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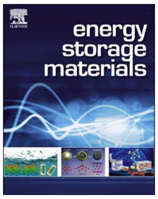

Growth and comparison of single crystals and polycrystalline brownmillerite $Ca_2Fe_2O_5$

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ABSTRACT

Brownmillerite $Ca_2Fe_2O_5$ is a mixed ionic electronic material with interesting electrical properties. In this report, the properties of $Ca_2Fe_2O_5$ single crystals are compared with bulk polycrystalline $Ca_2Fe_2O_5$ samples. Powder X-ray diffraction (PXRD), Scanning electron microscopy, Optical microscopy and Energy dispersive X-ray spectroscopy (EDX) have been performed on the as prepared samples. XPS full survey spectra confirm the presence of constituent elements and reveal the peak binding energy of calcium, iron and oxygen. EDX was also used to trace the distribution of constituent elements. Images of crystal surfaces and interiors by polarized optical microscopy have been presented.

1. Introduction

Perovskite-type ferrite oxide materials with general formula $AFeO_{3-\delta}$ (A=rare or alkaline earth metals) and their derivatives have attracted attention for applications such as ceramic membranes for oxygen separations, electrodes of solid oxide fuel cell (SOFC), catalyst for oxidation of hydrocarbons, removal of gaseous pollutants, dehydrogenation of alkanes, photocatalysis and oxygen sensors. These applications are associated with general requirements such as thermal stability at high temp, reactivity with CO_2 and water vapor, thermal and chemical expansion as well as high oxygen permeability combination of transport properties and thermodynamic stability. One such compound is the Brownmillerite compound $Ca_2Fe_2O_5$ which is an oxygen deficient perovskite with general formula $A_2BB'O_5$ (where A=Alkaline earth metals; B,B′=transition metals/group III elements). The compound has a perovskite derived structure and results from 1/6 order vacancies along [101] direction of unit cell. By introducing ordered vacancies, a stacking sequence of octahedrally coordinated B-site cations alternating with tetrahedrally coordinated B-site cations, along the b-axis is obtained. Brownmillerite $Ca_2Fe_2O_5$ is an antiferromagnetic materials and adopts *Pnma* ($a < c$) and *Pcmn* ($a > c$) space group. It has a Neel temperature of 720 K along with a weak ferromagnetic moment and melting point ~1722 K [1–5]. $Ca_2Fe_2O_5$ is studied for its diverse application and structural features. One of the attractive features of this material is mixed ionic electronic conductivity. Most of the physical property investigation on $Ca_2Fe_2O_5$ has been carried out on polycrystalline form of this compound. It is well known that single crystals are essential to investigate the true property of a compound, motivating us to grow $Ca_2Fe_2O_5$ crystals [6–9] and compare the results with its polycrystalline counterpart. The growth of many oxides by flux method has been hindered by contamination with the crucible material and the high melting temperature. Floating zone (FZ) technique is one of the best suited technique for synthesis of growing high-quality oxide single crystals. Main advantage of this technique is that there is no contamination from a crucible used during growth. Other advantages include, the relatively high-temperature attainable controlled atmosphere and easily separable crystals along with flux-free surfaces. Such conditions allow for more stable and faster crystal growth. Further, the size of as grown crystals by the optical floating zone method is usually more suitable for experimental measurements [10–15]. In the present work crystals of $Ca_2Fe_2O_5$ with well developed morphology, were successfully grown by Optical floating zone method under controlled atmosphere (Oxygen/Air) in order to explore and investigate the structure for physical and chemical properties. These crystals were black, shiny with smooth surface. The crystals have been characterized and compared with those obtained from polycrystalline material.

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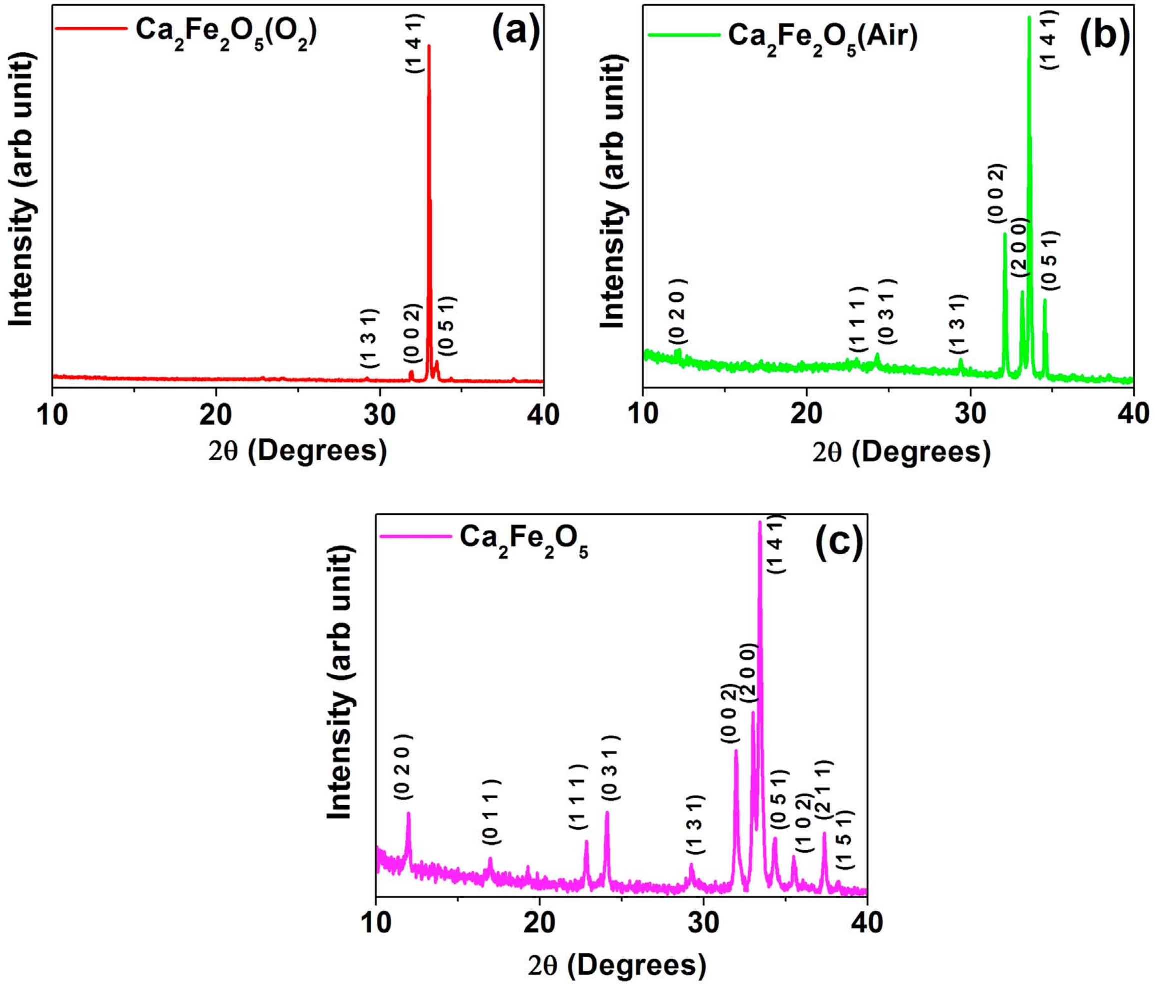

Fig. 1. Powder XRD patterns of the $Ca_2Fe_2O_5$ crystals in different growth atmosphere (a) Oxygen (b) Air (c) Polycrystalline sample.

2. Experiment details

2.1. Synthesis

The Polycrystalline powder of $Ca_2Fe_2O_5$ was prepared by chemical route using nitrates of the metal components. In the course of the synthesis process the respective nitrates were mixed in deionized water on a hot plate with subsequent addition of citric acid and ammonia to adjust pH (6–7). Further Ethylene Glycol (EG) was added to the solution. At last the temperature of hot plate is increased to 200 °C to evaporate water. Thus we obtained a dry mass which is further heated to 1000 °C for 12 h in order to remove all organic residuals and to get the final products.

Single phase bulk polycrystalline powder sample was used further to prepare feed and seed rods for crystal growth. The polycrystalline powder was sealed in a rubber tube and evacuated using vacuum pump. Further, cold isostatic press was utilized to obtain cylindrical rods. These seed rods and feed rods were sintered at high temperature of about 1100 °C. After sintering, these rods were used for crystal growth in an optical floating zone furnace M/S Crystal Systems Corp., Japan (FZ-T-4000-H-VII-VPO-PC- equipped with four 1000 W halogen lamps as heat source). Power supplied for crystal growth was kept at 40–42% and the growth rate was kept at 4 mm/h. The gas flow rate was maintained at 1 bar. The feed rod is rotated in clockwise directions while the seed rod is rotated in anticlockwise direction.

2.2. Characterization

Single crystals $Ca_2Fe_2O_5$ have been successfully grown under a controlled atmosphere of oxygen and air. Both the polycrystalline and single crystal samples were characterized by Powder X-ray diffraction (PXRD- X′Pert Pro) equipped with a Cu Kα X-ray source with a wavelength of 1.5453 Å. Crossectional SEM images were also recorded (Zeiss make) along with elemental mapping of the samples. Quantitative energy-dispersive X-ray absorption spectroscopy (Oxford Instruments Nanoanalysis INCA Energy EDS) was also used to trace the distribution of constituent elements. Raman spectroscopy studies on polycrystalline samples were carried out with the help of Argon ion laser using polarized 514 nm radiation (Instrument – Renishaw InVia) and compared with those of crystals. The macroscopic defects were checked with a Polarized Light Microscope (Zeiss Axio Scope A1) in cross transmission configuration.

3. Results and discussions

X-ray diffraction (XRD) patterns were collected with X′Pert Pro diffractometer, using Cu Kα radiation operating at 40 kV and 30 mA, with a wavelength of 1.545 Å. A small piece of the crystals was grinded into powder and XRD pattern was measured. The powder XRD pattern of single crystals and polycrystalline samples is shown in Fig. 1. No secondary phase was revealed and the diffraction peaks were indexed to that of $Ca_2Fe_2O_5$ (Ref: PDF Number: 96-901-3470) having orthorhombic structure with *Pnma* Space group. In all the three cases we observe the presence of (131) peak, whose broadening gives a measure