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# p-Type thermoelectric properties of the oxygen-deficient perovskite $Ca_2Fe_2O_5$ in the brownmillerite structure

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ABSTRACT

Brownmillerite calcium ferrite was synthesized in air at 1573 K and thermoelectric properties (direct current electrical conductivity $\sigma$, Seebeck coefficient $\alpha$, thermal conductivity $\kappa$, thermal expansion $\alpha_L$) were measured from 373 to 1050 K in air. Seebeck coefficient was positive over all temperatures indicating conduction by holes, and electrical properties were continuous through the *Pnma–Imma* phase transition. Based on the thermopower and conductivity activation energies as well as estimated mobility, polaron hopping conduction was found to dominate charge transport. The low electrical conductivity, $<1$ S/cm, limits the power factor ($\alpha^2\sigma$), and thus the figure of merit for thermoelectric applications. The thermal conductivity values of $\sim$2 W/mK and their similarity to Ruddlesden–Popper phase implies the potential of the alternating tetrahedral and octahedral layers to limit phonon propagation through brownmillerite structures. Bulk linear coefficient of thermal expansion ($\sim 14\times10^{-6}\,K^{-1}$) was calculated from volume data based on high-temperature *in situ* X-ray powder diffraction, and shows the greatest expansion perpendicular to the alternating layers.

## 1. Introduction

The ongoing investigation of oxide ceramics for thermoelectric applications seeks to support alternative energy power generation from excess heat: solar and geothermal heat sources, or waste heat from factories and automobiles, by incorporating oxide materials for their increased thermal and chemical stability. The actual efficiency of a thermoelectric material is proportional to a dimensionless figure of merit given by $ZT=\alpha^2\sigma T/\kappa$, where $\alpha$ is the Seebeck coefficient also known as thermopower, $\sigma$ is the electrical conductivity, and $\kappa$ the total thermal conductivity ($\kappa=\kappa_{el}+\kappa_{ph}$), which is a sum of the lattice (phonon) and electronic contributions. Target values include: $\kappa<1$ W/mK, $\sigma>10$ S/cm, $\alpha>150\,\mu V/K$, with the goal of designing oxide materials that exhibit $ZT>1$ to compete with traditional intermetallic thermoelectrics [1]. These values illustrate the fundamental requirements of thermoelectric materials: simultaneous occurrence of high electrical conductivity and Seebeck coefficient, with low thermal conductivity. Ultimately it has been realized that thermoelectric materials must behave as a crystal electronically, and a glass thermally [2].

The voltage output by a thermoelectric pair (essentially a thermocouple) is maximized for materials with Seebeck coefficients that are similar functions of temperature [3]. Likewise, thermal expansion behavior of thermoelectric materials must be considered as these oxides will be paired not just with other semiconducting oxides, but also with metal electrode and oxide substrate materials. Thermomechanical failure has been encountered in oxide thermoelectric devices, and attributed to poor thermal expansion compatibility between oxides and metal electrodes [4,5]. Accordingly, oxide/silver composites are being explored for their ability to narrow the gap between the thermal expansion of oxides and silver electrodes [6]. The aforementioned requirements restrict the number of optimal combinations of thermoelements, and support the development of an assortment of *p*- and *n*-type oxides. *p*-Type systems based on cobalt oxide continue to drive the development of thermoelectric oxides since the discovery of lucrative thermoelectric properties in $NaCo_2O_4$ [7–10].

Compounds with the brownmillerite structure ($A_2B_2O_5$) are named after the brownmillerite mineral [11] ($Ca_2AlFeO_5$), which is a perovskite-derivative structure resulting from ordered oxygen vacancies and/or reduction of the *B*-site cation from a IV oxidation state to III according to:

$$2ABO_3 \rightarrow 2B'_B + V_O^{\bullet\bullet} + \frac{1}{2}O_2(g) + 5O_O^{\times} + 2A_A^{\times} \tag{1}$$

The (1/6) oxygen vacancies order in the [101] direction of the perovskite unit cell, introducing a fraction of tetrahedrally coordinated *B*-site cations, which alternate in a stacking sequence with octahedrally coordinated *B*-site cations along the *b*-axis (Fig. 1). The possibility of right- and left-handed orientations of

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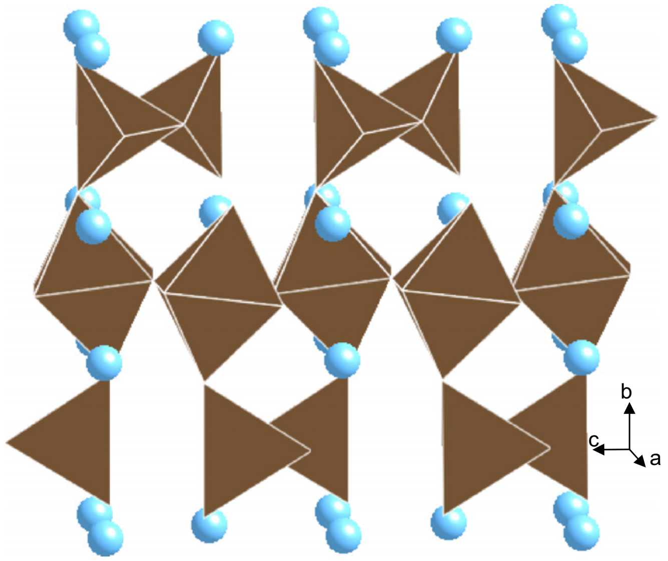

**Fig. 1.** Brownmillerite phase $Ca_2Fe_2O_5$, space group *Pnma*, showing alternating left- and right-handed tetrahedral chains. Light blue atoms represent $Ca^{2+}$ ions, polyhedra represent $Fe^{3+}$ ions, oxygen ions have been omitted for clarity.

the tetrahedra introduces polymorphic structures [12]. First, the low temperature phase, space group *Pnma* (*Pcmn*, number 62), contains alternating right- and left-handed configurations of tetrahedral chains. Depending on composition, two high temperature phases may exist: space group *I*2*mb* [13] containing tetrahedra that are all oriented in the same direction, and space group *Imma* [12], a phase with an aperiodic sequence of the tetrahedral chains [13,14]. Consistent with this view, a (3+1)-dimensional superspace group ($Imma(00\gamma)s00$) has been proposed [15] and recently confirmed in the $Ca_2Fe_2O_5$ composition [16]. Lastly, some brownmillerite structures may disorder at high temperatures [17] to form an oxygen-deficient cubic perovskite phase, marked by a shift in charge transport [18,19].

In general brownmillerite structures accommodate oxygen interstitials, charge compensated by holes, to exhibit *p*-type conduction according to:

$$\frac{1}{2}O_2(g) \Leftrightarrow O''_i + 2h^\bullet \qquad (2)$$

where in iron-containing compounds the holes may be associated with $Fe^{3+}$ cations, forming small polarons, to essentially produce a fraction of $Fe^{4+}$ cations

$$Fe^{3+} + h^\bullet \rightarrow Fe^{4+} \qquad (3)$$

with a resulting stoichiometry described as $Ca_2Fe_2O_{5+\delta}$ [20,21]. Loss of oxygen can be viewed as restoring stoichiometry by reducing Fe cations from the (IV) to (III) state. Finally, these structures are known to exhibit Jahn–Teller distortions, not due to the electronic nature of the constituent ions, but rather due to the existence of corner-shared octahedra and tetrahedra and their different inherent bond lengths which serve to trap charge carriers forming small polarons [22] and slowing charge transport [18].

The compound $Ca_2Fe_2O_5$ (mineral name srebrodolskite) is an antiferromagnetic mineral that crystallizes in the brownmillerite structure (space group *Pnma* shown in Fig. 1). It is characterized by a Néel temperature of ~720 K [13], and a congruent melting point of 1722 K [23]. Additionally, $Ca_2Fe_2O_5$ undergoes a phase transition from *Pnma* [16] (*Pcmn*) [24,25] to *Icmm* [25] (*I*2*mb* [24], $Imma(00\gamma)s00$ [16]) at ~950 K. This transition occurs over a 25 K temperature range, where both the low temperature and high temperature phases coexist [16]. The antiferromagnetic configuration of the $Fe^{3+}$ ions in this structure is a result of *super-exchange* through intermediate oxygen anions to increase the covalency of the Fe–O bonds, while the variable valence of Fe cations serve to facilitate charge transport by hopping [26,27]. Mössbauer studies have confirmed the high-spin state of Fe cations in the brownmillerite structure for both octahedral and tetrahedral sites [13], which results in electronic structure $(t_{2g})^3(e_g)^2$ with half-filled levels in both tetrahedral and octahedral coordination.

$Ca_2Fe_2O_5$ has been studied for oxygen ionic transport [20,22] and its applications to Li-ion batteries [28] and catalysis [29–31]. An investigation of the room temperature elastic properties of $Ca_2Fe_2O_5$ have found oxygen vacancies to decrease bulk modulus and increase anisotropy of compression as compared to stoichiometric calcium perovskites [32]. Studies to apply compounds with the brownmillerite structure to thermoelectric systems are limited. Kobayashi et al. developed a brownmillerite type compound ($Ca_{2-y}La_yCo_{2-x}Al_xO_5$) for *n*-type thermoelectrics, and observed *p*-type behavior above 500 K, but deemed the thermoelectric properties inadequate due to the high resistivity [33]. Zhou and Goodenough [21] used thermopower measurements to study the electronic behavior of $Fe^{3+}/Fe^{4+}$ calcium perovskites at low temperatures and report *n*-type behavior of $Ca_2Fe_2O_{5.16}$ below 300 K, with the Seebeck coefficient approaching positive values near 300 K.

Layered oxide structures have been used to achieve minimal thermal conductivity through increased phonon scattering introduced by the interfacial regions between layers. Due to the layered nature of brownmillerite structures, the potential of the octahedral–tetrahedral interfaces to reduce thermal conductivity through phonon scattering exists. Kobayashi et al. [33] found transport within the layers was 100 times higher than perpendicular to the layers, thus pointing to the potential of the layers to scatter phonons. However, in bulk polycrystalline materials, this anisotropy will certainly be averaged, which may limit the overall effect that the layers have to decrease thermal conductivity in bulk samples.

Due to the stringent thermal, electrical, and mechanical requirements on thermoelectric materials, an increase in the repertoire of *p*-type materials is advantageous to the realization of oxide thermoelectric devices. Herein we report on the thermoelectric properties of the brownmillerite compound $Ca_2Fe_2O_5$ prepared and analyzed in air for its application as a *p*-type thermoelectric material. The goal of this study is to expand the possible compositions of *p*-type thermoelectric materials to include those composed of materials with low toxicity, high natural abundance, and improved thermomechanical properties.

## 2. Experimental

### 2.1. Synthesis

Samples of $Ca_2Fe_2O_5$ were prepared using solid-state synthesis techniques. Stoichiometric proportions of $CaCO_3$ (Alpha Aesar, 99.9%) and $Fe_2O_3$ (Aldrich, 99.9%) were hand mixed in an agate mortar and pestle with isopropanol additions as necessary to facilitate mixing. After drying, powders were sieved to $<30\,\mu m$ and ~2.0 g portions were pressed uniaxially to ~12 MPa using a Carver Model M die press. The pressed pellets were calcined in air at 1272 K (10 K/min, 12 h), followed by reprocessing and reaction firing to 1373 K. Sintered compacts were formed as described above, followed by additional cold isostatic pressing to ~140 MPa. Samples were then sintered to 1573 K (10 K/min, 12 h) in air. Final densities of sintered compacts were >90% theoretical ($4.035\,g\,cm^{-3}$, calculated from refined lattice parameters), as found by the Archimedes method (ASTM Standard C 373-88).