \right) \frac{\Delta t}{|\Delta V|} + Q_F
\]

where \( c \) is the capacitance; \( V \) is the bias voltage, \( Q_F \) which is here can be expressed as polarization \( P \) (stands for the polarization intensity), is caused by ferroelectric effect, and is the polarized charge quantity nonlinear to \( V \); \( R \) is the resistance of the conductive layer, \( \Delta V/\Delta t \) is the scan velocity of \( V \), \( A \) is the scan speed of voltage, and \( Q_T \) is the total charge quantity. If \( Q_F \) is negligible, in other words, the material don’t have obvious ferroelectric effect, the \( Q_T -E \) curve will be parabolic, like the Fig. 1 (c) in the ref. 37. Therefore, the \( E-P \) curve of Sr₂Fe₈O₁₈ suggested that it was a ferroelectric semiconductor.
which do showed the ferroelectric effect but was smaller than the traditional one. The remanent polarization $P_r$ was around $0.1737 \mu C/cm^2$, and the coercive field $E_c$ was around $1.9309 \, kV/cm$. The dielectric spectroscopy shows the dynamical dielectric, which is important for discussing the physical properties of ionic crystal material at the molecular level. Fig. 4 (b) and (c) show the dielectric response of frequency and the Cole-Cole plot [38] of Sr$_2$Fe$_8$O$_{18}$, respectively. Fig. 46 (a) shows the dielectric response of frequency (form 40Hz to 110MHz) of Sr$_2$Fe$_8$O$_{18}$. The pink area is the relaxation rang of Sr$_2$Fe$_8$O$_{18}$. The $\varepsilon'$ (the real part of the complex dielectric constant) decrease with increase of frequency, and the $\varepsilon''$ (the imaginary part of the complex dielectric constant) first increase and then decrease with increase of frequency. Thus, the $\varepsilon''$ has the maximum value, and at this point of frequency, there is a following relationship:

$$\omega \tau = \frac{\varepsilon_s}{\varepsilon_\infty}$$

where $\omega$ is the frequency; $\tau$ is the relaxation time; $\varepsilon_s$ is the shunt dielectric constant; $\varepsilon_\infty$ is the dielectric constant at infinity frequency. Therefore, the relaxation time could be calculated via this relationship, and the value of relaxation time $\tau$ was $0.6007 \times 10^{-7}$. Fig. 4 (b) shows the Cole-Cole plot from the data of Fig. 4 (a). It can be seen that Sr$_2$Fe$_8$O$_{18}$ had two separated relaxation time, and each one contained a group of relaxation. As previous report, the first group relaxation times were from grain, and the second group were from grain boundary.

Fig. 5 shows a typical impedance plot obtained at room temperature for a Sr$_2$Fe$_8$O$_{18}$ sample with thickness of 1mm and sectional area of 0.1cm$^2$. Fig. 5 (a) shows the Nyquist plot and the fitting curve with the equivalent circuit shown in Fig. 5 (b). According to the test method described at experiment, the equivalent circuit could be shown as Fig. 5(b). $R_b$ is the resistance of solid electrolyte; $V_{oigt}$ component composed by $C_{bi}$ and $R_{bi}$ is the interface impedance between solid electrolyte and electrode; $V_{oigt}$
component composed by $C_{be}$ and $R_{be}$ is the interface impedance between solid electrolyte and liquid electrolyte; $R_e$ is the resistance of liquid electrolyte; $V_{eig}$ component composed by $C_{ei}$, $R_{ei}$ and $Z_w$ is the interface impedance between liquid electrolyte and electrode; $Z_w$ is the Warburg impedance. After fitting with equivalent circuit the $R_b$, $R_{bi}$, $R_{be}$, $R_e$, and $R_{ei}$ of 0.4554, 0.1927, 1292, 0.5453, 0.0645 MΩ were obtained, respectively. The ionic conductivity of the sample was calculated by the following formula:

$$\sigma = \frac{L}{R \times S} = \frac{L}{R_b \times S}$$

where: $L$ is the sample thickness, $S$ is the sample area, $R$ is the sample resistance. The ionic conductivity $\sigma$ of the sample was calculated to be $0.2196 \times 10^{-4}$ S/cm.

Analysis of application on solid electrolytes for Sr$_2$Fe$_8$O$_{18}$ was shown in Fig. 6. Fig. 6 (c) shows the velocity autocorrelation function (VACF) from Molecular Dynamics (MD) calculation of Sr$_2$Fe$_8$O$_{18}$ at 300K. It is known that the self-diffusion coefficient $D$ can be calculated from VACF by the following function[39]:

$$D = \frac{1}{3} \int_0^\infty \langle v(t) \cdot v(0) \rangle dt$$

Where $v(0)$ and $v(t)$ are the initial particle velocity and at time $t$, respectively. $\langle v(t) \cdot v(0) \rangle$ is the value of VACF. Therefore, the cation self-diffusion coefficient of Sr$_2$Fe$_8$O$_{18}$ can be calculated as $1.794 \times 10^{-5}$ cm$^2$/s. Fig. 6(b)–(d) show the cation diffusion velocities on the (100), (001), and (010) direction, respectively. It can be seen that on the (001) direction, there were three position had zero velocity which means there were no cation diffusion path on the (001) direction. There were different cation diffusion velocity distributed on the (100) and (010) direction. It was indicated that ion diffusion path existed in both (100) and (010) direction. The highest diffusion velocity on (100) and (010) direction were $3.62 \times 10^4$ cm/s, and $4.76 \times 10^4$ cm/s, respectively. The average diffusion velocity on (100) and (010)
direction were $1.98 \times 10^4$ cm/s and $2.21 \times 10^4$ cm/s, respectively. Therefore, (010) direction (y axis direction) had the higher ion diffusion velocity. This result can be analysis through crystal structure of Sr$_2$Fe$_8$O$_{18}$.

There are three ion diffusion mechanism in the ionic crystal: (1) vacancy diffusion; (2) interstitial diffusion; (3) sublattice diffusion. The sublattice diffusion has the lowest diffusion activation energy and the fastest diffusion velocity. The interstitial diffusion has the highest diffusion activation energy and hard to proceed. As discussed before, the intrinsic cation vacancy in Sr$_2$Fe$_8$O$_{18}$ structure provides the possibility for sublattice vacancy cation diffusion. Both FeO$_4$ and SrO$_6$ were connected in the (010) direction, providing the diffusion path along the (010) direction for Fe ion and Sr ion. Both FeO$_4$ and SrO$_6$ were not connected in the (100) and (001) direction (x and z axis direction). But FeO$_4$ had the short interval along the (100) direction, providing the possibility for Fe ion diffusion along the (100) direction. However, this diffusion had the higher diffusion activation energy than the sublattice diffusion. Therefore, (010) direction had the higher ion diffusion velocity than the (100) direction. Fig. 6 (e) ~ (h) show the schematic diagram of ion diffusion path. Fe ion had the two-dimension diffusion path on both (100) and (010) direction (x and y axis direction). Sr ion had the one-dimension diffusion path on (010) direction (y axis direction).

Conclusions

In summary, a new oxygen-deficient perovskite compound Sr$_2$Fe$_8$O$_{18}$ which can be a promising solid electrolyte, its microstructure and its physical properties were reported for the first time. It shows a layered monoclinic crystal structure with $a=8.4009 \, \text{Å}$, $b=8.4623 \, \text{Å}$, $c=6.4648 \, \text{Å}$, $\beta=111.676$, and $V_{\text{cell}}=427.09 \, \text{Å}^3$. The resistivities of Sr$_2$Fe$_8$O$_{18}$ in the temperature range of 20~145°C are from $10^8$ to $10^7$ Ω·cm. The microstructure of Sr$_2$Fe$_8$O$_{18}$ was flaky with the size of 1μm ~ 5μm. The $E$- $P$ curve results indicated that Sr$_2$Fe$_8$O$_{18}$ was a ferroelectric semiconductor. The Cole-Cole plot showed that Sr$_2$Fe$_8$O$_{18}$
had two separated relaxation time, and each one contained a group of relaxation. Sr$_2$Fe$_8$O$_{18}$ has a large ionic conductivity $\sigma$ with value of $0.2196 \times 10^{-4}$ S/cm. The conductive mechanism is mainly sublattice vacancy cation diffusion with self-diffusion coefficient $D$ of $1.794 \times 10^{-5}$ cm$^2$/s. Fe ion has two dimensional diffusion path (x and y axial), and Sr ion has on dimensional diffusion path (x axial).

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Fig. 1 (a) The XRD pattern of the Sr$_2$Fe$_8$O$_{18}$ sample. Fig. 1 (b)–(e) The graphical results of refinement and the detail of crystal structure of Sr$_2$Fe$_8$O$_{18}$. (b) shows the graphical results of refinement; (c)–(e) show the detail of crystal structure of Sr$_2$Fe$_8$O$_{18}$: (c) labeled unit cell of Sr$_2$Fe$_8$O$_{18}$, (d) view of FeO$_6$, (e) view of 2*2*2 supercell in the direction of (010).
Fig. 2 The results of First principle calculation and resistivities of Sr$_2$Fe$_8$O$_{18}$ in the temperature range of room temperature to 435°C. (a) shows the energy optimizing results during the last time of geometry optimization; (b)–(e) shows the final crystal structure after geometry optimization: (b) and (c) FeO$_4$ and Sr in the view of (001) and (010) direction, respectively, (d) and (e) SrO$_6$ and Fe in the view of (100) and (010) direction, respectively; (f) the resistivities of Sr$_2$Fe$_8$O$_{18}$ in the temperature range of room temperature to 435°C, the inset of (f) shows the resistivities of Sr$_2$Fe$_8$O$_{18}$ in the temperature range of 20 to 435°C.
Fig. 3 The SEM photographs of the surfaces of the Sr$_2$Fe$_8$O$_{18}$ samples.
Fig. 4 The dielectric response of frequency, the Cole-Cole plot and ferroelectric property of Sr$_2$Fe$_8$O$_{18}$.

(a) the dielectric response of frequency (form 40Hz to 110MHz) of Sr$_2$Fe$_8$O$_{18}$; (b) the Cole-Cole plot from the data of (a); (c) the Polarization Electric field (P-E) hysteresis loops of the Sr$_2$Fe$_8$O$_{18}$ samples tested at room temperature.
Fig. 5 The typical impedance plot obtained at room temperature for a Sr$_2$Fe$_8$O$_{18}$ sample; (a) Nyquist plot and the fitting curve; (b) equivalent circuit. $R_b$ is the resistance of solid electrolyte; $V_{\text{oigt}}$ component composed by $C_{bi}$ and $R_{bi}$ is the interface impedance between solid electrolyte and electrode; $V_{\text{oigt}}$ component composed by $C_{be}$ and $R_{be}$ is the interface impedance between solid electrolyte and liquid electrolyte; $R_e$ is the resistance of liquid electrolyte; $V_{\text{oigt}}$ component composed by $C_{ei}$, $R_{ei}$ and $Z_w$ is the interface impedance between liquid electrolyte and electrode; $Z_w$ is the Warburg impedance.
Fig. 6 Analysis of application on solid electrolytes for Sr$_2$Fe$_8$O$_{18}$. (a) VACF (velocity autocorrelation function) curve; (b) Ion diffusion velocity on the (100) direction; (c-d) Ion diffusion velocity on the (001) direction; (d) Ion diffusion velocity on (010) direction; (e) Fe ion diffusion path on x direction; (f) Fe ion diffusion path on y direction; (g) Sr ion diffusion path on y direction; (h) we intended to show that Sr ion don’t have any diffusion path on x or z direction.
Table 1: The structure parameters of the Sr$_2$Fe$_8$O$_{18}$ and agreement factors from refinement.

| Structure | Cell parameters | Agreement factors |
|-----------|-----------------|-------------------|
|           | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\alpha$ (°) | $\beta$ (°) | $\gamma$ (°) | $V_{cell}$ (Å$^3$) | $R_p$ | $R_{wp}$ | $R_e$ | $\text{Chi}^2$ |
|           | 8.4009 | 8.4623 | 6.4647 | 90 | 111.676 | 90 | 427.09 | 5.81 | 7.39 | 5.42 | 1.86 |

| Atom | X | Y | Z |
|------|---|---|---|
| Sr1  | 0.024 | 0.723 | -0.016 |
| Fe1  | 0.522 | 0.984 | 0.328 |
| Fe2  | -0.145 | 0.536 | 0.520 |
| Fe3  | 0.403 | 0.505 | 0.014 |
| Fe4  | 0.454 | 0.789 | 0.146 |
| O1   | 0.383 | 0.873 | 0.404 |
| O2   | -0.064 | 0.484 | -0.134 |
| O3   | -0.093 | 0.753 | -0.473 |
| O4   | 0.313 | 0.654 | -0.024 |
| O5   | 0.475 | 0.704 | 0.319 |
| O6   | 0.302 | 0.864 | -0.034 |
| O7   | 0.106 | 0.627 | -0.249 |
| O8   | 0.543 | 0.755 | 0.567 |
| O9   | -0.242 | 0.863 | -0.493 |