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# Synthesis, sintering, transport and thermal properties of $Na_2Fe_2Ti_6O_{16}$ freudenbergite

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## HIGHLIGHTS

- A dense freudenbergite ceramic has been obtained with a relative density of 95%.
- Electrical transport properties are dominated by small polaron hopping.
- The thermal conductivity is only 3.4 W $m^{-1}.K^{-1}$ at 1000 K.

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## ABSTRACT

$Na_2Fe_2Ti_6O_{16}$ freudenbergite has been synthesized using a simple solid-state route and conventionally sintered to reach 94% density ceramics. High temperature electrical and thermal transport properties have been investigated for the first time. In the temperature range of 468 K–1000 K, the electrical conductivity of $Na_2Fe_2Ti_6O_{16}$ can be well fitted with small polaron hopping model. For a further verification of the model, we measured the room-temperature optical reflectivity and derived the optical conductivity ($\sigma(\omega)$) with Kramers–Kronig analysis. A mid-infrared peak in $\sigma(\omega)$ confirms the presence of small polarons. From 468 K to 1000 K, $Na_2Fe_2Ti_6O_{16}$ is an n-type oxide and exhibits a temperature-independent Seebeck coefficient (~−590 μV $K^{-1}$), in agreement with the small polaron hopping mechanism. The thermal conductivity decreases with increasing temperature from 16.5 W $m^{-1}.K^{-1}$ (373 K) to 3.4 W $m^{-1}.K^{-1}$ (1000 K). $Na_2Fe_2Ti_6O_{16}$ shows a maximum figure of merit (ZT) ~ $3 \times 10^{-4}$ at 1000 K.

## 1. Introduction

Freudenbergite compounds have a general formula of $A_2B_2Ti_6O_{16}$, where A = $Na^+$, and B = $Mg^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Al^{3+}$, $Ga^{3+}$, $Ti^{3+}$, $Cr^{3+}$, $Fe^{3+}$, etc [1]. They have been widely studied as components of synroc to immobilize radioactive waste [1–5]. Among them, $Na_2(Al,Fe)_2Ti_6O_{16}$ shows good leach resistance, reasonable radiation resistance, and could be incorporated into synroc to immobilize nuclear waste containing a high amount of sodium. $Na_2Fe_2Ti_6O_{16}$ has also been investigated as an ion exchanger to remove nickel from potassium solutions [6]. Recently, $Na_2Fe_2Ti_6O_{16}$ shows prospects for application as anode materials in sodium-ion batteries due to its good cycle stability [7].

$Na_2Fe_2Ti_6O_{16}$ is mainly studied regarding its crystal structure, in addition to the aforementioned applications. Freudenbergite is a black mineral first described by Frenzel (1961) [8]. $Na_2Fe_2Ti_6O_{16}$ is a ferric freudenbergite with a monoclinic crystal structure and a space group *C*2/*m* [9–11]. The cell parameters are a = 12.267 (6) Å, b = 3.823 (5) Å, c = 6.483 (3) Å, β = 107.16 (5)° [10]. There are two octahedral sites occupied by randomly distributed $Fe^{3+}$ and $Ti^{4+}$. The (Fe, Ti)$O_6$ octahedra share edges in the ab plane, and double sheets of octahedra share corners in the c direction, forming a 3-dimensional framework. The channels of highly distorted cubes along b axis are almost fully occupied by Na ions.

The electrical and thermal transport properties of freudenbergite have not been reported yet. Such information is required to advance its application in sodium-ion batteries and other fields of research. Indeed, oxides with low thermal conductivity can find applications as thermal barrier coating materials [12,13] and with

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additionally high electrical conductivity and high Seebeck coefficient values, they could be promising thermoelectric materials. Thermoelectric materials can contribute to the improvement of energy efficiency as they are able to directly transform heat into electrical energy without any emissions ($CO_2$, other gases, radiations, …), vibrations or moving parts. Efficiency of thermoelectric materials is evaluated by the figure of merit $ZT = S^2\sigma T/\kappa$, where T is the absolute temperature, S the Seebeck coefficient, σ the electrical conductivity and κ the thermal conductivity. Oxides are considered as potential thermoelectric materials since 1997 [14]. Many compositions and structures have been studied [15] and especially: $Na_xCoO_2$ [14,16], $Ca_3Co_4O_9$ [17–21], $Bi_2Sr_2Co_2O_y$ [22], doped ZnO [23–26], doped $In_2O_3$ [27–29], $CaMnO_3$ [30,31] or $SrTiO_3$ [32–35]. Many efforts have been made to improve ZT values of such oxide ceramics but the highest value at 1000 K is 0.5 for a silver doped silver composite ($Ca_{2.7}Ag_{0.3}Co_4O_9$/Ag 10 wt%) sample [36]. Therefore, more recently, several new oxide systems have been studied for promising thermoelectric properties such as $(K_{0.5}Na_{0.5})NbO_3$ [37], $Ba_{6\text{-}3x}Nd_{8+2x}Ti_{18}O_{54}$ tungsten bronze [38] or $Ba_2Co_9O_{14}$ [39,40].

In this study, we report the electrical and thermal transport properties of $Na_2Fe_2Ti_6O_{16}$ for the first time. $Na_2Fe_2Ti_6O_{16}$ was prepared by solid-state reaction combined with conventional sintering. The electrical conductivity and Seebeck coefficient were measured in the temperature range of 468 K–1000 K, while the thermal conductivity was measured in the temperature range of 373 K–1000 K.

### 1.1. Experiment

$Na_2CO_3$ (Chempur, ≥ 99.9%), $Fe_2O_3$ (Sigma Aldrich, ≥ 99%), and $TiO_2$ (Sigma Aldrich, ≥ 99.9%) were used to synthesize $Na_2Fe_2Ti_6O_{16}$ by solid state reaction. Stoichiometric amount of precursor oxides were mixed at 250 rpm for 5 min in a tungsten carbide ball mill (Retsch PM 100). The powder was then calcined at 1223 K for 12 h in air. The powder was ball milled again and pressed into pellets by a uniaxial pressing machine under 80 MPa. The pellets were sintered at 1423 K for 6 h in air in a platinum wrapped $Al_2O_3$ crucible. The sintering temperature was determined by dilatometry analysis (Netzsch DIL 402).

X-ray diffraction (XRD) was performed at room temperature, on the powder after calcination and the pellet after sintering, using a BRUKER D8 Advance θ/2θ diffractometer equipped with a Linxeye energy-dispersive one-dimensional detector. The data have been recorded, using Cu-Kα radiation, from 10 to 85° (2θ) with a step of 0.02° and a counting time of 1 s per step. Rietveld refinement was carried out using Fullprof Suite [41] for the powder sample after calcination.

Microstructure was examined by field emission scanning electron microscopy (FE-SEM, Tescan MIRA3) coupled with a backscattered electron detector (BSD) and an Energy-dispersive X-ray spectroscopy (EDS, Oxford INCA X-act) without prior coating of the samples. The sample for the observation was prepared by polishing and thermal etching at 1323 K for 15 min in air.

Near normal incidence reflectivity spectra were measured at room temperature with a BRUKER IFS 66 v/S in the range 50–8000 $cm^{-1}$. The sample was polished to have a mirror-like surface. The spectrum of a gold mirror was used as the reference for normalization of the sample spectrum. Both Kramers-Kronig analysis and Drude-Lorentz fit procedure was applied to obtain the optical conductivity spectra, σ(ω).

The electrical conductivity and Seebeck coefficient were measured simultaneously by ULVAC ZEM-3 twice in low pressure He atmosphere from high temperature (1000 K) to low temperature (468 K). The thermal conductivity is the product of density, thermal diffusivity, and specific heat capacity. Bulk density was determined from the dry mass and the geometric dimensions of pellets. Thermal diffusivity has been measured from 373 K to 1000 K in air (Netzsch LFA457). The value is an average of three measurements at each temperature. The specific heat capacity was measured from room temperature up to 1073 K, with a heating rate of 20 K $min^{-1}$ in platinum crucibles with alumina liners in argon atmosphere (NETZSCH DSC 404F1 Pegasus).

## 2. Results and discussion

The XRD patterns in Fig. 1a show similar peaks for the powder after calcination and for the pellet after sintering. All of diffraction peaks can be assigned to the monoclinic freudenbergite (space group *C*2/*m*), $Na_2Fe_2Ti_6O_{16}$ (PDF 01-070-0637). Pure phase has been obtained without the appearance of impurities. The XRD pattern of powder $Na_2Fe_2Ti_6O_{16}$ after calcination was analyzed by Rietveld refinement based on Ishiguro et al. [10]. The refinement result displayed in Fig. 1b confirms the monoclinic structure of the sample. Na is slight deficient and its chemical formula is $Na_{1.74}Fe_2Ti_6O_{16}$, which agrees with the study by Bruhn et al. [11]. The refined

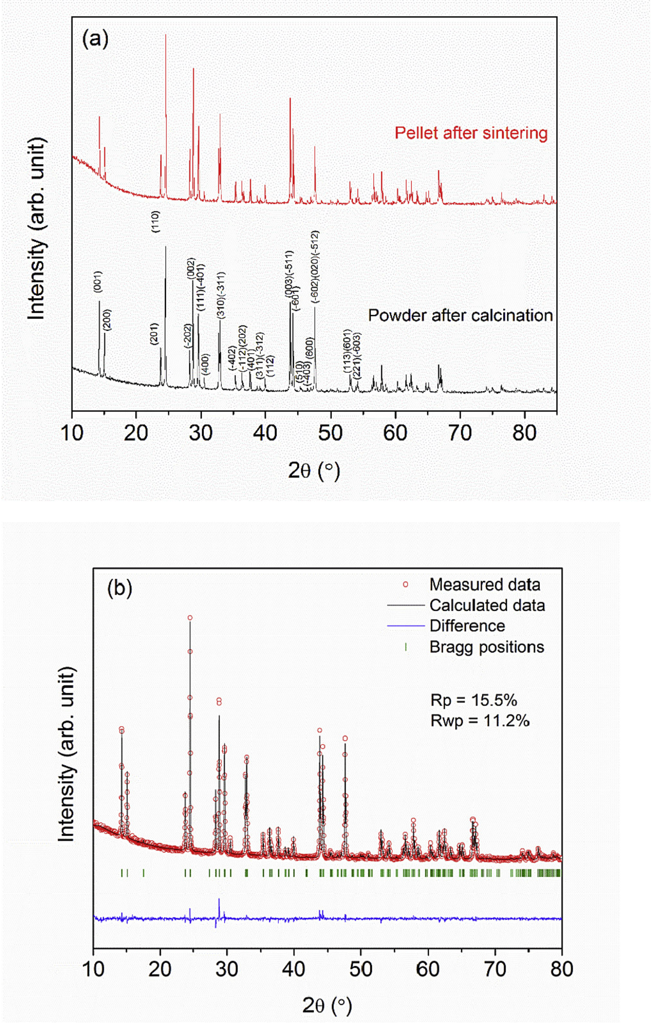

**Fig. 1.** (a) XRD patterns of powder $Na_2Fe_2Ti_6O_{16}$ after calcination and pellet $Na_2Fe_2Ti_6O_{16}$ after sintering. (b) Rietveld refinement of powder $Na_2Fe_2Ti_6O_{16}$ after calcination. The measured XRD pattern (red dots), calculated XRD pattern (black line), difference between these two (blue line) and Bragg peak positions (green vertical bars) are shown here.