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Electrical properties of murataite modules with complex and large-volume fluorite-type superstructures

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ABSTRACT

We have synthesized murataite modules with oxygen-deficient fluorite-type superstructures by a solid-state reaction method and investigated their electrical properties. The multiples of the fluorite-type unit-cell were determined using X-ray diffraction (XRD) and transmission electron microscope-selected area electron diffraction (TEM-SAED). They revealed that well-crystalized $3 \times 3 \times 3$ (M3) and $8 \times 8 \times 8$ (M8) fluorite-type superstructures were successfully synthesized with minor impurities. The calculated lattice constants of the M3 and M8 were 1.4589 and 3.9269 nm, respectively. Based on four-probe D.C. method and two-probe A.C impedance spectroscopy measurement, the electrical conductivity was measured as functions of temperature and oxygen partial pressure. The electrical conductivities of murataite modules increased with elevating temperature, which indicated typical semiconducting behavior. Impedance spectra suggested that either electronic or hole conduction must be superior to the ionic conduction in M3 phase. The M3 phase demonstrated good thermal stability under oxidizing and reducing atmosphere at 573–973 K.

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1. Introduction

The natural murataite, now defined as a derivative of the fluorite-type structure, was discovered by Adams et al. in 1974 [1]. Ercit and Hawthorne [2] solved the crystal structure of natural murataite ($F43m$, a = 14.886 Å, Z = 4), and it was recognized as an anion-deficient $3 \times 3 \times 3$ fluorite-type superstructure (M3) with an ordered arrangement of cations [3]. In 1982, Morgan and Ryerson [4] first identified synthetic murataite in complex radwaste ceramics. The crystal structure of the synthetic murataite is very similar to that of the natural murataite, but with surprisingly different elemental content, less number of cation vacancies and five symmetrically independent cation sites [5,6]. In addition, other murataite modules, $5 \times 5 \times 5$, $7 \times 7 \times 7$ and $8 \times 8 \times 8$ fluorite-type superstructures referred to as M5, M7 and M8, also have been confirmed by transmission electron microscopy (TEM) [7,8]. It is well-known that these superstructures are built up from murataite and pyrochlore structures. The detailed crystal structures of M3 and M5 were reported [9,10].

Murataite ceramics are constituted of various elements including rare-earth and actinide [11,12],which make it difficult to obtain a single murataite phase. Furthermore, depending on the synthesis conditions, the cation occupancy of specific sites and the superstructures easily change. Recently, we have synthesized very complex oxide crystal with an $8 \times 8 \times 8$ fluorite-type superstructure built up from two murataite and one pyrochlore structures [13]. This modular structure contains $8 \times 8 \times 8 = 512$ basic sub-cells, about 5250 atoms and 40 distinct symmetry cation positions [10,14].

In this paper, we focus on the electrical properties of murataite ceramics. Anion-deficient fluorite-related structures, such as yttrium-stabilized zirconia, are well-known for their potential applications, *e.g.* oxygen gas sensors and catalysts [15,16]. In addition to these, the materials with fluorite-type superstructure (*e.g.* pyrochlore) have been investigated for functional materials such as the electrolyte of solid oxide fuel cells [17]. The electrical conductivity of murataite modules, M3 and M8, under various temperatures and atmospheres are first presented to clarify its electrical conductivity and charge carrier because no report ever attempted as a functional ceramics despite its unique crystal structure. Furthermore, we discuss the potential applications of murataite ceramics by taking account of their electrical properties, thermal stability and distinct lattice parameters. Murataite

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structure, M3, and the largest murataite module, M8, were individually obtained by the standard ceramic procedure of co-firing oxides. Unlike conventional procedures, synthesis of murataite samples were carried out without rare-earth elements (REE) and actinide, resulting in a low cost and environmentally friendly processing.

2. Materials and methods

2.1. Sample preparation

Commercial α-Al_2O_3 (99.99% purity, Taimei Chemicals Co. Ltd., Saitama, Japan), TiO_2 anatase (99% purity, Kojundo Chemical Laboratory Co. Ltd.), CaO (99.9% purity, Kojundo Chemical Laboratory Co. Ltd.), MnO_2 (99% purity, Kojundo Chemical Laboratory Co. Ltd.), ZrO_2 (98% purity, Kojundo Chemical Laboratory Co. Ltd.) and α–Fe_2O_3 (99.9% purity, Wako Pure Chemical Industries Ltd.) powders were used as starting materials. The starting powders were mixed by planetary ball-milling with ZrO_2 media for 1.8×10^3 s (acceleration: 4 g). The powder mixtures were sieved through a 150-mesh screen. Cylindrical pellets (diameter of 15 mm) and rectangular specimens ($4 \times 6 \times 50$ mm) were prepared by the uniaxial and the cold isostatic pressing of the mixed oxides at 200 MPa for 6.0×10^2 s. The green compacts were then sintered at 1573 K for 1.8×10^3 s (Sample A) and 2.16×10^4 s (Samples B and C) in air in an alumina crucible coated with Pt foil. The compositions and synthesis conditions of murataite samples in the Al_2O_3-CaO-TiO_2-MnO_2-Fe_2O_3-ZrO_2 system are shown in Table 1.

2.2. Microstructural characterizations

TEM-SAED patterns of the crushed samples were observed by aberration-corrected transmission electron microscopy (JEOL, JEM-2200FS, operated at 200 kV), in order to discover the superstructure of these particular murataites.

The phases in the pulverized samples were analyzed by XRD (Rigaku, Multiflex, counter diffractometer with graphite-monochromatized Cu-$K_{\alpha1\alpha2}$ radiation, operated at 40 kV and 40 mA), using a reflection-free single-crystal silicon stage. A step scan (step: 0.01°) was done in a range of $2\theta = 2$–10° with judicious masking of the incident beam and background forward scatter. A normal scan (*viz.* without masking) was done in a range of $2\theta = 10$–150° with the background removed. $K_{\alpha2}$ lines were removed by the Rachinger algorithm. The lattice constant, *a*, of the murataite superstructure was calculated using a Nelson–Riley extrapolation. The ICDD-JCPDS database was used for identifying non-murataite phases. Indexing for peaks of murataite phases were carried out from the superstructures observed by TEM-SAED pattern. The atomic composition on the polished section of the bulk samples were measured by scanning electron microscopy (Hitachi TM3000, operated at 15 kV) equipped with energy dispersive X-ray spectrometry (SEM–EDS).

Table 1
Compositions of murataite samples (in mol.%).

	Samples		
	A	B	C
α-Al_2O_3	8.8	8.7	5.8
CaO	14.0	15.1	16.0
TiO_2	41.9	41.4	43.9
MnO_2	9.3	9.0	7.6
α-Fe_2O_3	14.9	12.6	10.0
ZrO_2	11.2	13.2	16.7

2.3. Electrical conductivity measurement

For the electrical conductivity measurements, the surface of the samples were polished by waterproof abrasive paper to enhance electrode adhesion. Platinum paste electrodes was attached to the surfaces of sintered samples and then heated up to 1473 K. The electrical conductivity measurement was carried out in air using conventional four-probe D.C. method (34410A, Agilent, Japan). The rectangular sample was positioned in the center of a tubular furnace. The measurement temperature range was from 573 to 1273 K monitored with a K-type thermocouple placed at the vicinity to the sample. Prior to the measurement, the temperature was kept at the target temperature for 1.2×10^3 s to stabilize the sample temperature. In order to confirm the long-term stability, the electrical conductivity was continuously measured every 10 s at 1073 K. Before and after 3.6×10^5 s aging, the coefficient of thermal expansion (CTE) was measured twice under atmospheric pressure in air by thermomechanical analysis (Thermoplus EVO II, Rigaku, Japan) to determine the influence of microcracks induced by minor impurity phase (pseudobrookite). These microcracks strongly affect the electrical conductivity and thermal expansion coefficient of specimen [18].

Oxygen partial pressure (P_{O_2}) dependence of the electrical conductivity was measured at 573–973 K by combination of the frequency response analyzer (1255, SolarTron, UK) and the potentio/galvanostat (1287, SolarTron, UK) over the frequency ranging from 1 MHz to 0.1 Hz under flowing O_2, air, Ar, and Ar-H_2 gas mixture under fixed water vapor pressure. Water vapor pressure was controlled by the following step: the sample gas was mixed with water vapor above 313 K, and then the mixed gas was flowing through the Liebig condenser line at 293 K; the water vapor pressure is 0.02 atm ($\log P_{H_2O} = -1.63$).

The oxygen partial pressure of the outlet gas was measured using the zirconia oxygen sensor set at downstream of the conductivity measurement cell. Temperature of the oxygen sensor was fixed at about 1173 K. In the case of O_2, air, and Ar containing water vapor gaseous, P_{O_2} measured at the oxygen sensor is the same with the P_{O_2} at the vicinity of the sample because no chemical reaction among the gas species were made. On the other hand, the P_{O_2} measured using the sensor is different from the P_{O_2} at the vicinity of the sample when the sample temperature is different from the sensor temperature using Ar + H_2 + H_2O gas mixture due to the chemical equilibrium among H_2, H_2O, and O_2. Hence, the P_{O_2} at the vicinity of the sample under Ar + H_2 + H_2O gas mixture was calculated based on the chemical thermodynamics as following procedures.

The P_{O_2} at the vicinity of the sample was calculated from the thermodynamic data using the following equation:

$$K = \frac{(P_{H_2O})^2}{(P_{H_2})^2 \cdot (P_{O_2})}$$

$$\left(\frac{P_{H_2O}}{P_{H_2}}\right)^2 = K_{sensor} \cdot P_{O_2}(\text{sensor})$$

and

$$P_{O_2}(\text{sample}) = \frac{1}{K_{sample}} \cdot \left(\frac{P_{H_2O}}{P_{H_2}}\right)^2$$

by monitoring the temperature close to the sample and oxygen sensor. The specimen for the two-probe A.C. impedance measurement was prepared by attaching the platinum paste electrode to both sides of the cylindrical pellet. In order to calculate the

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