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Ionic Conductivity in the Lu_2O_3–TiO_2 System

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Abstract—Nanocrystalline Lu_2O_3–TiO_2 (33.3–44 mol % Lu_2O_3) materials with a partially disordered pyrochlore structure, prepared via heat treatment in the range 1400–1750°C, are found to possess high oxygen ionic conductivity. Their 740°C conductivity is 10^{-3} to 10^{-2} S/cm, depending on the heat-treatment temperature and composition, which is comparable to that of the well-known fluorite solid electrolyte ZrO_2–9 mol % Y_2O_3.

INTRODUCTION

Many anion-conducting solid electrolytes have a cubic fluorite structure, in which fluoride or oxide ions migrate with relative ease. Oxygen ionic transport through vacancies is particularly effective in zirconia, ceria, and thoria stabilized with impurities and also in δ-Bi_2O_3 [1, 2].

Recently, $Gd_2(Zr_xTi_{1-x})_2O_7$ and $Y_2(Zr_xTi_{1-x})_2O_7$ pyrochlores with $x \geq 0.4$ have been reported to possess high ionic conductivity [3, 4]. As shown by Masasi Mori *et al.* [5], undoped $Gd_2Ti_2O_7$ is an ionic conductor, but its conductivity, $\kappa = 1.8 \times 10^{-4}$ S/cm, is too low for solid oxide fuel cell (SOFC) applications.

$Lu_2Ti_2O_7$ was found to undergo low-temperature (~800°C) and high-temperature (~1700°C) phase transitions accompanied by changes in structural order [6, 7]. It is disordering processes that are responsible for the marked (by two orders of magnitude) increase in the conductivity of $Lu_2Ti_2O_7$ upon an increase in synthesis temperature from 1400 to 1650°C. The 740°C conductivity of $Lu_2Ti_2O_7$ ceramics prepared by sintering at 1650°C is 10^{-2} S/cm [6, 8]. It seems likely that the electrical transport in this material is dominated by oxygen ionic conduction, just as in the earlier studied systems $Gd_2(Zr_xTi_{1-x})_2O_7$ and $Y_2(Zr_xTi_{1-x})_2O_7$.

Although the Lu_2O_3–TiO_2 phase diagram has not yet been studied in sufficient detail, it is reasonable to expect, by analogy with the Yb_2O_3–TiO_2 system [9], that $Lu_2Ti_2O_7$ has a broad homogeneity range (33.3 to 50 mol % Lu_2O_3). Therefore, conductivity measurements on solid solutions in this system may reveal new oxygen-ion conductors.

In this paper, we report the high-temperature (1400–1750°C) synthesis, microstructure, and electrical properties of $Lu_{2+x}Ti_{2-x}O_{7-x/2}$ materials with compositions (x = 0–0.94) near the pyrochlore–fluorite phase boundary.

EXPERIMENTAL

Lu(III) and Ti(IV) hydroxides (Lu : Ti atomic ratio of 1 : 1) were coprecipitated by adding solutions of Ti and Lu chlorides to aqueous ammonia at pH 11. The precipitate was washed several times with hot water to remove chloride ions and then separated from the wash water by centrifugation. Next, the precipitate was freeze-dried for 48 h at 5 Pa between –30 and 30°C.

We prepared Lu_2O_3–TiO_2 powders with the following compositions: $Lu_2Ti_2O_7$ (33.3 mol % Lu_2O_3), $Lu_{2.072}Ti_{1.928}O_{6.964}$ (34.5 mol % Lu_2O_3), $Lu_{2.132}Ti_{1.868}O_{6.934}$ (35.5 mol % Lu_2O_3), $Lu_{2.4}Ti_{1.6}O_{6.8}$ (40 mol % Lu_2O_3), $Lu_{2.643}Ti_{1.357}O_{6.68}$ (44 mol % Lu_2O_3), and $Lu_{2.94}Ti_{1.06}O_{6.53}$ (49 mol % Lu_2O_3). After prefiring at 740°C for 2 h, the powders were pressed at 10 MPa into pellets 10 mm in diameter, which were then sintered in the range 1400–1750°C.

The resultant ceramics were characterized by x-ray diffraction (XRD) on a DRON-3M diffractometer (CuK_α radiation, $2\theta = 15°$–$45°$). Microstructures were examined by scanning electron microscopy. The defect structure of the samples was inferred from Rietveld analysis data for powders prepared by grinding ceramic pellets (DRON-3M diffractometer, CuK_α radiation, $2\theta = 10°$–$80°$, step size of 0.05°, counting time of

3 s/step). In structure refinement, we used Fullprof software [10].

In two-probe conductivity measurements (air, 300–950°C), we used samples in the form of disks (low conductivity) or cylinders sandwiched between electrodes (high conductivity). Low-resistance electrodes blocking ionic transport were made by firing Pt paste. Electronic conductivity was determined by dc measurements. Total conductivity was measured at frequencies from 1 kHz to 1 MHz using a computer-based automatic system, which incorporated R5083, E7-12, and Tesla BM 431 E ac bridges.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of Lu_2O_3–TiO_2 samples (33.3–49 mol % Lu_2O_3) synthesized at 1600°C. The presence of superlattice reflections (with respect to the fluorite structure) points to a doubling of the cubic-cell parameters, characteristic of the pyrochlore structure. With increasing Lu_2O_3 content, the intensity of the pyrochlore superlattice reflections (111, 311, 331, and others) decreases. Starting above 49 mol % Lu_2O_3, only diffraction peaks from the fluorite phase are present.

The systematic increase in lattice parameter with Lu_2O_3 content attests to the formation of $Lu_2Ti_2O_7$-based pyrochlore-like solid solutions up to 44 mol % Lu_2O_3 (Fig. 2). The lattice parameter of $Lu_{2.94}Ti_{1.06}O_{6.53}$ (49 mol % Lu_2O_3) is not indicated in Fig. 2 because this solid solution has the fluorite structure, with a factor of 2 smaller lattice parameter: $a = 5.063$ Å.

The data in Figs. 1 and 2 provide clear evidence for the existence of $Lu_{2+x}Ti_{2-x}O_{7-x/2}$ pyrochlore-like solid solutions in the composition range $0 < x \le 0.643$ (33.3–44 mol % Lu_2O_3). Characteristically, the intensity of the pyrochlore reflections decreases with increasing Lu_2O_3 content.

Microstructural examination showed that, in the sample prepared by firing for 2 h at 740°C and 4 h at 1600°C and containing 34.5 mol % Lu_2O_3, the average grain size was about 40 nm (Fig. 3a). The same grain size was found in the sample of the same composition sintered at a 100°C lower temperature (2 h at 740°C + 4 h at 1500°C) (Fig. 3b). In earlier studies [7, 8], the grain size of an analogous material prepared by firing for 2 h at 740°C and 10 h at 950°C was 15–20 nm. Thus, increasing the sintering temperature from 950 to 1600°C causes a relatively small increase in grain size, by about a factor of 2. The small grain size (20–40 nm) is responsible for the considerable broadening of the XRD peaks from the samples studied (Fig. 1).

With increasing Lu_2O_3 content, the relative density of the $Lu_{2+x}Ti_{2-x}O_{7-x/2}$ (x = 0–0.643) samples decreases from 94 to 84%.

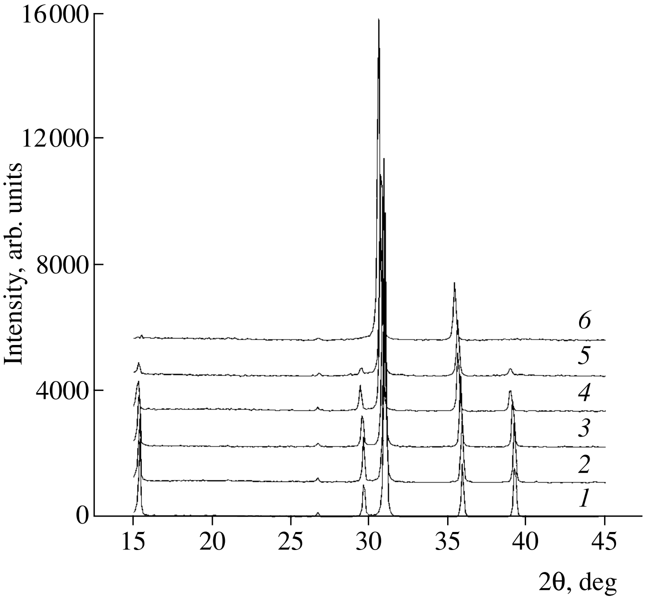

Fig. 1. XRD patterns of Lu_2O_3–TiO_2 samples containing (*1*) 33.3, (*2*) 34.5, (*3*) 35.5, (*4*) 40, (*5*) 44, and (*6*) 49 mol % Lu_2O_3; synthesis at 1600°C, 4 h.

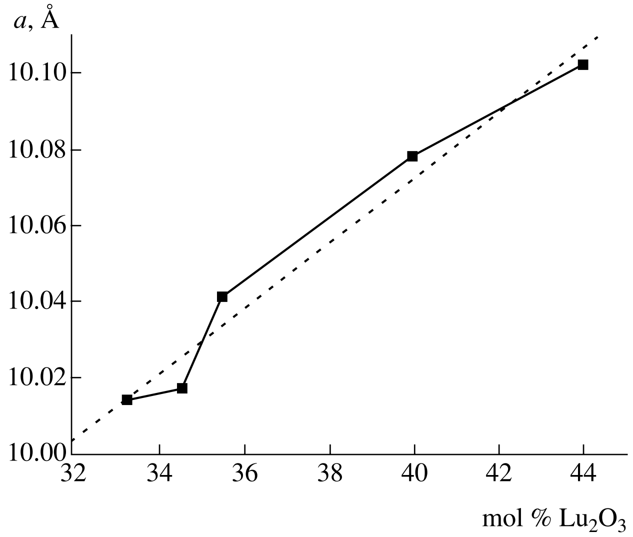

Fig. 2. Composition dependence of the lattice parameter for Lu_2O_3–TiO_2 samples (33–44 mol % Lu_2O_3).

To separately evaluate the electronic and ionic components of conductivity in the $Lu_{2+x}Ti_{2-x}O_{7-x/2}$ (x = 0–0.4) samples prepared in the range 1400–1750°C, we carried out ac (total conductivity) and dc (blocking electrodes) measurements. The ionic conductivity was determined as the difference between the total conductivity and ionic component.

Figure 4 shows the Arrhenius plots of conductivity for $Lu_{2.132}Ti_{1.868}O_{6.934}$ (x = 0.132, 35.5 mol % Lu_2O_3), and $Lu_2Ti_2O_7$ (x = 0, 33.3 mol % Lu_2O_3) sintered at 1600°C and for $Lu_{2.4}Ti_{1.6}O_{6.8}$ (x = 0.4, 40 mol % Lu_2O_3) sintered at 1750°C. In the range 20–900°C, the electronic conductivity of $Lu_{2.132}Ti_{1.868}O_{6.934}$ (x = 0.132, sin-

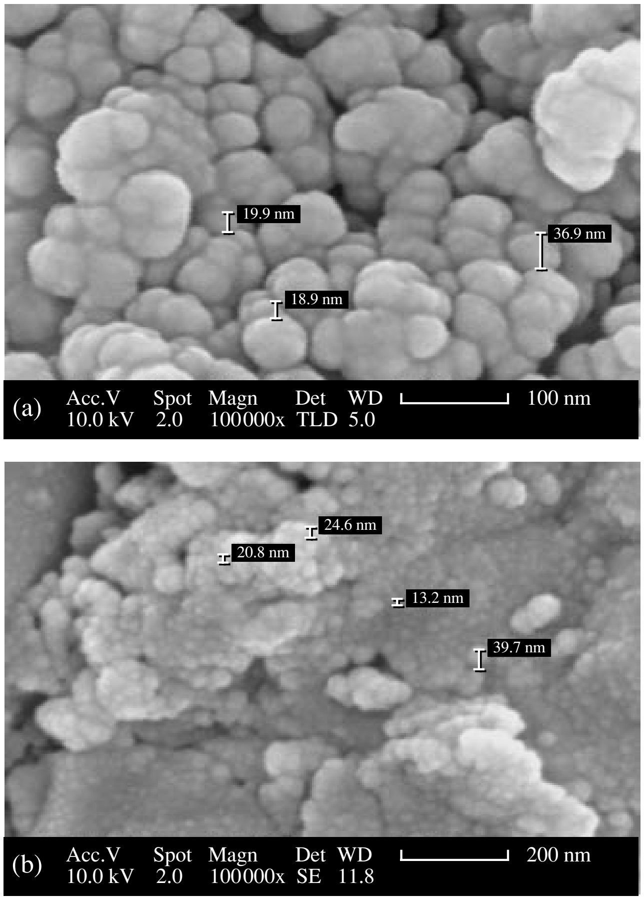

Fig. 3. Microstructures of $Lu_{2.072}Ti_{1.928}O_{6.964}$ (34.5 mol % Lu_2O_3) ceramics prepared by sintering for 4 h at (a) 1600 and (b) 1500°C.

tering at 1600°C) and $Lu_{2.4}Ti_{1.6}O_{6.8}$ ($x = 0.4$, sintering at 1750°C) is insignificant: at 740°C, no more than 1–3% of the total conductivity. Above 300°C, the conductivity of these samples is a weak function of frequency in the range 1–1000 kHz and exhibits Arrhenius behavior, with activation energies for conduction of 0.89 (Fig. 4a) and 0.99 eV (Fig. 4b), typical of oxygen-ion conductors. The 740°C ionic conductivity is $\sim 10^{-3}$ S/cm. The electronic conductivity of $Lu_2Ti_2O_7$ prepared at 1600°C almost coincides with its total conductivity at 900°C and is 10^{-5} S/cm at 740°C (Fig. 4c). Thus, $Lu_2Ti_2O_7$ is a *p*-type electronic conductor, just as $Ln_2Ti_2O_7$ with Ln = Sm, Ho, and Er [11].

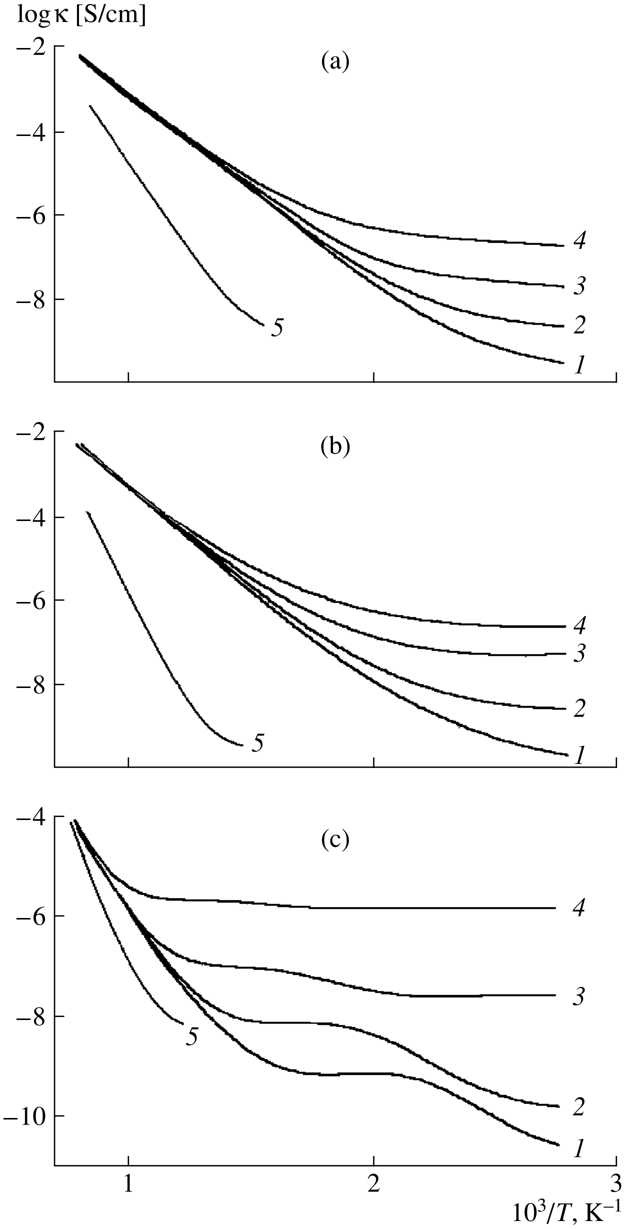

Fig. 4. Arrhenius plots of (*1–4*) ac (1, 10, 100, and 1000 kHz, respectively) and (*5*) dc conductivity for $Lu_{2+x}Ti_{2-x}O_{7-x/2}$: (a) $Lu_{2.132}Ti_{1.868}O_{6.934}$ (35.5 mol % Lu_2O_3), 2 h at 740°C + 4 h at 1600°C; (b) $Lu_{2.4}Ti_{1.6}O_{6.8}$ (40 mol % Lu_2O_3), 2 h at 740°C + 4 h at 1750°C; (c) $Lu_2Ti_2O_7$ (33.3 mol % Lu_2O_3), 2 h at 740°C + 4 h at 1600°C.

The total conductivity data for $Lu_{2+x}Ti_{2-x}O_{7-x/2}$ ($x = 0$–0.94) sintered at 1600°C (Fig. 5) demonstrate that a deviation from the stoichiometric composition $Lu_2Ti_2O_7$ (33.3 mol % Lu_2O_3) by as little as 1.2 mol % Lu_2O_3 ($Lu_{2.072}Ti_{1.928}O_{6.964}$, $x = 0.072$, 34.5 mol % Lu_2O_3) sharply increases conductivity. The stoichiometric material $Lu_2Ti_2O_7$ ($x = 0$, 33.3 mol % Lu_2O_3) is an electronic conductor with $\kappa = 9 \times 10^{-5}$ S/cm at 740°C (~1000 K) (Fig. 4c). $Lu_{2.072}Ti_{1.928}O_{6.964}$ ($x = 0.072$, 34.5 mol % Lu_2O_3) is an ionic conductor with $\kappa = 1.5 \times 10^{-3}$ S/cm. The conductivity of $Lu_{2.132}Ti_{1.868}O_{6.934}$ ($x = 0.132$, 35.5 mol % Lu_2O_3) attains 2.5×10^{-3} S/cm. As shown earlier, this material is a purely ionic conductor (Fig. 4a). The same refers to $Lu_{2.4}Ti_{1.6}O_{6.68}$. Further increase in the Lu_2O_3 content of $Lu_{2+x}Ti_{2-x}O_{7-x/2}$ ($x = 0.643$–0.94, 44–49 mol % Lu_2O_3) is accompanied by a gradual reduction in ionic conductivity.

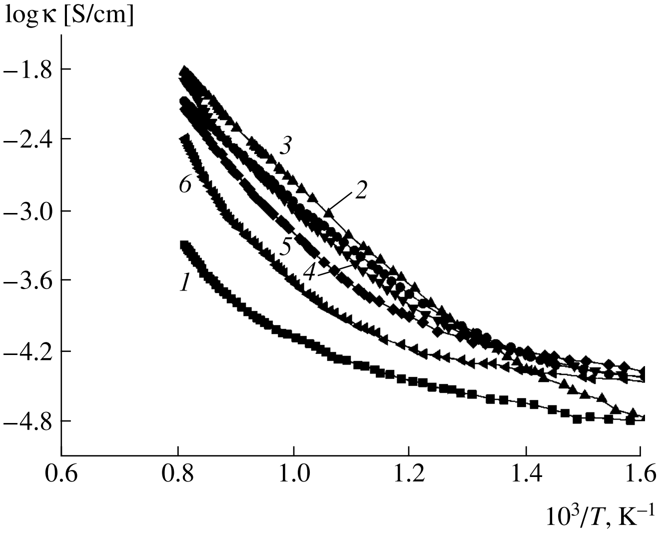

Fig. 5. Arrhenius plots of 1-MHz conductivity for Lu_2O_3–TiO_2 samples sintered at 1600°C for 4 h: (*1*) 33.3, (*2*) 34.5, (*3*) 35.5, (*4*) 40, (*5*) 44, and (*6*) 49 mol % Lu_2O_3.

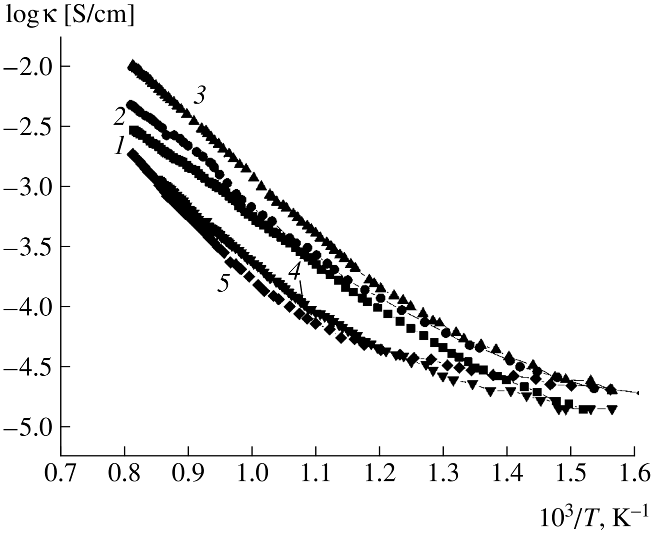

Fig. 6. Arrhenius plots of 1-MHz conductivity for Lu_2O_3–TiO_2 samples sintered at 1500°C for 4 h: (*1*) 34.5, (*2*) 35.5, (*3*) 40, (*4*) 44, and (*5*) 49 mol % Lu_2O_3.

The $Lu_{2+x}Ti_{2-x}O_{7-x/2}$ (x = 0.072–0.4, 34.5–40 mol % Lu_2O_3) samples sintered at 1500°C for 4 h also possess high ionic conductivity, ~10^{-3} S/cm at 740°C (Fig. 6).

The conductivity of $Lu_{2.132}Ti_{1.868}O_{6.934}$ (x = 0.132, 35.5 mol % Lu_2O_3) (Fig. 7a) and $Lu_{2.4}Ti_{1.6}O_{6.8}$ (x = 0.4, 40 mol % Lu_2O_3) (Fig. 7b) sintered at 1400°C for 4 h is dominated by the ionic component, with an electronic contribution of up to 10%. Thus, the conductivity of these materials has a significant electronic component, in contrast to that of the ceramics prepared at 1600 and 1750°C (Figs. 4a, 4b). These results suggest that 1400°C is the lower boundary of high ionic conductivity at the compositions in question.

The conductivity data for Lu_2O_3–TiO_2 (33.3–40 mol % Lu_2O_3) ceramics prepared at different temperatures demonstrate that the highest ionic conductivity (~10^{-2} S/cm at 740°C) is offered by the stoichiometric material $Lu_2Ti_2O_7$ sintered at 1650°C (near its melting point) (Fig. 8). The conductivity of $Lu_2Ti_2O_7$ sintered at 1600°C is two orders of magnitude lower. Thus, increasing the synthesis temperature from 1600 to 1650°C increases the conductivity of $Lu_2Ti_2O_7$ by two orders of magnitude, owing to the development of ionic conduction.

Lu_2O_3–TiO_2 samples containing 33.3, 34.5, 35.5, and 40 mol % Lu_2O_3 were heat-treated at 1750°C for 1 h. During heat treatment, the first three samples were observed to melt. The conductivity of $Lu_{2.4}Ti_{1.6}O_{6.8}$ (40 mol % Lu_2O_3) sintered at 1600°C (4 h) and 1750°C (1 h) is independent of the firing temperature and is 1.5×10^{-3} S/cm at 740°C (Fig. 8). It follows from Fig. 7b that the ionic conductivity of $Lu_{2.4}Ti_{1.6}O_{6.8}$

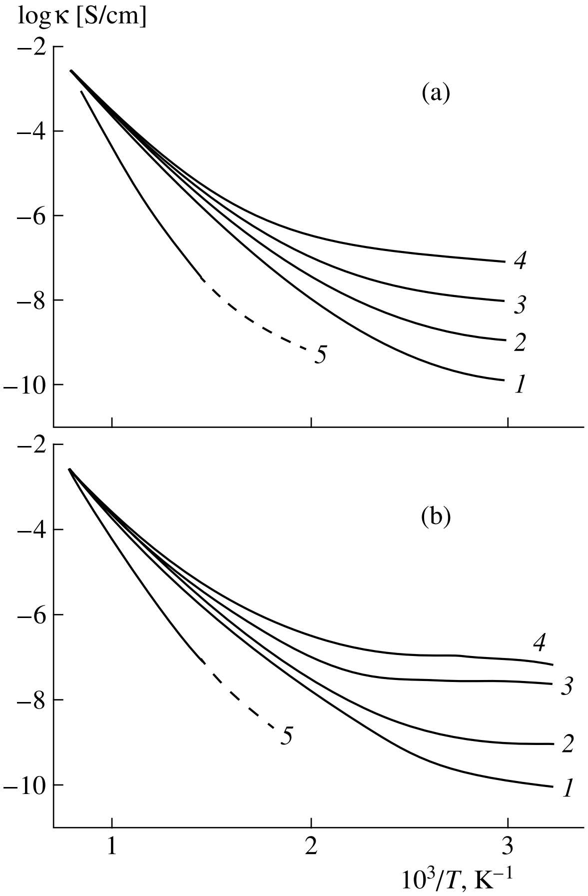

Fig. 7. Arrhenius plots of (*1–4*) ac (1, 10, 100, and 1000 kHz, respectively) and (*5*) dc conductivity for (a) $Lu_{2.132}Ti_{1.868}O_{6.934}$ (35.5 mol % Lu_2O_3) sintered for 2 h at 740°C + 4 h at 1400°C and (b) $Lu_{2.4}Ti_{1.6}O_{6.8}$ (40 mol % Lu_2O_3) sintered for 2 h at 740°C + 4 h at 1400°C.

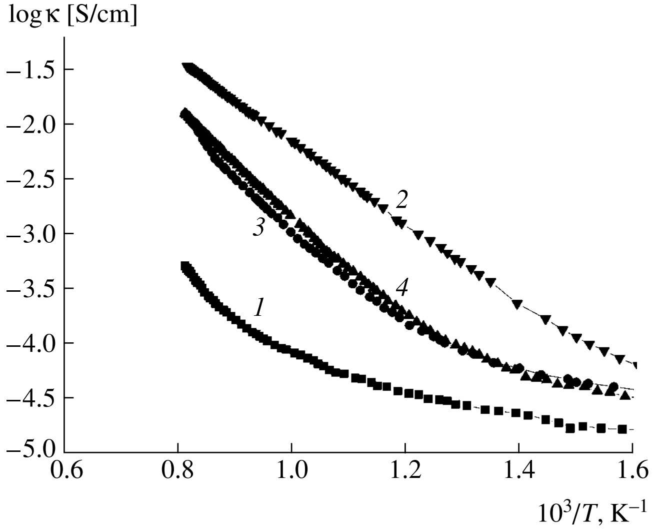

Fig. 8. Arrhenius plots of 1-MHz conductivity for (*1*, *2*) $Lu_2Ti_2O_7$ and (*3*, *4*) $Lu_{2.4}Ti_{1.6}O_{6.8}$ sintered at (*1*, *3*) 1600, (*2*) 1650, and (*4*) 1750°C.

remains high after heat treatment at 1400°C, indicating that its crystal structure changes little in the range 1400–1750°C.

Thus, the stoichiometric material $Lu_2Ti_2O_7$ (33.3 mol % Lu_2O_3) sintered at 1650°C (near its melting point, 1670°C) has high ionic conductivity. At higher Lu_2O_3 concentrations (34.5–40 mol %), high conductivity is observed between 1400 and 1750°C. In the composition and temperature ranges studied here, the conductivity of our samples ranges from 10^{-3} to 10^{-2} S/cm (740°C).

The assumption made earlier [6–8] that the high conductivity of $Lu_2Ti_2O_7$ at high temperatures is associated with the structural transition in this material is supported by the present data on the composition variation of conductivity for a large number of Lu_2O_3–TiO_2 samples. Our results demonstrate that, at Lu_2O_3 contents above 33.3 mol %, ceramic electrolytes with a 740°C ionic conductivity on the order of 10^{-3} S/cm can be prepared via heat treatment in the range 1400–1750°C.

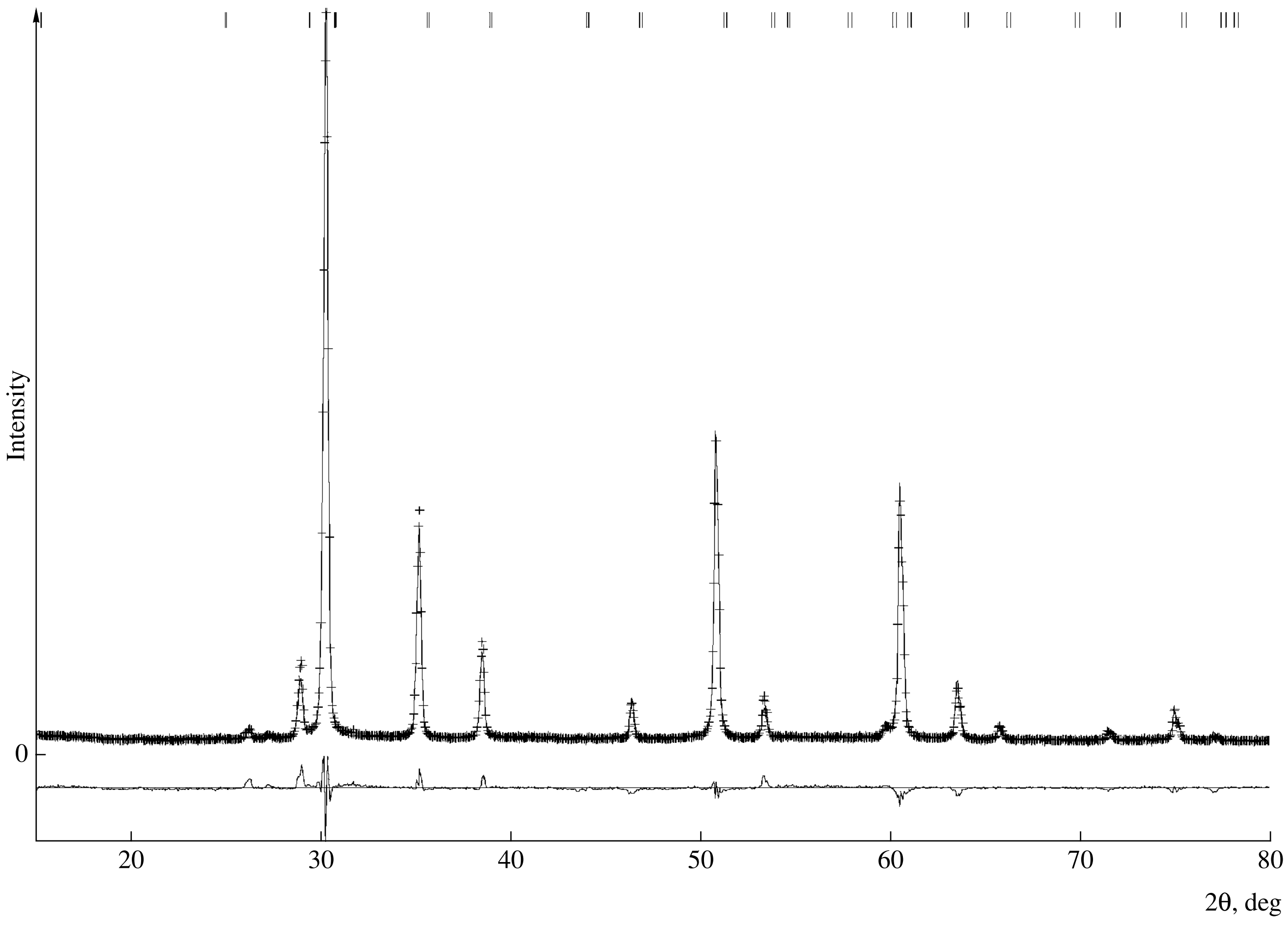

Fig. 9. Rietveld refinement profile for $Lu_{2.4}Ti_{1.6}O_{6.8}$.

Rietveld analysis data for $Lu_{2+x}Ti_{2-x}O_{7-x/2}$ (x = 0–0.643)

Composition	Atom	Position	Occupancy	X	Y	Z	B, Å^2	R_{wp}, %	a, Å
$Lu_2Ti_2O_7$ $x = 0$	Lu(1)	16	0.992(4)	0.625	0.625	0.625	0.02	10.69	10.0141 (0.0004)
	Ti(1)	16	0.008	0.625	0.625	0.625	0.02		
	Ti(2)	16	0.992	0.125	0.125	0.125	0.02		
	Lu(2)	16	0.008	0.125	0.125	0.125	0.02		
	O(1)	8	1	0.5	0.5	0.5	0.02		
	O(2)	48	1	0.201 (0.002)	0	0	0.02		
$Lu_{2.072}Ti_{1.928}O_{6.964}$ $x = 0.072$	Lu(1)	16	1	0.625	0.625	0.625	0.02	13.16	10.0172 (0.0006)
	Ti(1)	16	0	0.625	0.625	0.625	0.02		
	Ti(2)	16	0.964	0.125	0.125	0.125	0.02		
	Lu(2)	16	0.036	0.125	0.125	0.125	0.02		
	O(1)	8	0.946	0.5	0.5	0.5	0.02		
	O(2)	48	1	0.203	0	0	0.02		
$Lu_{2.132}Ti_{1.868}O_{6.934}$ $x = 0.132$	Lu(1)	16	0.997(2)	0.625	0.625	0.625	0.02	6.34	10.0413 (0.0004)
	Ti(1)	16	0.003	0.625	0.625	0.625	0.02		
	Ti(2)	16	0.949	0.125	0.125	0.125	0.02		
	Lu(2)	16	0.051	0.125	0.125	0.125	0.02		
	O(1)	8	0.952	0.5	0.5	0.5	0.02		
	O(2)	48	1	0.212 (0.001)	0	0	0		
$Lu_{2.4}Ti_{1.6}O_{6.8}$ $x = 0.4$	Lu(1)	16	1	0.625	0.625	0.625	0.02	7.38	10.078 (0.0004)
	Ti(1)	16	0	0.625	0.625	0.625	0.02		
	Ti(2)	16	0.8	0.125	0.125	0.125	0.02		
	Lu(2)	16	0.2	0.125	0.125	0.125	0.02		
	O(1)	8	0.8	0.5	0.5	0.5	0.02		
	O(2)	48	1	0.208 (0.001)	0	0	0		
$Lu_{2.643}Ti_{1.357}O_{6.68}$ $x = 0.643$	Lu(1)	16	0.919(5)	0.625	0.625	0.625	0.02	8.24	10.1016 (0.0007)
	Ti(1)	16	0.081	0.625	0.625	0.625	0.02		
	Ti(2)	16	0.598	0.125	0.125	0.125	0.02		
	Lu(2)	16	0.402	0.125	0.125	0.125	0.02		
	O(1)	8	0.956	0.5	0.5	0.5	0.02		
	O(2)	48	0.987	0.203	0	0	0.02		

Comparison of the conductivity data for samples prepared at 1600°C (Fig. 4) with XRD results indicates that the highest ionic conductivity is offered by slightly (1–2%) Lu_2O_3-enriched samples, as well as by stoichiometric samples prepared at 1650°C (near the melting point of $Lu_2Ti_2O_7$) (Fig. 8).

The defect structure of nanocrystalline $Lu_{2+x}Ti_{2-x}O_{7-x/2}$ (x = 0–0.643) samples sintered at 1600°C for 4 h was studied by XRD using Rietveld analysis (table) [10]. The results demonstrate that $Lu_2Ti_2O_7$, an electronic conductor, contains a low density of Lu_{Ti} + Ti_{Lu} antistructure pairs (~0.8%). In contrast, the ionic conductors $Lu_{2.072}Ti_{1.928}O_{6.964}$ (34.5 mol % Lu_2O_3), $Lu_{2.132}Ti_{1.868}O_{6.934}$ (35.5 mol % Lu_2O_3), and $Lu_{2.4}Ti_{1.6}O_{6.8}$ (40 mol % Lu_2O_3) contain significant amounts of Lu_{Ti} antisite defects (3.6, 5.1, and 20%,

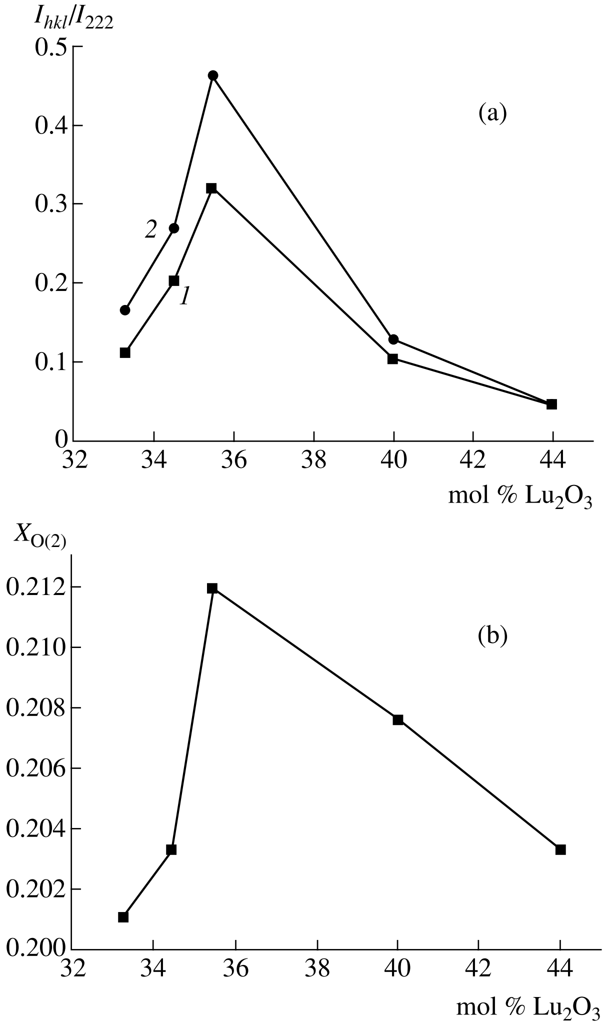

Fig. 10. Composition dependences of the (a) (*1*) I_{311}/I_{222} and (*2*) I_{331}/I_{222} intensity ratios and (b) variable positional parameter of O(2) (position 48*f* in the pyrochlore structure), $X_{O(2)}$, for $Lu_{2+x}Ti_{2-x}O_{7-x/2}$ (x = 0–0.643) sintered at 1600°C for 4 h.

respectively). In addition, the Lu-enriched materials contain oxygen vacancies in the O(1) site. The ionic conduction in these materials is due Lu_{Ti} antisite defects (≥3%) and oxygen vacancies (≤20%). The Rietveld refinement profile for $Lu_{2.4}Ti_{1.6}O_{6.8}$ (40 mol % Lu_2O_3) is displayed in Fig. 9.

Higher Lu_{Ti} defect densities, e.g., ~40% in $Lu_{2.643}Ti_{1.357}O_{6.68}$ (x = 0.643, 44 mol % Lu_2O_3), lead to disordering of the pyrochlore structure. Thus, a pronounced Lu_2O_3 enrichment (>10 mol %) gives rise to strong structural distortions, suppressing ionic conduction.

Figure 10 displays the composition dependences of the I_{311}/I_{222} and I_{331}/I_{222} intensity ratios and variable positional parameter of O(2) (position 48*f* in the pyrochlore structure), $X_{O(2)}$, inferred from XRD data for $Lu_{2+x}Ti_{2-x}O_{7-x/2}$ (x = 0–0.643) prepared at 1600°C. As seen, I_{311}/I_{222} and I_{331}/I_{222} correlate well with $X_{O(2)}$.

The conductivity of the 49 mol % Lu_2O_3 (fluorite-like) material is substantially lower than that of the pyrochlores (33.3–44 mol % Lu_2O_3), which supports the assumption that the ionic conductivity reaches a maximum in distorted pyrochlores, which contain relatively low levels of cation antisite defects [12].

CONCLUSIONS

Lu_2O_3–TiO_2 materials are shown to be ionic conductors in a rather broad composition range. According to their ionic conductivity and its activation energy, some of these materials can be classed with superionic conductors. In the composition range 33.3–49 mol % Lu_2O_3 (within the homogeneity range of $Lu_2Ti_2O_7$), high oxygen-ion conductivity can be ensured by heat treatment between 1400 and 1750°C. Within this T–x region, ionic conductivity is a weak function of the heat-treatment temperature. Ionic conduction in $Lu_{2+x}Ti_{2-x}O_{7-x/2}$ with x = 0–0.643 is due to Frenkel defects in the anion sublattice and antisite defects in the cation sublattice. Among nonstoichiometric $Lu_{2+x}Ti_{2-x}O_{7-x/2}$ (x = 0–0.94) materials, the highest ionic conductivity (~10^{-3} S/cm at 740°C) is offered by samples with small deviations from stoichiometry (x = 0.072–0.4), which contain relatively low levels of Lu_{Ti} antisite defects, 3 to 20%. The maximum ionic conductivity in the system is exhibited by stoichiometric samples prepared at 1650°C (near their melting point), which contain Lu_{Ti} + Ti_{Lu} antistructure pairs. In particular, the 740°C conductivity of nanocrystalline $Lu_2Ti_2O_7$ is ~8.5×10^{-3} S/cm, which is comparable to that of the well-known solid electrolyte ZrO_2–9 mol % Y_2O_3.

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