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Structures and electrical conductivity of $CaNdFeO_4$ ceramics

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Abstract $CaNdFeO_4$ ceramics were prepared using a solid-state process, and their crystal structure was identified by Rietveld method, while the electrical conductivity was evaluated as a function of sintering and testing temperatures. $CaNdFeO_4$ ceramics had an orthorhombic K_2NiF_4 structure, and a secondary perovskite phase $(Ca,Nd)FeO_{3\pm\delta}$ was observed in the samples. The DC electrical conductivity of $CaNdFeO_4$ ceramics increased firstly to a maximum value, 0.065 Scm^{-1}, and then decreased with increasing sintering temperature. The relationship between electrical conductivity of $CaNdFeO_4$ ceramics and testing temperature obeyed the Arrhenius law.

Keywords $CaNdFeO_4$ · K_2NiF_4 structure · Rietveld method · Electrical conductivity · Arrhenius law

1 Introduction

Many compounds with the K_2NiF_4-type structure have attracted much attention from the discovery of the high temperature superconductivity in $La_{1.85}Ba_{0.15}CuO_4$ ceramics [1]. The structure can be described as NiF_6 octahedra interleaved with the rocksalt KF layers along the c-direction. The space group of ideal K_2NiF_4 structure is I4/mmm, and it will be translated to orthorhombic Bmab through the distortion of NiF_6 octahedra, which is originated from the two-dimensional lattice mismatch between two intergrowth layers [2].

Among the K_2NiF_4-type $ARMO_4$ ceramics (A = Sr, Ca; R = rare earth; M = Ni, Mn, Fe, Co, Cr), $CaNdMO_4$ ceramics have been relatively less investigated [2–5]. The space group of $CaNdCoO_4$ is I4/mmm, while it is Bmab for $CaNdCrO_4$ and $CaNdFeO_4$. Although Oyama et al. have reported the crystal structure and spin orientation of $CaNdFeO_4$, the electrical properties of the ceramics have not been investigated.

In the present paper, $CaNdFeO_4$ ceramics were prepared, and the crystal structure and electrical conductivity were characterized.

2 Experimental procedure

Reagent-grade $CaCO_3$ (99%), Nd_2O_3 (99%) and Fe_2O_3 (99%) in a 2:1:1 molar ratio were mixed by ball milling in deionized water using zirconia balls for 24 h. The slurry was dried and then calcined at 1100°C in air for 3 h to prepare $CaNdFeO_4$ powders. The calcined powders, with 8 wt% PVA (polyvinyl alcohol) added, were pressed into disc compacts of 12 mm in diameter and around 5 mm in height, and these compacts were sintered at temperatures from1225°C to 1325°C in air for 3 h.

The phase constitution of the composite ceramics was characterized by powder X-ray diffraction (XRD, RIGAKU D/max 2550 PC, Rigaku Co., Tokyo, Japan) analysis using Cu$K\alpha$ radiation. XRD data for Rietveld refinement were collected on the sample sintered at 1325°C in air for 3 h, and the intensity data were collected over a range 8–130° with a step interval of 0.02° and a counting time of 5 s per step. The Rietveld refinement was performed using the

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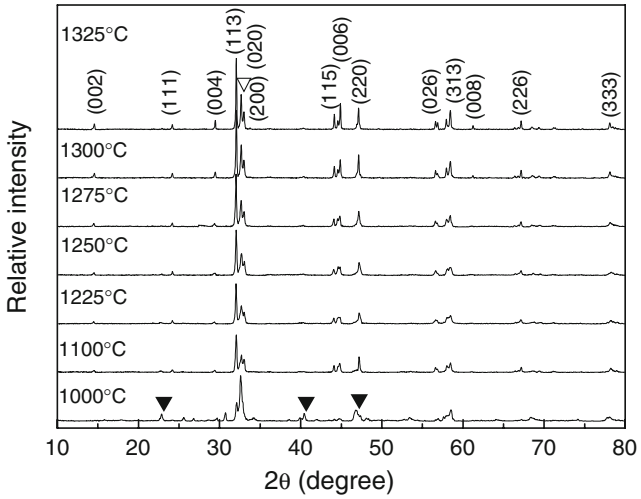

Fig. 1 XRD patterns for $CaNdFeO_4$ calcined at 1000°C, 1100°C and ceramics sintered at different temperatures (*inverted shaded triangle*, perovskite; *inverted open triangle*, Bragg reflection of two phases)

FULLPROF program [6], and a pseudo-Voigt profile function with preferred orientation was used.

The DC conductivity was measured by a digital multimeter (Agilent 34401A) from room temperature to 550°C with an interval of 50°C.

3 Results and discussion

$CaNdFeO_4$ with K_2NiF_4 structure can not be obtained when the calcining temperature is lower than 1100°C, and the dominated phase is perovskite (Ca,Nd)$FeO_{3\pm\delta}$ phase as shown in Fig. 1. There is also minor perovskite (Ca, Nd)$FeO_{3\pm\delta}$ phase indicated as inverted open triangle in Fig. 1 even when the calcining temperature reaches 1100°C. Dense $CaNdFeO_4$ ceramics with minor secondary phase can be obtained by sintering at 1225–1325°C in air for 3 h.

The Rietveld refinement results of $CaNdFeO_4$ ceramics sintered at 1325°C in air for 3 h are shown in Fig. 2 and Table 1. A (Ca,Nd)$FeO_{3\pm\delta}$ perovskite secondary phase is present in the sample. The results show that $CaNdFeO_4$ has orthorhombic K_2NiF_4 structure (Bmab), with lattice parameters of a=5.4115(1) Å, b=5.4713(1) Å, and c=12.0820(2) Å. The orthorhombic distortion can be evaluated through the orthorhombic strain parameter S_o [2], and $CaNdFeO_4$ ceramics (S_o=1.098(9)×10^{-2}) have a larger orthorhombic distortion than $CaNdCrO_4$ ceramics. This structure should be originated from the ideal tetragonal K_2NiF_4 structure via the FeO_6 octahedra titling at the same angle clockwise and counterclockwise alternatively in [010] direction. The tilting can be quantified by α_1 and α_2 angles, where α_1 is formed by the equatorial plane of the octahedron and the basal plane *ab* of the unit cell, and α_2 is defined by the Fe–O axial bond of the octahedron and the *c*-axis of the unit cell [2]. The values of α_1 and α_2 are 6.62 and 7.58° (see Table 2), respectively, which are larger than those of $CaNdCrO_4$, and this is consistent with the result of orthorhombic strain parameter S_o. The neodymium and calcium atoms are nine-fold coordinated polyhedron, and the polyhedron is strongly distorted with six different distances (see Table 2). While there are only two different distances of Fe–O bond, and this shows that the FeO_6 octahedra are tetragonally distortion with a d_{Fe-Oa}/d_{Fe-Oe}=1.098.

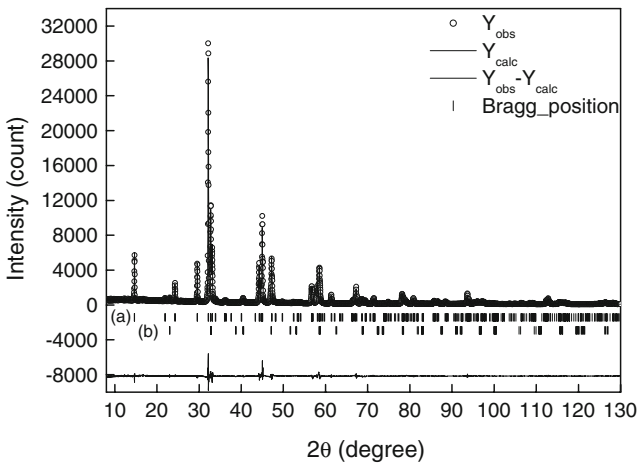

Fig. 2 X-ray powder diffraction patterns obtained at room temperature (*circles*) and calculated (*solid line*) of $CaNdFeO_4$ ceramics. *Vertical marks* show the position of allowed structural Bragg reflections for (*a*) $CaNdFeO_4$ and (*b*) (Ca,Nd)$FeO_{3\pm\delta}$ ceramics. A difference curve is plotted at the bottom of the pattern

Table 1 Experimental parameters for X-ray powder diffraction of $CaNdFeO_4$ ceramics.

Parameters	Values
Unit cell (space group Bmab, 64)	a=5.4115 (1) Å
	b=5.4713 (1) Å
	c=12.0820 (2) Å
Volume	357.72 (1) $Å^3$
Minimum 2θ	8
Maximum 2θ	130
Total refined variables	40
Number of reflections	173
Profile function	Pseudo-Voigt, 0.13(2)
Gaussian U, V, W	0.002(2), 0.021(2), 0.068(4)
Asymmetry corrections (P1, P2)	−0.009(7), 0.036(2)
Preferred orientation (modified March)	[001] direction, 0.735(1)
R_p (profile)	0.0602
R_{wp} (weighted profile)	0.0776
R_B (Bragg)	0.0435
R_F	0.0470
Reduced χ^2	2.55

Table 2 Refined structural parameters from X-ray powder diffraction data for the $CaNdFeO_4$ ceramics.

Atom	Site	x	y	z	B_{iso} (Å^2)	Occupancy
Fe	4a	0.0	0.0	0.0	1.93(6)	1.0
Ca/Nd	8f	0.0	0.0124(3)	0.35682(4)	1.56(2)	0.493/0.507
O1	8e	0.25	0.25	0.0131(5)	0.9(1)	1.0
O2	8f	0.0	0.955(2)	0.1742(4)	2.6(1)	1.0
4×Fe–O1=1.9303(5) Å				2×Ca/Nd–O1=2.523(4) Å		
2×Fe–O2=2.1189(5) Å				2×Ca/Nd–O1=2.662(4) Å		
				1×Ca/Nd–O2=2.229(5) Å		
α_1=6.62(1)°				1×Ca/Nd–O2=2.450(9) Å		
α_2=7.58(3)°				1×Ca/Nd–O2=3.073(9) Å		
				2×Ca/Nd–O2=2.7373(9) Å		

The DC electrical conductivity of $CaNdFeO_4$ ceramics at room temperature is shown in Table 3. The conductivity increases firstly and then decreases with increasing sintering temperature. The maximum value of conductivity reaches 0.065 Scm^{-1} for the ceramics sintered at 1250°C for 3 h, and this value is larger than that of $SrNdFeO_4$ [7] and $CaNdCoO_4$ [8] ceramics. The electrical conductivity of $CaNdFeO_4$ ceramics should be affected by three different factors: the relative density, the content of oxygen vacancy and secondary phase. The relative densities of $CaNdFeO_4$ ceramics increase to a maximum value then decrease with increasing sintering temperature (see Table 3), so the variation of electrical conductivities should obey the same law as that of relative density. During cooling after sintering, re-oxidation will occur to compensate oxygen vacancies generated during soaking, and the concentration of oxygen vacancy is in proportion to the grain size since the re-oxidation process will be more difficult to penetrate the coarse grains. The grain sizes of $CaNdFeO_4$ ceramics should increase with increasing sintering temperature, and this will lead to the increased content of oxygen vacancies and in turn the electrical conductivities of ceramics. The contents of $(Ca,Nd)FeO_{3\pm\delta}$ secondary phase increase with the sintering temperature (see Fig. 1), and the electrical conductivity should decrease for $(Ca,Nd)FeO_{3\pm\delta}$ phase is an antiferromagnetic insulator [9]. The variation of electrical conductivity of $CaNdFeO_4$ ceramics should be the combined effects of above three factors. Figure 3 shows the relationship between the logarithm of the electrical conductivity of $CaNdFeO_4$ ceramics sintered under different conditions and the reciprocal of testing temperature. The logσ−1000/T curves of all samples are almost linear below 550°C and it obeyed the Arrhenius law. These results indicate that the $CaNdFeO_4$ ceramics is capable of a semiconductive behavior. The activation energy E_a and the pre-factors σ_0 calculated from the linear portion of logσ−1000/T curves are shown in Table 3. The E_a values of $CaNdFeO_4$ ceramics are in the range from 0.038 to 0.057 eV, which are one magnitude lower than those of $CaNdCoO_4$ ceramics.

Table 3 Relative densities, DC conductivities at room temperature and parameters of Arrhenius model for $CaNdFeO_4$ ceramics.

Sintering temperature	Relative density (%)	Conductivity (Scm^{-1})	Ea (eV)	σ_0 (Scm^{-1})
1225°C	91.7	0.058	0.057	0.275
1250°C	93.6	0.065	0.038	0.344
1275°C	94.5	0.049	0.049	0.279
1300°C	93.5	0.025	0.050	0.236
1325°C	93.3	0.030	0.040	0.286

4 Conclusions

$CaNdFeO_4$ ceramics with a $(Ca,Nd)FeO_{3\pm\delta}$ perovskite secondary phase had been obtained using a solid-state process. $CaNdFeO_4$ ceramics had an orthorhombic K_2NiF_4

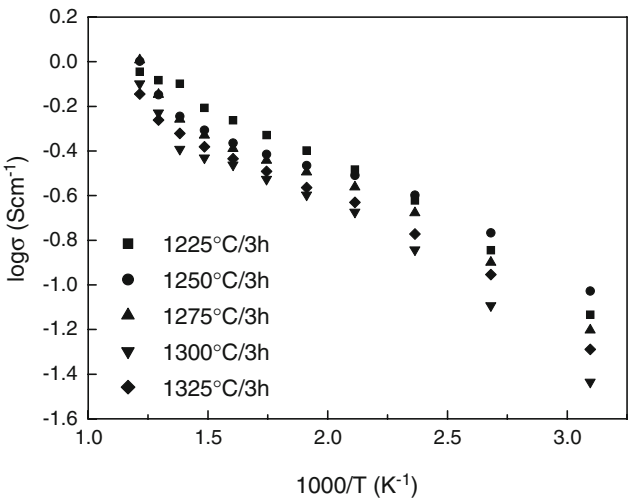

Fig. 3 Relationship between the logarithm of the electrical conductivity of $CaNdFeO_4$ ceramics sintered under different conditions and the reciprocal of testing temperature

structure which was deduced from the ideal tetragonal phase by the FeO_6 octahedra tilt. The DC electrical conductivity of $CaNdFeO_4$ ceramics increased firstly to a maximum value, 0.065 Scm^{-1}, and then decreased with increasing sintering temperature, which should be contributed from the combined effects of the relative density, the content of oxygen vacancy and secondary phase. The relationship between the electrical conductivity and testing temperature obeyed the Arrhenius law, and the activation energies were very low.

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