Conference Paper

Oxygen-conducting Composites Based on $Me_2(WO_4)_3$ (Me = Sm, Al)

D. A. Lopatin, E. L. Vostrotina, D. D. Otcheskih, N. N. Pestereva, and A. F. Guseva

Institute of Natural Sciences and Mathematics, Ural Federal University, 620000 Ekaterinburg, Russia

Abstract

Composites $Sm_2(WO_4)_3$-WO_3 and $Al_2(WO_4)_3$-WO_3 were prepared by the solid-state method and a systematic study of their electrotransport properties has been carried out. A sharp increase in the oxygen-ion conductivity is observed in composites $Sm_2(WO_4)_3$–WO_3 at small WO_3 values (about 10 mol.%). This effect is probably caused by formation of the non-autonomous interface phase covering grain boundaries of $Sm_2(WO_4)_3$. These composite O^{2-} – electrolytes are perspective materials for high temperature fuel cells. The composite effect is absent in the $Al_2(WO_4)_3$–WO_3 system. This is probably due to the negative thermal expansion coefficient of $Al_2(WO_4)_3$, which prevents the formation of a continuous high-conducting microphase film.

Keywords: composites, ionic conductivity, heterogeneous doping, microphase

Corresponding Author:
N. N. Pestereva
Natalie.Pestereva@urfu.ru

Received: 14 September 2018
Accepted: 1 October 2018
Published: 14 October 2018

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the ASRTU Conference Committee.

1. Introduction

Recently, special attention has been paid to high-temperature oxygen conductive solid electrolytes, which is due to their application for solid oxide fuel cells and oxygen sensors [1, 2]. Composite solid electrolytes with oxygen ion conductivity have been investigated by Neiman, et al. [3–6]. A sharp increase in the oxygen ion conductivity was observed, when tungsten oxide was added to alkaline earth tungstates with the scheelite structure. The effect was explained by easy spreading of WO_3 along the grain boundaries of tungstate with formation of the oxygen ion conducting interface phase.

$Sm_2(WO_4)_3$ and $Al_2(WO_4)_3$ as was shown earlier in our works [7–8] are low-conductive oxygen-ionic conductors; therefore, to improve the ion transport parameters, a heterogeneous doping method was used to obtain composites with acceptable values of ionic conductivity. Since the structure of $Sm_2(WO_4)_3$ and $Al_2(WO_4)_3$ is similar to those of alkaline earth metals, it can be expected that the conduction increase effect will also be observed in the systems $Sm_2(WO_4)_3$–WO_3 and $Al_2(WO_4)_3$–WO_3.

How to cite this article: D. A. Lopatin, E. L. Vostrotina, D. D. Otcheskih, N. N. Pestereva, and A. F. Guseva, (2018), “Oxygen-conducting Composites Based on $Me_2(WO_4)_3$ (Me = Sm, Al)” in *Sino-Russian ASRTU Conference Alternative Energy: Materials, Technologies, and Devices*, KnE Materials Science, pages 92–97. DOI 10.18502/kms.v4i2.3042

2. Methods

$Sm_2(WO_4)_3$and $Al_2(WO_4)_3$ powder samples were prepared by the solid-state method from Me_2O_3 (Me = Sm, Al) and WO_3 of 'extra-pure grade' qualification. The mixture of the oxides taken in stoichiometric amounts was heated in air with the gradual increase of temperature from 700 to 1000°C in four steps with intermediate grindings in ethanol media. Annealing time at each stage was varied from 24 to 48 h. Composites $Me_2(WO_4)_3$-WO_3 (Me = Sm, Al) were prepared by mechanical mixing of $Me_2(WO_4)_3$(Me = Sm, Al) and WO_3powders. The mixtures were compacted into disc pellets (10 mm in diameter and 2 mm thick) under a pressure of 64 MPa, and the pellets were sintered at 900^{o}C for 10 h. Porous Pt electrodes were deposited on the faces of the pellets from suspension of the platinum black in organic solvent, evaporated, and annealed at 900°C for 6 hours.

The samples were characterized by X-ray diffraction method by using a Bruker D8 ADVANCE diffractometer with Cu*K*α-radiation at the 40 kV voltage on the tube and the 40 mA current with the step of 0.05/s in the angle range of $15 \leq 2\theta \leq 65$. X-ray patterns were interpreted using the FullProf Suite software. The accuracy of detection was 5%.

$Me_2(WO_4)_3$–WO_3(Me = Sm, Al) samples resistance was measured by impedance spectroscopy with the Immittance Parameters Meter IPI1 (Trapeznikov Institute of Control Sciences, Moscow) at frequencies of 100 Hz – 1 MHz (the test signal amplitude automatically varied within the range from 3 to 300 mV) in the temperature range of 400–900°C.

The conductivity dependence on oxygen partial pressure P_{O_2} was studied at a fixed temperature 800°C. The oxygen pressure was set and controlled by an oxygen pump and a sensor made of a solid electrolyte based on yttrium-stabilized zirconia ZrO_2–10%Y_2O_3.

3. Results

3.1. Phase identification

$Sm_2(WO_4)_3$ and $Al_2(WO_4)_3$ were confirmed to be a single phase by XRD analysis (Figure 1). The unit cell parameters of the synthesized phases are in good agreement with those published earlier [7, 8]. All composites $Me_2(WO_4)_3$–WO_3 (Me = Sm, Al) under study were biphasic and contained only $Me_2(WO_4)_3$ (Me = Sm, Al) and WO_3 (Figure 1).

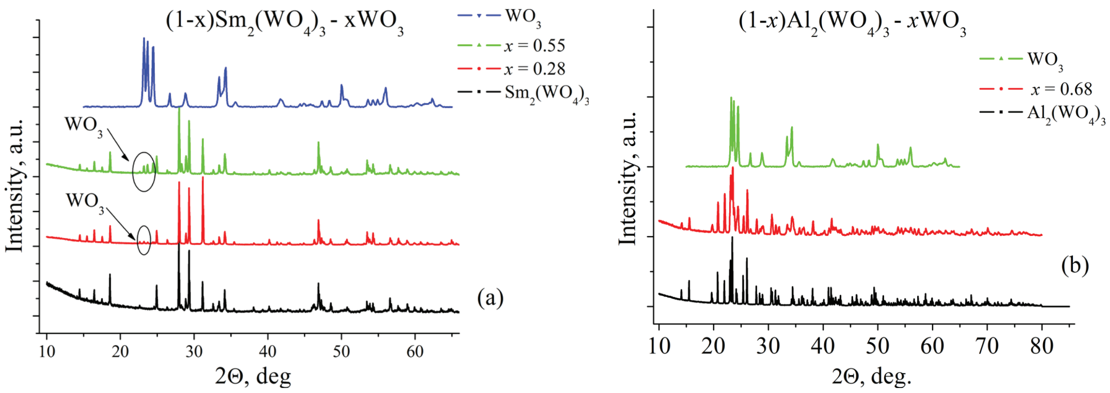

Figure 1: XRD patterns of (a) $Sm_2(WO_4)_3$–WO_3 and (b) $Al_2(WO_4)_3$–WO_3 composites.

3.2. $Me_2(WO_4)_3$–WO_3 composites conductivity polytherms

The resistance of $Me_2(WO_4)_3$–WO_3 (Me = Sm, Al) composites was measured by impedance spectroscopy. The temperature dependences of the conductivity of the $Me_2(WO_4)_3$–WO_3 are shown in Figure 2. As seen, activation energy is equal 1.1 eV for the $Sm_2(WO_4)_3$–WO_3 composites in the range 400–700°C, whereas for the $Al_2(WO_4)_3$–WO_3 composites E_A = 0.75 eV. The proximity of the activation energies to 1 eV indirectly indicates the O^{2-}-type of the conductivity in the subjects under study. It has been shown that the addition of a WO_3 semiconductor to $Sm_2(WO_4)_3$ leads to a sharp increase in conductivity. It is established that the conductivity of composites increases with the increase in the amount of WO_3, approaching the electrical conductivity of tungsten oxide.

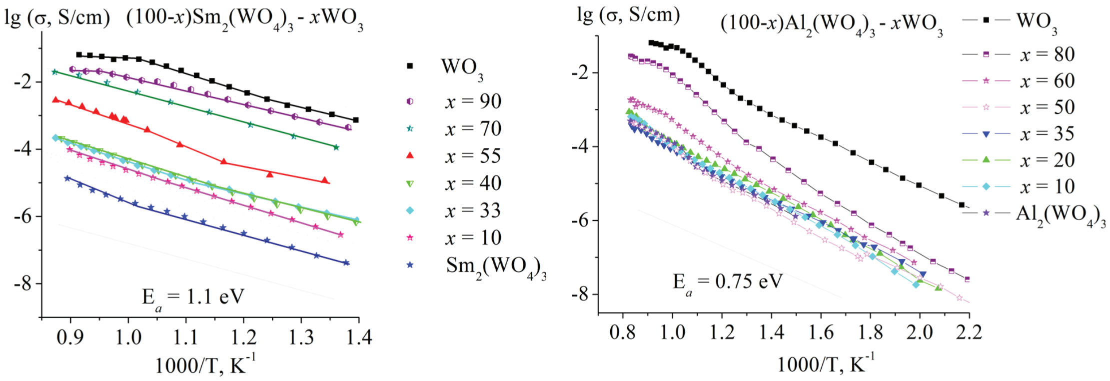

Figure 2: Temperature dependence of conductivity for (a) $Sm_2(WO_4)_3$–WO_3 and (b) $Al_2(WO_4)_3$–WO_3 composites; x – molar content of WO_3 in composites, %.

It has been found that the introduction of up to 50 mol.% in the $Al_2(WO_4)_3$ ceramic practically does not affect the conductivity value. When adding more than 50 mol.% of WO_3 to aluminum tungstate, the composite conductivity increases, gradually approaching to the WO_3 conductivity.

3.3. Conductivity of $Me_2(WO_4)_3$–WO_3 composites versus oxygen partial pressure

To determine the electrolytic conductivity region of the $Me_2(WO_4)_3$–WO_3 composites, its electrical conductivity versus oxygen partial pressure in the gas phase was measured (Figure 3). Conductivity of $Al_2(WO_4)_3$–WO_3 composites with a WO_3 content up to 50 mol.% does not depend on the oxygen pressure, which indicates its ionic character. Increasing WO_3 content, the $\log\sigma - \log P_{O_2}$ dependence has a negative slope, which indicates the presence of an n-type electron conduction contribution (WO_3 is an n-type electron conductor).

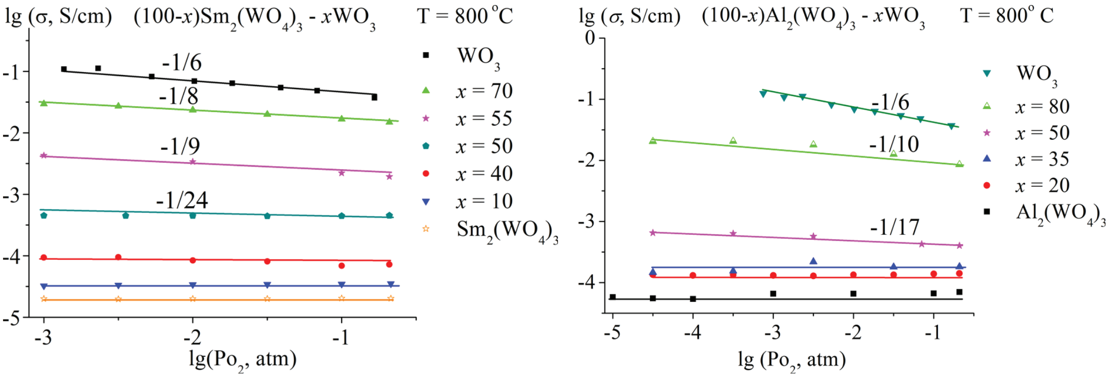

Figure 3: Conductivity of composites versus oxygen partial pressure: (a) $Sm_2(WO_4)_3$–WO_3 and (b) $Al_2(WO_4)_3$–WO_3.

A similar behavior has been observed for $Sm_2(WO_4)_3$–WO_3 composites: conductivity of composites with a WO_3 content up to 40 mol.% does not depend on the oxygen pressure; increase in the content of tungsten oxide led to the appearance of the negative slope of the $\log\sigma - \log P_{O_2}$ dependences.

3.4. Concentration dependence of the conductivity

Figure 4 shows that for $Sm_2(WO_4)_3$–WO_3 composites a sharp increase in the O^{2-}-conductivity is observed by more than an order of magnitude when the tungsten oxide conductor is added 10 mol.% (composite effect is detected). With the further addition of WO_3 up to 40 mol.% conductivity remains unchanged. When adding more than 40 mol.% WO_3, conductivity of composites becomes ion-electronic.

In contrast, the addition of tungsten oxide to aluminum tungstate up to 50 mol.% (Figure 4) does not lead to an increase in ion conductivity (composite effect is not observed). More than 50 mol.% conductivity type becomes mixed. Thus, the region of

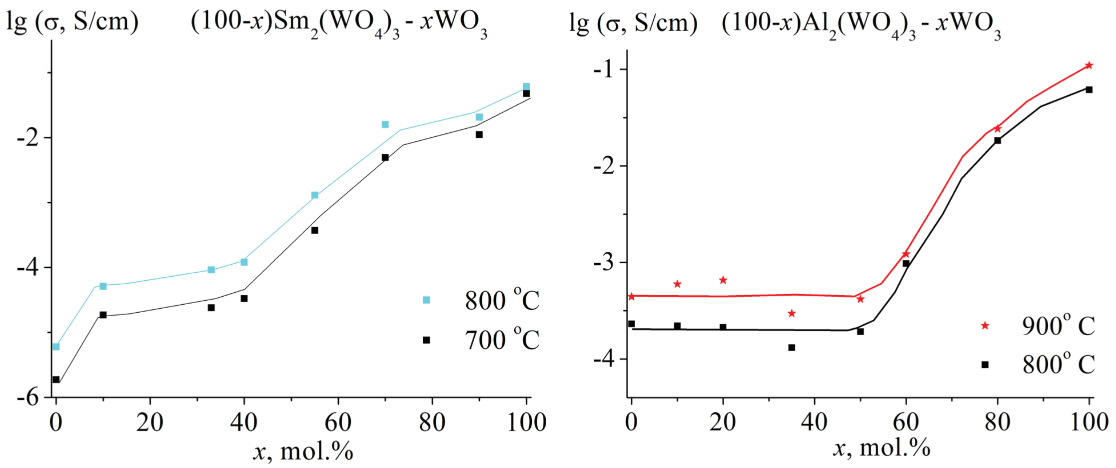

Figure 4: Concentration dependence of electrical conductivity of $Me_2(WO_4)_3$–WO_3 composites (Me = Sm, Al); x – molar content of WO_3 in composites, %.

electrolytic conductivity of composites is limited to 40 mol.% of the WO_3 fraction for $Sm_2(WO_4)_3$–WO_3 and 50 mol.% for $Al_2(WO_4)_3$–WO_3.

4. Conclusion

A composite effect was found in the system $Sm_2(WO_4)_3$–WO_3: adding up to 40 mol.% of the WO_3 semiconductor to the ionic conductor $Sm_2(WO_4)_3$ leads to an increase in the oxygen-ionic conductivity of the system by more than an order of magnitude. So, the obtained composites have application prospect as solid electrolytes for fuel cells. By analogy with MWO_4–WO_3 composites (M – alkaline earth metal) investigated earlier this phenomenon can be probably explained by the formation of a high-conductivity surface microphase at the $Sm_2(WO_4)_3|WO_3$ interface, which plays the role of a connected matrix in the composite $Sm_2(WO_4)_3$–WO_3 and responsible for its high transport properties. As a result, a Maxwell-type composite is formed in this system.

There is no composite effect in the $Al_2(WO_4)_3$–WO_3 system: the conductivity of the composite containing up to 50 mol.% is close to the $Al_2(WO_4)_3$ conductivity; adding more amount of WO_3 leads to a sharp increase in the electronic conductivity due to the formation of a continuous WO_3 matrix. The absence of a composite effect in the $Al_2(WO_4)_3$–WO_3 system can be explained by the negative thermal expansion coefficient of $Al_2(WO_4)_3$, which prevents the formation of a continuous microphase film on the $Al_2(WO_4)_3|WO_3$ interface. As a result, a statistical distributed composite is formed in this system.

Acknowledgement

The research results were obtained in the framework of the State Task of the Ministry of Education and Science of Russia. The equipment of the Ural Center for Shared Use 'Modern nanotechnology' UrFU was used.

References

[1] Ishihara, T. (2009). *Perovskite Oxide for Solid Oxide Fuel Cells*, p. 302. Boston, MA: Springer.

[2] Tarancón, A. (2009). Strategies for lowering Solid Oxide Fuel Cells operating temperatures. *Energies*, vol. 2, pp. 1130–1150.

[3] Neiman, A. Ya., Pestereva, N. N., Sharafutdinov, A. R., et al. (2005). Conduction and transport numbers in metacomposites $MeWO_4$–WO_3 (Me = Ca, Sr, Ba). *Russian Journal of Electrochemistry*, vol. 41, no. 6, pp. 598–611.

[4] Neiman, A. Ya., Uvarov, N. F., and Pestereva, N. N. (2007). Solid state surface and interface spreading: An experimental study. *Solid State Ionics*, vol. 177, pp. 3361–3369.

[5] Pestereva, N., Zhukova, A., and Neiman, A. (2007). Transport numbers and ionic conduction of eutectic methacomposites $\{(1\text{–}x)MeWO_4\text{–}xWO_3\}$ (Me=Sr, Ba; x=0-0.55). *Russian Journal of Electrochemistry*, vol. 43, no. 11, pp. 1305–1313.

[6] Pestereva, N. N., Safonova, I. G., Nokhrin, S. S., et al. (2010). Effect of MWO_4 (M = Ca, Sr, Ba) dispersion on the interfacial processes in $(+/–)WO_3|MWO_4|WO_3(–/+)$ cells and transport properties of metacomposite phases. *Zhurnal Neorganicheskoi Khimii*, vol. 55, no. 6, pp. 876–882.

[7] Neiman, A. Ya., Pestereva, N. N., Zhou, Y., et al. (2013). The nature and the mechanism of ion transfer in tungstates $Me^{2+}\{WO_4\}$ (Ca, Sr, Ba) and $Me_2{}^{3+}\{WO_4\}_3$ (Al, Sc, In) according to the data acquired by the tubandt method. *Russian Journal of Electrochemistry*, vol. 49, no. 9, pp. 895–907.

[8] Pestereva, N., Guseva, A., Vyatkin, I., et al. (2017). Electrotransport in tungstates $Ln_2(WO_4)_3$ (Ln = La, Sm, Eu, Gd). *Solid State Ionics*, vol. 301, pp. 72–77.