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**Preparation and properties of endothermic functional ceramics with iron tailings as raw materials**

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**Abstract**

The present work attempts to utilize iron tailings as the main raw materials for preparation of functional ceramics as a means of resource utilization. A new type of endothermic functional ceramics, which can be used in the field of solar energy, was prepared via semi-dry pressing followed by pressureless sintering. The results show that the functional ceramics made of 68 wt% iron tailings, 26 wt% iron ore, 3 wt% alumina, 1 wt% potash feldspar and 2 wt% kaolin, sintered at 1185°C exhibited the best overall performance. Visual observation reveals that there were no cracks on the surface of the samples even after 20 cycles of intense thermal shock. Other attributes could be summarized as follows: Infrared emissivity in mid-infrared region: 0.85; thermal conductivity at 500°C: 2.066 W/ (m·K); flexural strength: 119.03 MPa. XRD analysis indicates that the main crystalline phases in the samples are augite, magnetite and a small amount of hematite. An increase in the proportion of iron oxide contributed to lower melting temperature of the functional ceramics, deepen color, promote densification and increase infrared emissivity. In short, the introduction of iron tailings improves the thermal and physical properties to a certain extent.

**1. Introduction**

The increased consumption of non-renewable energy sources such as petroleum and coal, is well known to contribute to a series of environmental problems such as greenhouse effect, which demands development of suitable technologies to increase the renewable energy sources so as to replace non-renewable energy sources [1, 2]. Renewable energy sources such as solar, wind, hydropower and biogas are well known potential sources to meet the global energy requirements in a sustainable way. As solar energy resources are abundant and cheap, intensified attempts are being made by the scientific community so as to harness its benevolence.

Solar collectors are an important component that can effectively utilize solar energy. The material type largely governs the absorption efficiency of solar energy. At present, the conventional solar collector materials are highly priced, easily corrode and inconvenient to replace, having low solar energy absorption efficiencies in the mid-infrared band [3–6].

Ceramics are a kind of corrosion-resistant materials which are high temperature resistance, low priced and high in hardness, which have the potential to gradually replace the traditional solar collectors materials [7, 8]. At present, the primary examples of materials used in solar collectors are graphite, silicon nitride, silicon carbide, graphene, and other materials. Due to its high thermal conductivity and heat storage density, these materials find increasing application in preparation of solar functional ceramics. However, they have some obvious disadvantages such as high cost, high sintering temperature, low flexibility, low flexural strength and compressive strength [9–11].

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Iron tailings are a kind of solid wastes. The main components of iron tailings are silica, alumina, magnetite, hematite, etc. Since these iron tailings are being generated continuously in large quantities dumped as solid waste, they contribute to heavy metal pollution, which endangers the environment and the safety of residents. Currently, the iron tailings are widely utilized as raw materials in the manufacture of sintered brick, cement and functional ceramics so as to alleviate the solid waste issues. In this work, the endothermic functional ceramics were prepared from iron tailings is reported for the first time.

In the present work iron tailings were utilized as the main raw materials for preparation of endothermic functional ceramics. Additionally, potash feldspar was added to help melt, kaolin was added to increase plasticity, iron ore and alumina were added to increase the hardness and the bulk density. Due to the presence of iron oxide in raw materials, the color is deepened, infrared absorption is increased, and the heat absorption property is indirectly improved. The phase composition and microstructures of ceramics were assessed utilizing a range of advanced characterization techniques.

### 2. Materials and methods

#### 2.1. Materials and preparation methods

The raw materials iron tailings and iron ore were supplied by Luanping Jianlong Mining Co., Ltd, Hebei, China, Al₂O₃ was supplied by Tianjin Bodi Chemical Co., Ltd Tianjin, China, kaolin was supplied by Tianjin Fuchen Chemical Reagent Factory. Tianjin, China and potash feldspar was supplied by Xingtang Xinlei Mineral Powder Processing Plant, Shijiazhuang, China.

The raw materials were crushed utilizing ball mill supplied by QM-L, Mi Qi Instrument and Equipment Co., Ltd, Hunan, China. The crushed raw materials were screened to size less than 300 mesh and were dry mixed with the other desired ingredients (tables 1 and 2) and ground again in the same ball mill for a duration of 45 min. The pressure testing machine supplied by TYE-300B, Jianyi Instrument Machinery Co., Ltd, Jiangsu, China was used to compress (the mixture) at a pressure of 30 MPa for 5 min to produce cuboid bodies (40 × 7 × 8 mm³). The compressed bodies were dried for 10 h in an oven (YH-2BS, Tianjin Zhonghuan Electric Furnace Co., Ltd, Tianjin, China) and subsequently sintered between 1000 °C and 1200 °C in a muffle furnace (SX-G12163, Tianjin Zhonghuan Electric Furnace Co., Ltd, Tianjin, China) for 2 h. The heating rate of muffle furnace was 5 °C min⁻¹ below 1000 °C, and turned into 3 °C min⁻¹ above 1000 °C. After sintering the samples were cooled to room temperature in the furnace, named A series samples.

#### 2.2. Characterizations

The chemical compositions of raw materials were analyzed by x-ray fluorescence spectrometer (XRF). The results are listed in table 1. Table 2 lists the composition of the A series samples. The phase compositions of all samples were characterized by x-ray diffraction (XRD), which covered the scanning angle from 10° to 80° (2θ). The micro-morphology and element mapping of the samples were performed using Scanning Electron Microscope (Nova Nano SEM 450, USA). Bulk density of the samples was measured by WT-51001S electronic water purification balance. The thermal conductivity and specific heat capacity of the samples were measured by LFA467 thermal conductivity meter, and the mid-infrared emissivity of the samples were measured by V80 Fourier infrared spectrometer. The flexural strength of the samples was measured by TYE-300B pressure tester. The thermal expansion coefficient of the samples from 50 °C to 500 °C were measured by DIL402 thermal

| Sample  | Iron tailings | Iron ore | Al₂O₃  | Potash feldspar | Kaolin |
|---------|--------------|----------|-------|-----------------|--------|
| A₁      | 69           | 27       | 1     | 1               | 1      |
| A₂      | 73           | 23       | 1     | 1               | 2      |
| A₃      | 77           | 19       | 1     | 1               | 2      |

**Table 1.** Chemical composition of raw materials (wt%).

| Chemical composition | SiO₂ | Al₂O₃ | MgO | TFe | CaO | K₂O | Na₂O | TiO₂ | Σ   |
|---------------------|------|-------|-----|-----|-----|-----|------|------|-----|
| Iron tailings        | 41.92| 7.51  | 11.64| 14.95| 17.74| 3.31| —    | 2.40 | 99.47|
| Iron ore             | 14.28| 4.28  | 1.89 | 76.64| 1.06 | 0.14| 1.23 | —    | 99.52|
| Kaolin               | 58.64| 39.04 | 0.19 | 0.42 | 0.13 | 0.25| —    | 1.19 | 99.86|
| Potash feldspar      | 64.71| 13.98 | 0.93 | 3.32 | 3.60 | 10.71| 1.81 | 0.35 | 99.41|

**Table 2.** Mineral compositions of A series samples (wt%).
dilatometer at 10 °C min⁻¹. The thermal shock resistance of the samples was tested by heating/cooling cycle in a box furnace. The samples were kept at 400 °C for 30 min, before quenched with water, which was repeated for 20 times.

3. Results and discussion

3.1. Phase composition and microstructure of the samples
As shown in figure 1, XRD analysis was carried out on the endothermic functional ceramics Sample A₁ at different temperatures. The main crystalline phases of the samples are augite, magnetite and hematite after sintering at the optimum sintering temperature. And augite phase has been formed at temperature below 1080 °C. With the increase in temperature, the diffraction peaks of hematite began to weaken at 1120 °C while the weakening amplitude increased at 1160 °C. Meanwhile, the appearance of the samples changed from reddish brown to black, indicating that hematite began to decrease and magnetite began to increase at 1080 °C.

Figures 2(a) and (b) show the surface and the cross section of the Sample A₁ at 1185 °C, respectively. It can be seen that the surface indicates distribution of pore in the size range of 16–33 microns, while the cross section has almost no pore, which is also the reason for its higher flexural strength. Figures 2(c) and (d) show the cross sections of the Sample A₁ at 1060 °C and 1185 °C, respectively. It is observed that the porosity and cracks disappear gradually with the increase in temperature [17, 18]. Figure 2(e) shows the amplification of a randomly chosen tiny aperture of the Sample A₁ at 1185 °C. It shows small particles being wrapped all over. EDAX spectroscopy analysis of the small particles indicated by red circle is shown in figure 3, which identifies the main elements to be O and Fe elements. The small particles are identified to hematite and magnetite from the results of XRD. The element mapping of the Sample A₁ presented in figure 4, shows the presence of large proportion of Si and O elements in the region, combined with the result that there is no silica diffraction peak in figure 1, it is concluded that silica is surrounded by iron oxide particles in glass phase.

3.2. Infrared emission performance
Color is known to be a main factor affecting endothermic ability. Because dark color can absorb more visible light and reflect less light, the endothermic ability of dark color is stronger. A series samples were all black, were tested for their infrared emissivity to further assess its ability to absorb heat. Figure 5 shows the infrared emissivity of A series samples sintered at 1185 °C in the wavelength range of 7.5–20 μm. The emissivity of the Sample A₁ increases gradually with the increase of wavelength from 7.5 to 15 μm, while it decreased progressively from 15 to 20 μm. The average infrared emissivity is about 0.85, with the highest emissivity being 0.88 at a wavelength of 17 μm. The average infrared emissivity of the Sample A₂ was about 0.80, with the highest 0.83 at 17.5 μm. The average emissivity of the Sample A₃ was about 0.79, with the highest 0.84 at 15 μm. It can be concluded that the infrared emissivity of A series samples increases gradually with increase in iron oxide content. It could be that there are a large number of transition metal oxides in ceramics, such as hematite and magnetite, which improve the infrared emissivity.
3.3. TG-DSC

The TG-DSC curves of the Sample A1 powders are shown in figure 6. The first endothermic peak appeared after 80 °C, which could be attributed to the evaporation of residual water, resulting in a mass loss of 0.5 wt%. The exothermic peak about 310 °C can be attributed to the combustion of some residual organic matter, with the mass loss contributing to 0.25 wt%. The mass loss of 1.35 wt% around 695 °C is the dehydroxylation reaction of the chlorite in iron tailings. The endothermic peak appeared at 1090 °C, combining with figure 1, is attributed to the transformation of Fe$_2$O$_3$–Fe$_3$O$_4$. This change is expressed in the form of a chemical reaction [18] (1).

$$6\text{Fe}_2\text{O}_3 \rightarrow 4\text{Fe}_3\text{O}_4 + \text{O}_2$$  \hspace{1cm} (1)

![Figure 2. SEM images of the surface of the Sample A1 at 1185 °C (a), the cross section of the Sample A1 at 1185 °C (b), the cross sections of the Sample A1 at 1060 °C (c), the cross sections of the Sample A1 at 1185 °C (d), the amplification of a randomly chosen tiny aperture of the Sample A1 at 1185 °C (e).](image-url)
3.4. Thermal conductivity of the samples
The presence of pores in ceramics, has an effect on the thermal conductivity of ceramics. Even presence of small number of pores can decrease the mean free path of photons and limit the heat conduction [19]. Thus, the thermal conductivity decreases with the increase of porosity. The thermal conductivity of the Sample A1 is shown in table 3. Compared with common cordierite-based ceramics and shale-based ceramics [18, 20], the thermal conductivity is slightly higher which could be attributed to the high melting temperature of iron oxide in...
Sample A1. The liquid phase such as the low-temperature eutectic mixture in iron ore and tailings, the feldspar and the silicon dioxide permeate into the pore fully, promotes the densification of the samples thereby improving the thermal conductivity.

3.5. Physical and mechanical properties of the samples

3.5.1. Volume shrinkage, bulk density and flexural strength of the samples

The volume shrinkage, bulk density and flexural strength of the samples are shown in figures 7, 8 and table 4, respectively. The volume shrinkage of the Sample A1 begins to increase from 1100 °C and stabilize at 1150 °C. Bulk density increases gradually while decreases marginally at 1200 °C. The flexural strength reaches its maximum until 1185 °C, while found to decrease at higher temperature. The reason could be due to the melting of low-temperature eutectic mixture in iron ore and tailings, as well as the feldspar at about 1100 °C, diffuse
through the porous matrix causing the pores to plug thereby increasing the bulk density [21]. At a temperature of 1200 °C, all the components in addition to low-temperature eutectic mixture began to melt reducing the properties. Hence the temperature of 1185 °C is identified to be the optimal.

3.5.2. Thermal shock resistance and thermal expansion coefficient of the samples
The thermal expansion coefficient and thermal shock resistance of the samples are shown in table 5 and figure 9, respectively. The thermal shock resistance of ceramics is also an important factor for its application as solar functional materials. Table 5 shows the flexural strength of the Sample A1 after 20 thermal shock tests. No obvious cracks were found on the surface of the samples after 20th thermal shock tests. The flexural strength was found to obviously reduce after the fifth thermal shock test, however it remained in the same order of magnitude with minor ups and downs until 20th thermal shock test. It should be noted that the reduced flexural strength after 20th thermal shock test can still meet the requirements of general solar functional ceramics. Figure 9 shows the thermal expansion coefficient of the Sample A1 from 50 °C to 500 °C, with the average value being around $9.3 \times 10^{-6} ^\circ\text{C}^{-1}$. The thermal expansion coefficient was observed to increase dramatically at lower temperatures until 100 °C, beyond which it was almost constant. However, as compared to mullite ceramics

| Table 4. Flexural strength of the Sample A1. |
|-----------------|-----------------|
| Temperature/°C  | Flexural strength/MPa |
| 1035            | 14.28            |
| 1060            | 22.24            |
| 1085            | 22.73            |
| 1110            | 29.75            |
| 1135            | 63.57            |
| 1160            | 89.35            |
| 1185            | 119.03           |
| 1200            | 109.71           |

| Table 5. Thermal shock resistance of the Sample A1. |
|-----------------|-----------------|
| Number of flexural strength | Flexural strength/MPa |
| 0                | 119.03           |
| 1                | 120.21           |
| 5                | 36.48            |
| 10               | 30.82            |
| 15               | 40.91            |
| 20               | 33.23            |

Figure 8. Relationship curves of flexural strength with the temperature of the Sample A1.
(5.3 × 10⁻⁶ °C⁻¹, 0 °C–1000 °C) and cordierite ceramics (1.1–2.0 × 10⁻⁶ °C⁻¹, 0 °C–1000 °C), the thermal expansion coefficient of the endothermic functional ceramics was still higher. The higher thermal expansion coefficient could be attributed to the larger proportion of iron oxide that lead to a higher thermal expansion coefficient [22]. The higher thermal expansion coefficient is detrimental to the thermal shock resistance as it can reduce the thermal shock resistance.

4. Conclusions

The endothermic functional ceramics were prepared from iron tailings. The optimum samples sintered at 1185 °C exhibited the best of properties that had proportion of various ingredients to be 68 wt% iron tailings, 26 wt% iron ore, 3 wt% alumina, 1 wt% potash feldspar and 2 wt% kaolin. The main components of sintered samples are augite, magnetite and a small amount of hematite, black in color having average infrared emissivity of 0.85 at wavelength 7–20 μm, a thermal conductivity of 2.308 W/(m·K) at room temperature and a flexural strength of 119.03 MPa.

The samples were subjected to thermal shock resistance tests up to a temperature of 400 °C. No cracks were observed even after 20th thermal shock resistance tests and the final flexural strength was stable between 30 MPa and 40 MPa. The higher thermal expansion coefficient was attributed to the presence of iron oxide which accounts for poor thermal shock resistance. Ceramics having these properties can well meet the demand of solar energy endothermic materials.

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Figure 9. Thermal expansion coefficient curve of the Sample A1.
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