

Magnetic and Electric Properties of $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$ Brownmillerites Obtained by Ball Milling High-Energy Process

T. LUCIŃSKI^{a,*}, E. MARKIEWICZ^a, B. ANDRZEJEWSKI^a,
M. PUGACZOWA-MICHALSKA^a, K. CHYBCZYŃSKA^a, V.H. TRAN^b,
R. IDCZAK^c, P. SKOKOWSKI^a, M. CHRUNIK^d AND B. KOŚCIELSKA^e

^a*Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179 Poznań, Poland*

^b*W. Trzebiatowski Institute for Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-422 Wrocław, Poland*

^c*Institute of Experimental Physics, University of Wrocław, pl. Maksa Borna 9, 50-204 Wrocław, Poland*

^d*Institute of Applied Physics, Military University of Technology, Kaliskiego 2, 00-908 Warszawa, Poland*

^e*Institute of Nanotechnology and Materials Engineering, Gdansk University of Technology, Narutowicza 11/12, 80-233, Gdańsk, Poland*

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*e-mail: lucinski@ifmpan.poznan.pl

The structural, magnetic, and electric properties of the $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$ ($0 \leq x \leq 1.2$) brownmillerites prepared by the method of mechanochemical synthesis were examined. It was confirmed that these compounds, at least for the Al doping level $x \leq 0.8$, adopt the orthorhombic *Pnma* structure. Undoped $\text{Ca}_2\text{Fe}_2\text{O}_5$ brownmillerite exhibits ferromagnetic-like properties up to room temperature. In contrast, only a marginal ferromagnetic contribution to magnetic properties is observed in samples with Al addition. The Mössbauer results also suggest that Al atoms substitute for Fe in both tetrahedral and octahedral positions, resulting in a reduction of the hyperfine field. These results are consistent with density functional theory calculations, confirming the Al substitution at two positions in the crystal structure and the presence of an energy barrier between the favored antiferromagnetic and ferromagnetic ordering in both $\text{Ca}_2\text{Fe}_2\text{O}_5$ and $\text{Ca}_2\text{Fe}_{1.75}\text{Al}_{0.25}\text{O}_5$ compounds. A set of complex impedance measurements on frequency and temperature, along with the analysis of the obtained data within the Nyquist plot and the models of Arrhenius and Jonscher, yielded information on the conductivity mechanisms, as well as the contributions of grains and grain boundaries. The addition of Al significantly enhances the conductivity of $\text{Ca}_2\text{Fe}_2\text{O}_5$ ceramics, particularly in grain boundaries. However, at high doping levels, the localization of oxygen holes takes place, thereby increasing the activation energy. The conductivity mechanism also changes character from diffusive-like below 380 K to hopping-like at higher temperatures.

topics: brownmillerite, magnetic properties, Mössbauer, conductivity

1. Introduction

It is well known that metal oxides composed of transition metals display miscellaneous and very interesting properties arising from many competitive mechanisms (see, for instance, [1]). Among these, brownmillerites, being non-stoichiometric perovskite oxides, attract much attention due to their potential applications in many areas of engineering and electronics, such as fuel cells, sensors, and membranes, to name only a few (see, for

instance, [1–3] and references therein). In addition to homogeneous brownmillerite compounds, the production of an ensemble of perovskite heterostructures with brownmillerite can lead to new and very interesting phenomena [4, 5]. For example, one of the most recent applications of brownmillerite structure is their implementation into heterostructures with perovskites. Such structures have exhibited excellent bipolar resistance switching characteristics and can be applied as resistive switching random access memory (RRAM), which is one of the very popular types of memristors [6, 7].

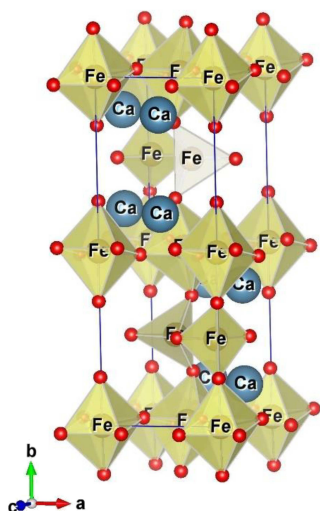


Fig. 1. Crystal structure of the $\text{Ca}_2\text{Fe}_2\text{O}_5$ in orthorhombic $Pnma$ structure. The structure was visualized using the VESTA package [24].

Brownmillerite $\text{A}_2\text{B}_2\text{O}_5$ oxides are formally a type of perovskite-related compound with an ABO_3 structure and oxygen deficiency. The first compound of this type, $\text{Ca}_2\text{AlFeO}_5$, was recognized as a common component of Portland cement and was named after Lorrin Thomas Brownmiller, chief chemist of the Alpha Portland Cement Company [8]. In 1962, Smith [9] proved that the $\text{Ca}_2\text{Fe}_2\text{O}_5$ structure represents the $Pnma$ space group. Less than a decade later, in 1970, Colville [10] determined the crystal structure of $\text{Ca}_2\text{Fe}_2\text{O}_5$. In 2004, G.J. Redhammer and coworkers [11] examined the structure variation of the brownmillerite series substituted by aluminum $\text{Ca}_2(\text{Fe}_{2-x}\text{Al}_x)\text{O}_5$ for $0.0 \leq x \leq 1.34$. In order to determine the structure of examined samples, they used both Mössbauer spectroscopy and X-ray powder diffraction and found that the examined samples with x up to $x = 0.56$ exhibit the $Pnma$ space group of the brownmillerite prototype. However, samples with $x > 0.56$ tended to reflect the symmetry of $I2mb$. The evolution of the $\text{Ca}_2(\text{Fe}_{2-x}\text{Al}_x)\text{O}_5$ structures was also studied by Colville and Geller [10, 12, 13], while M. Ceretti and coworkers [14] dealt with the influence of phase transformation on the crystal growth of stoichiometric $\text{Ca}_2\text{Fe}_2\text{O}_5$ and $\text{Sr}_2\text{ScGaO}_5$. They also found that $\text{Ca}_2\text{Fe}_2\text{O}_5$ reflected the $Pnma$ space group. Unlike $\text{Sr}_2\text{ScGaO}_5$, which exhibited a phase transition to cubic perovskite at 1400°C , $\text{Ca}_2\text{Fe}_2\text{O}_5$ did not undergo such a transformation.

The variety of brownmillerite properties was reported by N. Abe and coworkers [15], who studied the magnetic properties of the $\text{Ca}_2(\text{Fe}_{2-x}\text{Al}_x)\text{O}_5$ single crystal for $0.5 \leq x \leq 1$. They found not only the spin-flop transition induced by a magnetic field but also the antiferromagnetic transition occurring above room temperature and simultaneous

anomalies in electrical polarization and dielectric constant. Furthermore, the complex and specific structural, magnetic, and charge transport properties [2, 3] of brownmillerites appear to be highly dependent on their preparation technology, the most common of which are conventional solid-state reaction, chemical methods such as wet chemical synthesis, sol-gel, self-combustion, and high-energy mechanical milling combined with post-annealing [2]. The latter method was successfully used by Wang et al. [16] and Amorim et al. [17] to synthesize the $\text{Ca}_2\text{Fe}_2\text{O}_5$ brownmillerite, but to our knowledge, its potential has never been tested to obtain doped brownmillerites. Therefore, the main intention of our study was to determine the influence of both Al doping and high-energy mechanical processing on magnetic, structural, and charge transport properties of a series of the $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$ samples with aluminum content of $0 \leq x \leq 1.2$.

2. Experimental and computational methods

The investigated samples were prepared by high-energy ball milling using CaO , Fe_2O_3 , and Al_2O_3 powder substrates, followed by annealing in air at 800°C for 6 h. The mechanical milling was performed using a Pulverisette 6 (Fritsch) planetary ball mill equipped with a zirconia ZrO_2 reactor containing 5 ZrO_2 balls of 20 mm diameter. The ratio of ball mass to powder mass was 12.5:1. This stage of the reaction took place in air and at room temperature (however, the temperature of the powder substrates reached about 80°C during milling). Different milling times were tested, ranging from 5 to 40 h. The optimal processing time was 9 h, as it ensured a good quality of the final product with some amount of zirconium always added due to the abrasion of the reactor and the zirconia balls. After initial milling followed by the stage of annealing, the resulting powders were cold-pressed into tablets and then resintered in air and at 800° for 24 h.

The polycrystalline structure of all samples was characterized by $\text{Cu } K_\alpha$ X-ray diffraction (XRD) measurements. The magnetic measurements, such as the temperature dependence of magnetic moment and magnetic hysteresis loops, were recorded using a Quantum Design Physical Property Measurement System (PPMS) equipped with a VSM (Vibrating Sample Magnetometer). Magnetic characterization of all samples was supplemented by Mössbauer spectroscopy measurements performed at room temperature. The temperature dependencies of alternating current electric conductivity and impedance spectra of the samples were recorded using an Alpha-A high-performance frequency analyzer combined with Quatro Cryosystem for temperature control. The range of frequency used was varied from 1 Hz to 1 MHz.

Electronic structure calculations were applied to describe the ground state properties of Al-doped $\text{Ca}_2\text{Fe}_2\text{O}_5$ brownmillerites, with particular emphasis on the $\text{Ca}_2\text{Fe}_{1.75}\text{Al}_{0.25}\text{O}_5$ compound. The calculations were performed using the projector augmented wave method (PAW) [18], which is implemented in the Vienna *ab initio* Simulations Package (VASP) [19, 20]. Wave functions were represented in a plane-wave basis truncated at 520 eV. In the calculations, we used the orthorhombic cell (*Pnma* space group) with 36 atoms (Fig. 1, see also [21]). The cell and the atomic coordinates were optimized until the residual forces acting on constituent atoms (i.e., Ca, Fe, Al, O) became smaller than 10^{-6} eV/Å. The Brillouin zone (BZ) integrations were performed using a $7 \times 5 \times 7$ Monkhorst-Pack *k*-points mesh. Moreover, a total energy convergence threshold of 10^{-6} eV was taken into account. The calculations were performed within the recently developed non-empirical strongly constrained and appropriately normed (SCAN) meta-generalized gradient approximation (meta-GGA) [22]. The GGA introduces a dependence on the electron density gradient, which improves the description of examined systems compared to the local density approximation (LDA). However, the meta-GGA also includes a dependence on the Laplacian of the density and the Kohn–Sham kinetic energy density. Importantly, the SCAN functional satisfies all the 17 known constraints of an exchange-correlation functional, whereas GGA does not satisfy them [23].

3. Results and discussion

Figure 2 (see also [24]) shows examples of XRD measurements for the $\text{Ca}_2\text{Fe}_2\text{O}_5$, $\text{Ca}_2\text{Fe}_{1.6}\text{Al}_{0.4}\text{O}_5$, and $\text{Ca}_2\text{Fe}_{1.2}\text{Al}_{0.8}\text{O}_5$ samples. Rietveld analysis for these samples indicated the presence of the orthorhombic *Pnma* structure with similar values of the lattice parameters (see Fig. 2). More details of the $\text{Ca}_2\text{Fe}_2\text{O}_5$ crystal structure with *Pnma* unit cell are visualized in the graphics in Fig. 1. As can be seen, the structure contains eight Ca atoms, eight Fe atoms, and twenty O atoms.

Figure 3 presents the magnetic moment versus applied magnetic field and temperature ($m(H)$ and $m(T)$, respectively, in arbitrary units a.u.) for samples with aluminum content of $x = 0$, $x = 0.4$, and $x = 1.2$. These results prove that the addition of Al significantly changes the character of both $m(H)$ and $m(T)$ dependencies and that only the undoped ($x = 0$) compound exhibits ferromagnetic-like behavior up to room temperature. The conclusion about the ferromagnetic-like properties of the $\text{Ca}_2\text{Fe}_2\text{O}_5$ compound without no aluminum admixture is also supported by the $m(H)$ measurements, which show the existence of apparent hysteresis loops for $x = 0$ up to 300 K. It should be noted that the marginal $m(H)$ hysteresis loops were

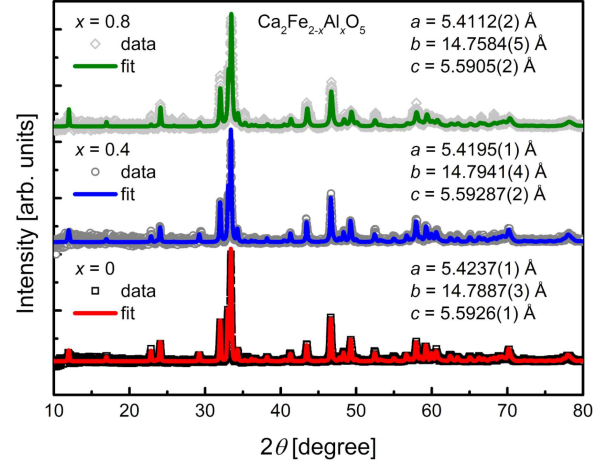


Fig. 2. X-ray diffraction patterns for the $\text{Ca}_2\text{Fe}_2\text{O}_5$, $\text{Ca}_2\text{Fe}_{1.6}\text{Al}_{0.4}\text{O}_5$, and $\text{Ca}_2\text{Fe}_{1.2}\text{Al}_{0.8}\text{O}_5$ samples. Open symbols denote XRD data and solid lines are fits of theoretical models performed in the FullProf software [24]. The lattice parameters a , b , and c of the orthorhombic *Pnma* crystal structure are presented. The XRD intensity is expressed in arbitrary units (a.u.).

also observed for samples with $x > 0$, but their contribution to the overall $m(H)$ curve was definitely less pronounced.

Figure 4 represents the results of Mössbauer spectra measurements for $\text{Ca}_2\text{Fe}_2\text{O}_5$ as-prepared, annealed, and Al-doped compounds at room temperature. The spectra of undoped brownmillerites are composed of two sextets, while the blue component corresponds to the octahedral position of Fe^{+3} ions (see Table I) whereas the red component corresponds to its tetrahedral position, i.e., the smaller isomer shift (IS) corresponds to the tetrahedral position, and larger IS stands for octahedral positions of the Fe^{+3} ions. The relative contributions of both sextets are very similar, and the acquired Mössbauer parameters have very similar values to those reported in [3]. For Al-doped samples, the two additional sextets appear with very broad lines and a lower hyperfine field B_{HF} . Our Mössbauer results suggest that the occurrence of Al atoms in the base $\text{Ca}_2\text{Fe}_2\text{O}_5$ structure decreases the B_{HF} , and Al atoms replace Fe atoms in both tetrahedral and octahedral positions. However, they more frequently “prefer” the tetrahedral positions than the octahedral positions, i.e., 18% and 14% of the Fe atoms in the tetrahedral and octahedral positions, respectively, are replaced by Al in the sample with $x = 0.4$ and 27% and 22% in the respective positions in the sample with $x = 0.8$.

The results found for $\text{Ca}_2\text{Fe}_{0.8}\text{Al}_{1.2}\text{O}_5$ seem to be similar to those obtained for the $\text{Ca}_2\text{Fe}_{1.6}\text{Al}_{0.4}\text{O}_5$ sample. The most puzzling result is that the samples with $x \neq 0$ exhibit the magnetic moment only at very low temperatures, and the hysteresis loop

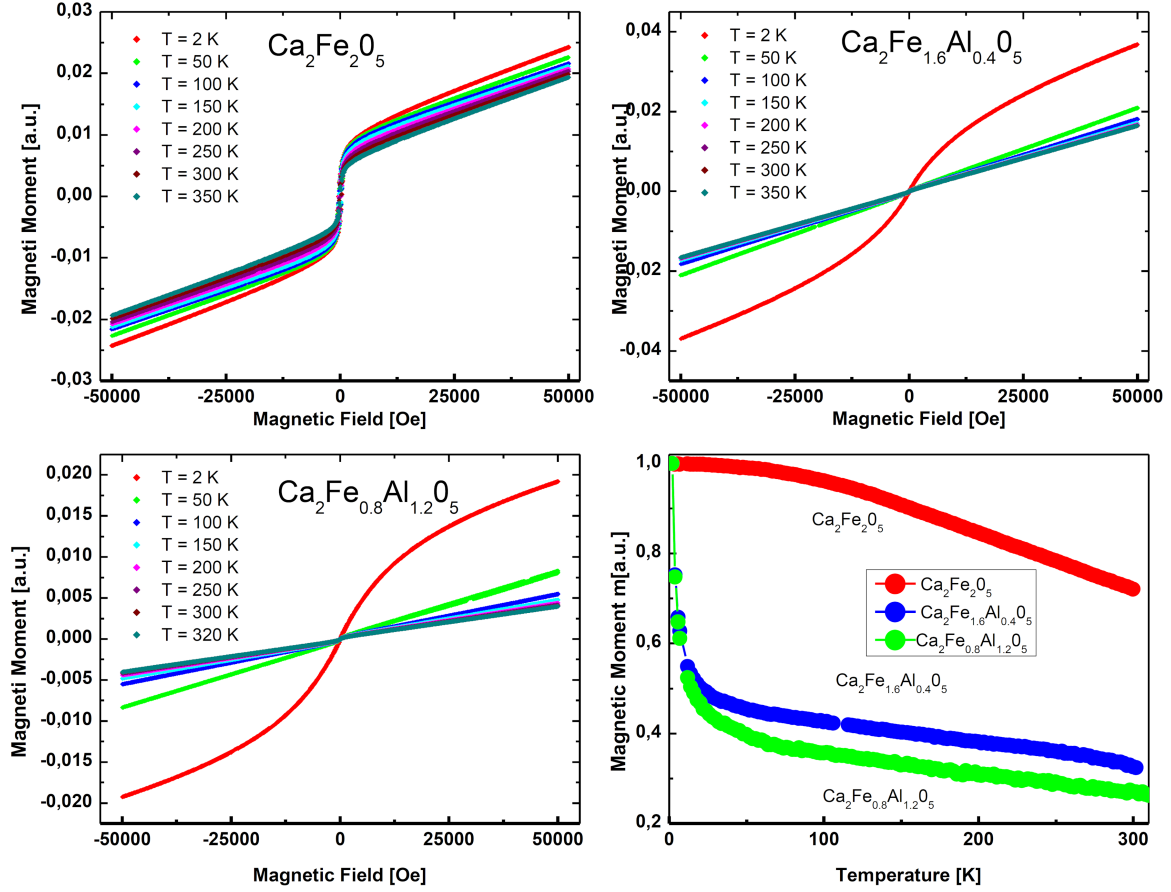


Fig. 3. The $m(H)$ and $m(T)$ dependencies for samples with $x = 0$, $x = 0.4$, and $x = 1.2$ for different temperatures. The values of the magnetic moment of different samples measured at $T = 0$ are normalized to 1. The moment is expressed in arbitrary units (a.u.).

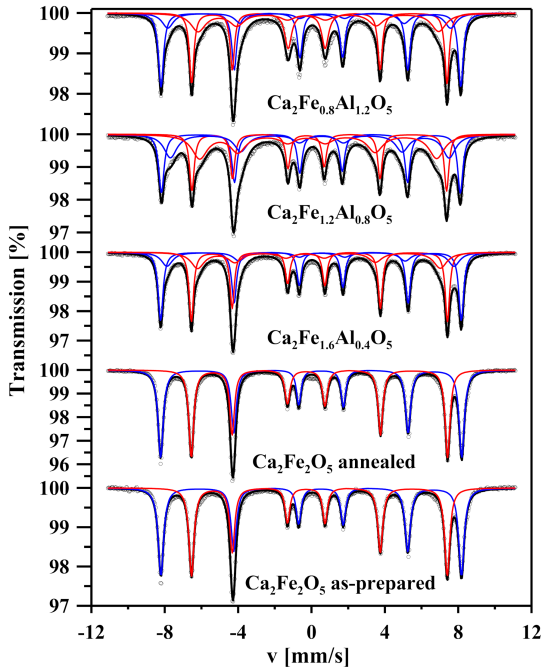


Fig. 4. The Mössbauer spectra of $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$ measured at room temperature.

is almost absent at higher temperatures. This is in contrast with the Mössbauer results recorded at room temperature, where the typical spectra reflecting ferromagnetic, antiferromagnetic, or even ferrimagnetic ordering were found for all examined samples with aluminum content of $0 \leq x \leq 1.2$.

The measurements of the electric alternating current (AC) conductivity σ_{ac} presented in Fig. 5a and b show that at low frequencies, all investigated samples exhibit a plateau in the dependence of conductivity on frequency, which is a characteristic feature of the direct current (DC) conductivity σ_{dc} satisfying the Arrhenius equation expressed in terms of reciprocal temperature, i.e., $\ln(\sigma_{dc}/\sigma_0) = -E_a/(k_B T)$ where σ_0 is a constant and k_B is the Boltzmann constant. The activation energies of conductivity for samples with Al content varying from 0 to 1.2 have been found by fitting this equation to the data in Fig. 5d.

For further analysis, the Jonscher equation $\sigma_{ac} = \sigma_{dc} + A\omega^s$ was fitted to the experimental results of the conductivity measurement (Fig. 5a–b), and Jonscher's exponent s , which indicates the character of conductivity mechanism, was calculated (Fig. 5c).

TABLE I

The fitting parameters of the Mössbauer spectra from Fig. 4.

Sample	Component	IS [mm/s]	QS [mm/s]	B_{HF} [T]	C [%]	Γ [mm/s]
$\text{Ca}_2\text{Fe}_2\text{O}_5$ annealed	blue sextet	0.355(2)	-0.522(4)	50.8(1)	51.5(2)	0.34(1)
	red sextet	0.183(2)	0.716(3)	43.2(1)	48.5(2)	0.32(1)
$\text{Ca}_2\text{Fe}_2\text{O}_5$	blue sextet	0.360(4)	-0.530(6)	50.9(1)	50.9(2)	0.32(1)
	red sextet	0.186(4)	0.716(5)	43.3(1)	49.1(2)	0.29(1)
$\text{Ca}_2\text{Fe}_{1.6}\text{Al}_{0.4}\text{O}_5$	blue sextet	0.358(4)	-0.554(5)	50.8(1)	35(1)	0.30(1)
	second blue sextet	0.37(2)	-0.63(5)	48.5(2)	14(1)	0.74(3)
	red sextet	0.185(4)	0.714(5)	43.3(1)	33(1)	0.29(1)
	second red sextet	0.15(2)	0.75(4)	41.0(2)	18(1)	0.86(3)
$\text{Ca}_2\text{Fe}_{1.2}\text{Al}_{0.8}\text{O}_5$	blue sextet	0.355(5)	-0.553(6)	50.5(2)	28(1)	0.33(1)
	second blue sextet	0.34(2)	-0.64(5)	47.1(3)	22(1)	0.85(3)
	red sextet	0.181(5)	0.706(6)	43.0(2)	23(1)	0.29(1)
	second red sextet	0.16(2)	0.64(6)	40.0(3)	27(1)	1.00(3)
$\text{Ca}_2\text{Fe}_{0.8}\text{Al}_{1.2}\text{O}_5$	blue sextet	0.355(5)	-0.552(6)	50.6(2)	35(1)	0.31(1)
	second blue sextet	0.34(1)	-0.71(4)	47.8(5)	13(1)	0.74(3)
	red sextet	0.182(5)	0.715(6)	43.1(2)	32(1)	0.28(1)
	second red sextet	0.16(1)	0.65(5)	40.6(4)	20(1)	0.96(3)

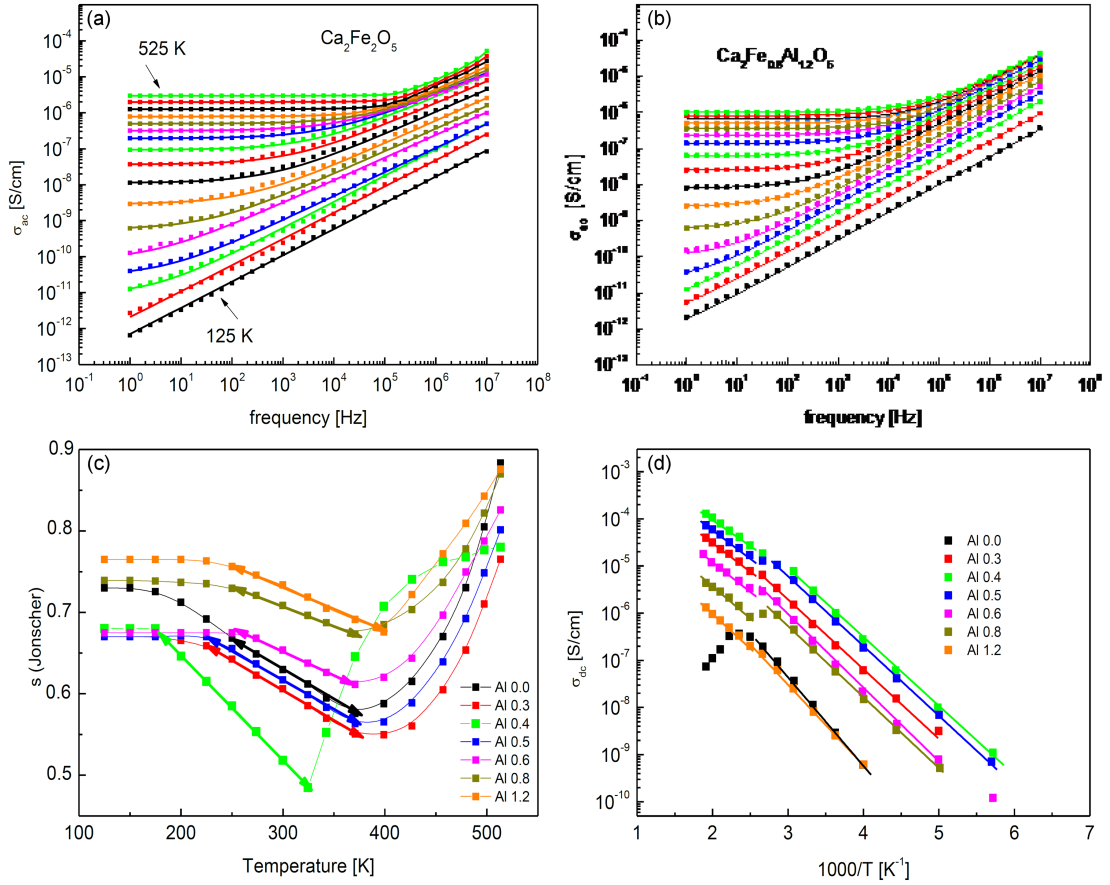


Fig. 5. The examples of AC conductivity dependence on frequency for various temperatures and samples with Al content $x = 0.0$ and 1.2 together with fitting to Jonscher equation (a, b). Panel c shows the values of Jonscher's exponent s . Panel d represents the values of DC conductivity versus reciprocal temperature for all examined samples.

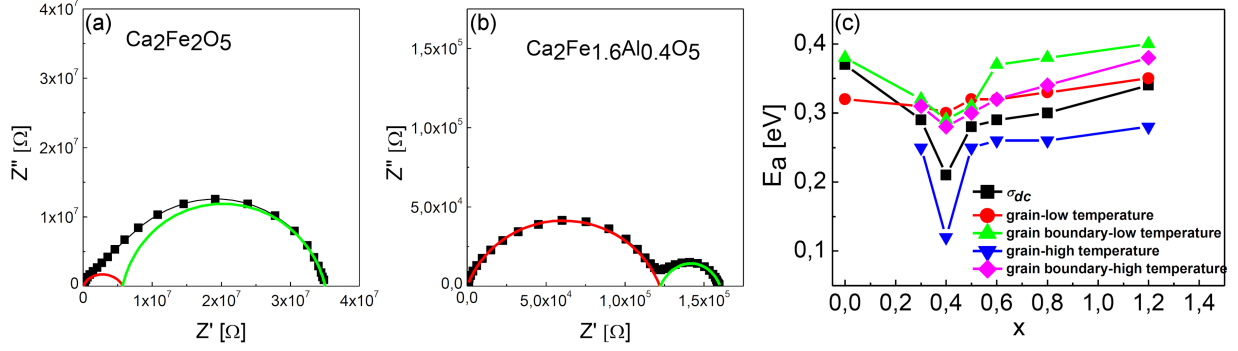


Fig. 6. Nyquist plots for $\text{Ca}_2\text{Fe}_2\text{O}_5$ and $\text{CaFe}_{1.6}\text{Al}_{0.4}\text{O}_5$ samples and deconvolution of the complex impedance to the grain and grain boundary contributions represented by the red and green semicircles, respectively (panels a and b). Panel c presents activation energies E_a of total σ_{dc} conductivity and oxygen ion conduction in grains and grain boundaries.

For each sample, two characteristic temperature ranges were observed. Below ~ 380 K, the s exponent decreased, and above ~ 400 K, it increased. The calculated values of s (varying between 0.5 and 0.9 depending on x and temperature range) show that at lower temperatures (below 380 K) the conductivity has a diffusive character, whereas at higher temperatures, it becomes more hopping-like. The sample with $x = 0.4$ is characterized by the lowest value of s in the low temperature and also by the lowest temperature range at which the plateau associated with σ_{dc} conductivity appears.

Figure 5d represents the DC conductivity σ_{dc} versus reciprocal temperature for all examined samples.

The activation energy E_a of σ_{dc} conductivity calculated based on the Arrhenius plot changes from 0.21 to 0.37 eV for the samples with different content of Al (Fig. 6c). The sample with $x = 0.4$ is characterized once again by the lowest activation energy.

The contributions of grains and grain boundaries to total conductivity can be determined using the Nyquist plots of complex conductivity $Z^*(\omega) = Z'(\omega) - iZ''(\omega)$ (where Z' is real and Z'' is imaginary component), as shown in Fig. 6a and b for pure $\text{Ca}_2\text{Fe}_2\text{O}_5$ and $\text{CaFe}_{1.6}\text{Al}_{0.4}\text{O}_5$ samples, respectively. The doping with aluminum exerts a substantial effect on the real part of the impedance $Z'(\omega)$, resulting in a decrease in resistivity by more than two orders of magnitude in the sample with an aluminum content of 0.4. The deconvolution of the Nyquist plots reveals two semicircles related to the grain and grain boundary contributions to complex impedance. The grain boundary contribution represented by the green semicircles is dominant in the case of pure $\text{Ca}_2\text{Fe}_2\text{O}_5$, whereas in all doped samples dominates grain contribution to the total resistivity, represented by the red semicircles in Fig. 6. This means that in doped samples, the Al content at the grain boundaries is higher than in the grain interiors, resulting in a lower resistivity

of the former. Within the lower temperature range (below ~ 380 K), the activation energies of the processes in grains and grain boundaries are very similar for $x = 0.3, 0.4$, and 0.5 with the minimum energy of 0.30 eV for the sample with $x = 0.4$ (see Fig. 6c). At higher temperatures, the energy required for the process in grain boundaries is higher than that required for the process in grains. The sample with Al content $x = 0.4$ seems to be the one in which the processes (oxygen ion conduction) require the lowest activation energy. This fact can be explained by assuming that at lower concentration of the dopants, the oxygen vacancies are randomly distributed and cannot interact with each other. In this case, oxygen can easily diffuse, which is likely to occur in the $\text{CaFe}_{1.6}\text{Al}_{0.4}\text{O}_5$ compound with an Al content $x = 0.4$. However, when the vacancy concentration increases, oxygen vacancies start to interact and form an ordered arrangement. Due to the two-dimensional structure of brownmillerite, the oxygen ions cannot diffuse to the adjacent layers.

In a typical brownmillerite structure, there are unique octahedral B1 and tetrahedral B2 sites arranged in layers parallel to the long axis (b axis in $Pnma$ structure in Fig. 1), whereas for compounds with different B1 and B2 ions, interlayer site ordering is observed. In fact, this structure type can accommodate both intra- and interlayer cation site ordering. To answer questions concerning the details of the crystal structure and site preferences for Al in $\text{Ca}_2\text{Fe}_2\text{O}_5$, a density functional theory (DFT) study of both $\text{Ca}_2\text{Fe}_2\text{O}_5$ and $\text{Ca}_2\text{Fe}_{1.75}\text{Al}_{0.25}\text{O}_5$ was performed. For the calculations, it was assumed that the unit cell of the $\text{Ca}_2\text{Fe}_2\text{O}_5$ base structure consists of four formula units (4 f.u.) in the $Pnma$ phase. Figure 1 presents a schematic drawing of the $Pnma$ unit cell of $\text{Ca}_2\text{Fe}_2\text{O}_5$ brownmillerite with eight Ca atoms, eight Fe atoms, and twenty O atoms. In Wyckoff notations, the eight Fe atoms occupy (4a) and (4c) sites, while eight Ca atoms occupy (8d) sites, and twenty O atoms occupy both (8d) and

(4c) sites.

TABLE II

Calculated a , b , c lattice parameters (in Å) and the bond angles of Fe–O–Fe (in degrees): $\theta_T = \text{Fe}_2\text{–O–Fe}_2$, $\theta_O = \text{Fe}_1\text{–O–Fe}_1$, and $\theta_{OT} = \text{Fe}_1\text{–O–Fe}_2$ for $\text{Ca}_2\text{Fe}_2\text{O}_5$ and $\text{Ca}_2\text{Fe}_{1.75}\text{Al}_{0.25}\text{O}_5$ for G-AFM magnetic order.

Sample	a [Å]	b [Å]	c [Å]	θ_T [°]	θ_O [°]	θ_{OT} [°]
$\text{Ca}_2\text{Fe}_2\text{O}_5$	5.403	14.708	5.571	126.44	165.32	140.31
$\text{Ca}_2\text{Fe}_{1.75}\text{Al}_{0.25}\text{O}_5$ Al(4c) (0.448, 1/4, 0.568)	5.388	14.626	5.583	126.038	166.1456	140.6651
$\text{Ca}_2\text{Fe}_{1.75}\text{Al}_{0.25}\text{O}_5$: Al(4a) (0,0,0)	5.365	14.751	5.526	125.8564	165.1780	143.2371

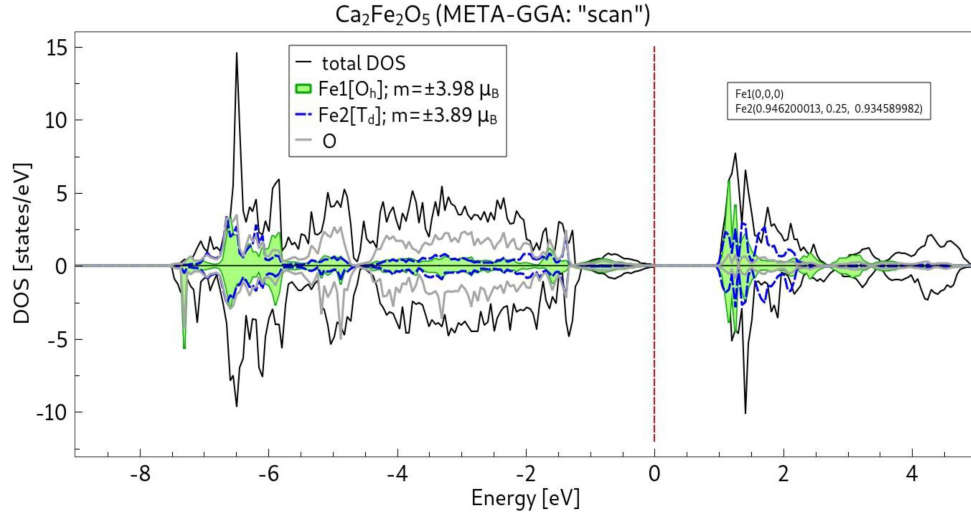


Fig. 7. The total density of states (DOS) of $\text{Ca}_2\text{Fe}_2\text{O}_5$ in $Pnma$ structure with G-AFM. The green and blue lines indicate the atomic contribution of Fe in octahedral and tetrahedral coordination, respectively. The gray line shows a sum of the atomic DOS contribution of oxygens. The positions occupied by Fe atoms (Fe1 and Fe2) in the cell are indicated in the right frame.

We realize that DFT calculations are restricted to 0 K. Thus, in calculations for $\text{Ca}_2\text{Fe}_2\text{O}_5$, we considered both ferromagnetic (FM) and antiferromagnetic G-type (G-AFM) collinear spin ordering on the Fe atoms with the magnetization pointing along the b axis. In the G-AFM type of arrangement of the unit cell of the brownmillerite, both the intra-plane and inter-plane coupling between Fe cations are antiferromagnetic. The total energy differences of two different magnetic orders (FM and G-AFM) calculated for parent $\text{Ca}_2\text{Fe}_2\text{O}_5$ in $Pnma$ structure is 28.9 meV/atom (or ~ 335 K). Thus, it can be concluded to some extent that from the DFT level, ferromagnetic spin alignment of Fe atoms could occur at slightly above room temperature. This is consistent with our experimental results (see Fig. 3).

In order to study the electronic structure of $\text{Ca}_2\text{Fe}_{1.75}\text{Al}_{0.25}\text{O}_5$ brownmillerite, two kinds of inequivalent sites for Al atom (4a) (octahedral site) and (4c) (tetrahedral one) are taken into consideration in the unit cell of $Pnma$. We substitute one of the Fe cations in the unit cell of parent $\text{Ca}_2\text{Fe}_2\text{O}_5$ with one Al atom. The cell shape, internal atomic positions, and volume were re-optimized during the

structural relaxations in both cases (Al in octahedral site and Al in tetrahedral site). Here, we note that the calculations carried out for the doped brownmillerite with $\text{Ca}_2\text{Fe}_{1.75}\text{Al}_{0.25}\text{O}_5$, assuming FM magnetic order, show that the total energy of the system will increase by at least 40 meV/atom compared to the G-AFM case. For this reason, we will further consider only the G-AFM magnetic order.

We found that the energy difference between the two $\text{Ca}_2\text{Fe}_{1.75}\text{Al}_{0.25}\text{O}_5$ systems with Al in octahedral coordination and Al in tetrahedral one is about 2.37 meV/atom. The proximity of these total energies can be explained by the coexistence of both Al coordination in $\text{Ca}_2\text{Fe}_{1.75}\text{Al}_{0.25}\text{O}_5$ and is thus consistent with our observation from the Mössbauer experiment. The calculated lattice parameters and the bond angles of Fe–O–Fe of the $\text{Ca}_2\text{Fe}_2\text{O}_5$ and $\text{Ca}_2\text{Fe}_{1.75}\text{Al}_{0.25}\text{O}_5$ for relaxed $Pnma$ structure with G-AFM order are presented in Table II.

In the unit cell of brownmillerite ($Pnma$ structure), the Fe atoms fall into two sets, namely four in octahedral coordination with Fe–O bond distances ranging from 1.9541 to 2.1037 Å and four in

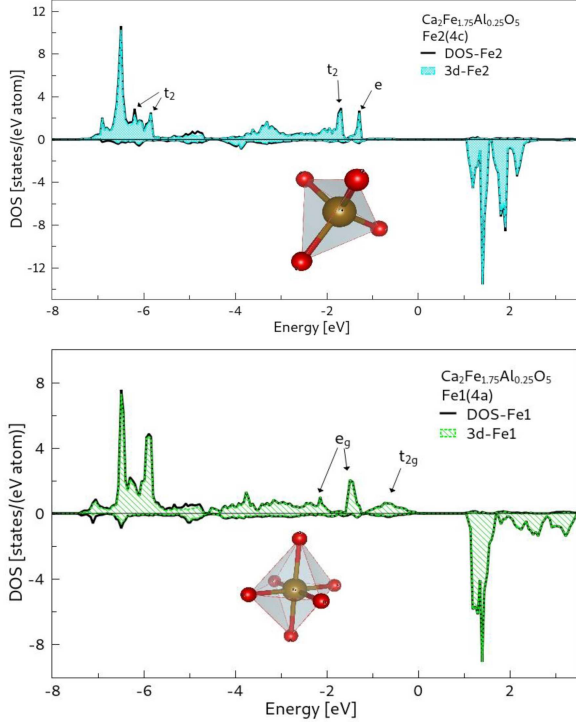


Fig. 8. The orbital resolved density of 3d states of Fe in tetrahedral and octahedral oxygen coordination in $\text{Ca}_2\text{Fe}_{1.75}\text{Al}_{0.25}\text{O}_5$.

tetrahedral environments with Fe–O bond distances ranging from 1.8365 to 1.9009 Å for $\text{Ca}_2\text{Fe}_2\text{O}_5$. The FeO_6 octahedra are not connected out-of-plane (along the b axis), which causes the apical oxygen atoms to displace more than the equatorial ones. In $\text{Ca}_2\text{Fe}_{1.75}\text{Al}_{0.25}\text{O}_5$, the bond lengths of the Fe1 with some apical oxygen increase to 2.175 Å and 2.128 Å when the Al atom is located in tetrahedral and octahedral oxygen coordination, respectively.

The magnetic arrangement of the Fe spins can be described as a G-type magnetic structure with antiferromagnetic (AFM) layers of FeO_6 octahedra alternating along the a direction with AFM layers of FeO_4 tetrahedra; the coupling of the octahedral and tetrahedral layers is also AFM. The calculated density of states (DOS) of $\text{Ca}_2\text{Fe}_2\text{O}_5$ (with G-AFM magnetic order) projected onto Fe-3d states is shown in Fig. 7. We found that the use of the meta-GGA [18] for $\text{Ca}_2\text{Fe}_2\text{O}_5$ drove the insulating band structure. The value of the band gap is 1.104 eV. The charge-transfer character of the band gap can be noticed by observing the O-2p character of the states close to the Fermi level and the large Fe-3d character of the conduction band. The top of the valence band is dominated by Fe(4a)-3d and O-2p states, while the Fe(4c)-3d states are pushed about 1 eV below the Fermi energy. On the other hand, the bottom of the conduction band is due to the 3d states of both Fe(4a) and Fe(4c) and O-2p states.

The results of our DFT calculation show that the hybridization between Fe-3d bands and O-2p orbitals in the studied $\text{Ca}_2\text{Fe}_2\text{O}_5$ insulator leads to the formation of a ligand hole in the surroundings of some O ions. In the $\text{Ca}_2\text{Fe}_2\text{O}_5$, the magnetic moment is only induced on the O ions (approximately $0.11 \mu_B$) that are located in apical positions of FeO_6 and FeO_4 cages (i.e., along b axes). However, in $\text{Ca}_2\text{Fe}_{1.75}\text{Al}_{0.25}\text{O}_5$, the polarization of the O anions can also be noticed by observing the depletion of spin-down (or spin-up) states close to the Fermi level in the DOS of the O atoms that are located at both apical and equatorial oxygen positions of FeO_6 or FeO_4 . For the equatorial oxygen atoms, the induced magnetic moments are about $0.12 \mu_B$. Due to the substitution of Al for Fe in the (4a) or (4c) position in the $Pnma$ structure of $\text{Ca}_2\text{Fe}_2\text{O}_5$, the value of the band gap decreases to 0.762 eV or 1.013 eV, respectively.

The magnetic moments of Fe1(4a) and Fe2(4c) are found to be $\pm 3.98 \mu_B$ and $\pm 3.89 \mu_B$, respectively. The presence of two different H_{hf} originating from Fe with the tetrahedral oxygen and octahedral oxygen coordination corresponds to the orbital resolved density of 3d states of Fe1(4a) and Fe2(4c). Due to the octahedral environment, the 3d states of Fe1(4a) are broadly split into $t_{2g}(d_{xy}, d_{yz}, d_{zx})$ and $e_g(d_{3z^2-r^2}, d_{x^2-y^2})$ states along the whole valence band from the bottom of the valence band to 0 eV (as marked in Fig. 8). However, the tetrahedral oxygen coordination of Fe2(4c) provides a split into e and t_2 states from the bottom of the valence band to the energy of about -1.22 eV.

4. Conclusions

The structural, magnetic, and electronic transport properties of $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$ structures were examined. The XRD measurements revealed that all these compounds, at least for $x \leq 0.8$, had orthorhombic $Pnma$ structures. Using magnetometric measurements, we found that undoped $\text{Ca}_2\text{Fe}_2\text{O}_5$ brownmillerite shows ferromagnetic-like behavior up to room temperature, while the addition of Al significantly changes the magnetic properties of this compound, and only the marginal ferromagnetic contribution to the magnetic properties could be observed for samples with $x > 0$. This is in line with the DFT calculation that proved that the G-AFM magnetic ordering is energetically favored in both $\text{Ca}_2\text{Fe}_2\text{O}_5$ and $\text{Ca}_2\text{Fe}_{1.75}\text{Al}_{0.25}\text{O}_5$. However, the energy barrier between the G-AFM and FM in $\text{Ca}_2\text{Fe}_2\text{O}_5$ is of the order of magnitude of 28.9 meV/atom only. Nevertheless, the fact that the energy barrier increases (at least to 40 meV/atom) in the doped $\text{Ca}_2\text{Fe}_{1.75}\text{Al}_{0.25}\text{O}_5$ compound is taken into account. The Mössbauer results suggest that the occurrence of the Al atoms in the base structure lowers the hyperfine field, and Al substitutes

Fe atoms in both tetrahedral and octahedral positions. Moreover, from DFT calculations, the small difference (~ 2.37 meV/atom) in total energy of $\text{Ca}_2\text{Fe}_{1.75}\text{Al}_{0.25}\text{O}_5$ with Al in both tetrahedral and octahedral coordination allowed us to conclude that both coordination occur with equal probability. From the same calculations, it was also found that for $\text{Ca}_2\text{Fe}_2\text{O}_5$, the magnetic moments of Fe1(4a) and Fe2(4c) are $\pm 3.98 \mu_B$ and $\pm 3.89 \mu_B$, respectively, and that some magnetic moment is induced only on the O ions (of about $0.11 \mu_B$) located in apical positions of FeO_6 and FeO_4 cages. This is different from the doped $\text{Ca}_2\text{Fe}_{1.75}\text{Al}_{0.25}\text{O}_5$ compound, where the equatorial oxygen atoms also exhibit magnetic moments about of $0.12 \mu_B$. Comparing the DFT calculations with the experimental results, which show marginal ferromagnetic properties in Al-doped compounds, we realize that our calculations were performed for ideal static systems, where the atoms are fixed in their crystallographic positions in the base structure without temperature fluctuations, but in fact, there is a larger disorder in the prepared sample, which we are only able to partially take into account in the DFT calculations.

The AC electric conductivity measurements data σ_{ac} showed at low frequencies a characteristic plateau in the dependence of conductivity on frequency for all samples studied, due to the significant contribution of the DC conductivity σ_{dc} . The analysis of these data within the Arrhenius and Jonscher models confirmed that at lower temperatures (below 380 K), the conductivity has a diffusive character, while at higher temperatures, it becomes more hopping. It turned out that for a sample with Al content $x = 0.4$, oxygen ion conduction processes required the lowest activation energy. This behavior was explained by the assumption that the number of free oxygen vacancies increases with the doping level; however, at high doping, the mutual interactions between vacancies lead to the localization and ordered distribution of oxygen holes. The DFT calculation confirmed that even for the undoped $\text{Ca}_2\text{Fe}_2\text{O}_5$ insulator, the hybridization between Fe-3d bands and O-2p orbitals leads to the formation of ligand holes in the surroundings of some O ions.

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