Conference Paper

Oxygen-conducting Composites Based on \( \text{Me}_2(\text{WO}_4)_3 \) (Me = Sm, Al)

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Abstract

Composites \( \text{Sm}_2(\text{WO}_4)_3\text{WO}_3 \) and \( \text{Al}_2(\text{WO}_4)_3\text{WO}_3 \) 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 \( \text{Sm}_2(\text{WO}_4)_3\text{WO}_3 \) at small \( \text{WO}_3 \) values (about 10 mol.%). This effect is probably caused by formation of the non-autonomous interface phase covering grain boundaries of \( \text{Sm}_2(\text{WO}_4)_3 \). These composite \( \text{O}^{2-} \)– electrolytes are perspective materials for high temperature fuel cells. The composite effect is absent in the \( \text{Al}_2(\text{WO}_4)_3\text{WO}_3 \) system. This is probably due to the negative thermal expansion coefficient of \( \text{Al}_2(\text{WO}_4)_3 \), which prevents the formation of a continuous high-conducting microphase film.

Keywords: composites, ionic conductivity, heterogeneous doping, microphase

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 \( \text{WO}_3 \) along the grain boundaries of tungstate with formation of the oxygen ion conducting interface phase.

\( \text{Sm}_2(\text{WO}_4)_3 \) and \( \text{Al}_2(\text{WO}_4)_3 \) 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 \( \text{Sm}_2(\text{WO}_4)_3 \) and \( \text{Al}_2(\text{WO}_4)_3 \) is similar to those of alkaline earth metals, it can be expected that the conduction increase effect will also be observed in the systems \( \text{Sm}_2(\text{WO}_4)_3\text{WO}_3 \) and \( \text{Al}_2(\text{WO}_4)_3\text{WO}_3 \).
2. Methods

Sm$_2$(WO$_4$)$_3$ and Al$_2$(WO$_4$)$_3$ powder samples were prepared by the solid-state method from Me$_2$O$_3$ (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$_3$ powders. 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°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 CuKα-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 $15^\circ \leq 2\theta \leq 65^\circ$. 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 IPh (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$_2$O$_3$.

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).
3.2. $\text{Me}_2(\text{WO}_4)_3$–WO$_3$ composites conductivity polytherms

The resistance of $\text{Me}_2(\text{WO}_4)_3$–WO$_3$ (Me = Sm, Al) composites was measured by impedance spectroscopy. The temperature dependences of the conductivity of the $\text{Me}_2(\text{WO}_4)_3$–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.

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 $\text{Me}_2(\text{WO}_4)_3$–$\text{WO}_3$ composites versus oxygen partial pressure

To determine the electrolytic conductivity region of the $\text{Me}_2(\text{WO}_4)_3$–$\text{WO}_3$ composites, its electrical conductivity versus oxygen partial pressure in the gas phase was measured (Figure 3). Conductivity of $\text{Al}_2(\text{WO}_4)_3$–$\text{WO}_3$ composites with a $\text{WO}_3$ content up to 50 mol.% does not depend on the oxygen pressure, which indicates its ionic character. Increasing $\text{WO}_3$ content, the $\log\sigma$–$\log P_{\text{O}_2}$ dependence has a negative slope, which indicates the presence of an n-type electron conduction contribution ($\text{WO}_3$ is an n-type electron conductor).

A similar behavior has been observed for $\text{Sm}_2(\text{WO}_4)_3$–$\text{WO}_3$ composites: conductivity of composites with a $\text{WO}_3$ 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 $\log\sigma$–$\log P_{\text{O}_2}$ dependences.

3.4. Concentration dependence of the conductivity

Figure 4 shows that for $\text{Sm}_2(\text{WO}_4)_3$–$\text{WO}_3$ composites a sharp increase in the $\text{O}^{2-}$-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 $\text{WO}_3$ up to 40 mol.% conductivity remains unchanged. When adding more than 40 mol.% $\text{WO}_3$, 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

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Figure 3: Conductivity of composites versus oxygen partial pressure: (a) $\text{Sm}_2(\text{WO}_4)_3$–$\text{WO}_3$ and (b) $\text{Al}_2(\text{WO}_4)_3$–$\text{WO}_3$. 

Figure 4 shows that for $\text{Sm}_2(\text{WO}_4)_3$–$\text{WO}_3$ composites a sharp increase in the $\text{O}^{2-}$-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 $\text{WO}_3$ up to 40 mol.% conductivity remains unchanged. When adding more than 40 mol.% $\text{WO}_3$, 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
electrolytic conductivity of composites is limited to 40 mol.% of the WO₃ fraction for Sm₂(WO₄)₃–WO₃ and 50 mol.% for Al₂(WO₄)₃–WO₃.

4. Conclusion

A composite effect was found in the system Sm₂(WO₄)₃–WO₃: adding up to 40 mol.% of the WO₃ semiconductor to the ionic conductor Sm₂(WO₄)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 MWO₄–WO₃ composites (M – alkaline earth metal) investigated earlier this phenomenon can be probably explained by the formation of a high-conductivity surface microphase at the Sm₂(WO₄)₃|WO₃ interface, which plays the role of a connected matrix in the composite Sm₂(WO₄)₃–WO₃ 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 Al₂(WO₄)₃–WO₃ system: the conductivity of the composite containing up to 50 mol.% is close to the Al₂(WO₄)₃ conductivity; adding more amount of WO₃ leads to a sharp increase in the electronic conductivity due to the formation of a continuous WO₃ matrix. The absence of a composite effect in the Al₂(WO₄)₃–WO₃ system can be explained by the negative thermal expansion coefficient of Al₂(WO₄)₃, which prevents the formation of a continuous microphase film on the Al₂(WO₄)₃|WO₃ interface. As a result, a statistical distributed composite is formed in this system.
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References


