Conference Paper

Electrical Properties of Tungstates Ln$_2$(WO$_4$)$_3$ (Ln – Gd, Ho)

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Abstract

Electrical properties of Gd$_2$(WO$_4$)$_3$ and Ho$_2$(WO$_4$)$_3$ were studied and the type of charge carriers was determined. The studied compounds have a salt-like isle structure with isolated tetrahedrons. It crystallises in the Eu$_2$(WO$_4$)$_3$ structural type, so-called ‘defective scheelite’, in which 1/3 of Ln sites are vacant, Ln$_{2/3}$[V$_{Ln}$]$_{1/3}$WO$_4$. Predominant ionic conductivity in Ln$_2$(WO$_4$)$_3$ (Ln = Gd, Ho) was established both by the EMF method and from independence of conductivity versus oxygen partial pressure. A minor contribution (4-11%) of the anion [WO$_4$]$^{2-}$ transport was detected by the Tubandt method, which along with the results of the EMF technique proves the predominant oxygen conductivity.

Keywords: lanthanide tungstates, ion transference numbers, Tubandt method, electrical conductivity versus temperature, oxygen partial pressure

1. Introduction

It has been established earlier [1, 2] that electromigration in tungstates with the structure of scheelite is carried by ions O$^{2-}$ and WO$_4^{2-}$. Since the polyanionic transfer is a rare and insufficiently studied phenomenon, that is of interest to investigate the type and the nature of the conductivity of trivalent metal tungstates, for example Gd$_2$(WO$_4$)$_3$ and Ho$_2$(WO$_4$)$_3$. This tungstates crystallizes in Eu$_2$(WO$_4$)$_3$ structural type, so-called ‘defective scheelite’, in which 1/3 of Me-sites are vacant, Me$_{2/3}$[V$_{Me}$]$_{1/3}$WO$_4$ [3, 4]. The crystal structure of ‘defective scheelite’ can be characterized by the presence of isolated tetrahedrons [WO$_4$], which have a common oxygen apex with [MeO$_8$] dodecahedrons [3, 4].

2. Methods

Gd$_2$(WO$_4$)$_3$ was prepared by the solid-state method from the powders of Gd$_2$O$_3$ and WO$_3$ of the ‘extra-pure grade’ qualification in air. The oxides Gd$_2$O$_3$ and WO$_3$ were previously calcinated for 6 hours to remove traces of moisture, Gd$_2$O$_3$ at 1100°C, WO$_3$ at 800°C. Synthesis was performed according to the equation:

$$Gd_2O_3 + 3WO_3 = Gd_2(WO_4)_3$$ (1)
with the gradual increase of temperature (600-1100°C) in six steps with intermediate grindings in the ethyl alcohol media; annealing time at each stage varied from 12 to 96 hours.

$\text{Ho}_2(\text{WO}_4)_3$ was prepared by glycerole-nitrate method described in Ref. [5]. The precursors for glycerole-nitrate method were $(\text{NH}_4)_10\text{W}_{12}\text{O}_{41}$, $\text{Ho}_2\text{O}_3$, $\text{C}_4\text{H}_6\text{O}_6$, and 57% HNO$_3$ (all of high purity grade). The phase purity of the samples was confirmed by X-ray diffraction (XRD) method (Bruker D8 ADVANCE, Cu-K$\alpha$ radiation, 40 kV, 40 mA, exposition 1 s, angles range $15 \leq 2\theta \leq 65$). The unit cell parameters were refined by the FullProf Package.

Compacted briquettes of $\text{Ln}_2(\text{WO}_4)_3$ with a diameter of 1 cm and 2 mm thickness were obtained by pressing of powders at 900 kg/cm$^2$ followed by sintering at 1100°C for 24 hours ($\text{Gd}_2(\text{WO}_4)_3$) and 900°C for 48 hours ($\text{Ho}_2(\text{WO}_4)_3$). The relative densities of the ceramic samples were 85% for $\text{Gd}_2(\text{WO}_4)_3$ and 60% for $\text{Ho}_2(\text{WO}_4)_3$. $\text{Ln}_2(\text{WO}_4)_3$ ($\text{Ln} = \text{Gd, Ho}$) samples resistance was measured by impedance spectroscopy with the Immittance Parameters Meter IP1 (Trapezinkov Institute of Control Sciences, Moscow) at frequencies of 100 Hz - 1 MHz in the temperature range 450-880°C.

The sum of ionic transference numbers was determined by the EMF method in the cell:

$$P'_O(Pt)\big|\text{Ln}_2(\text{WO}_4)_3\big| (Pt) P'_O$$

The effect of oxygen partial pressure $P_{O_2}$ on conductivity was measured at fixed temperature in the temperature range 700-940°C. The oxygen pressure was set and controlled by an oxygen pump and a sensor made of solid electrolyte on the basis of yttrium-stabilised zirconia ZrO$_2$(Y$_2$O$_3$).

The nature of mass and charge transfer was determined by the Tubandt method in a two-piece cell:

$$(-)Pt\big|\text{Ln}_2(\text{WO}_4)_3\big| \text{Ln}_2(\text{WO}_4)_3\big| Pt(+)$$

The experiment was carried out at 850°C; the voltage $U = 300$ V was applied to Cell with the current not exceeding 1 mA. The amount of electricity passing through the cell Q ranged from 10 to 86 C. The TG and DSC measurements were carried out with the simultaneous thermal analysis device NETZSCH STA 409 PC LUXX equipped with the Quadrupole Mass Spectrometer QMS 403 AÉOLOS.

### 3. Results

#### 3.1. Phase identification

$\text{Gd}_2(\text{WO}_4)_3$ and $\text{Ho}_2(\text{WO}_4)_3$ were confirmed to be a single phase by XRD analysis (Fig. 1). The unit cell parameters of the synthesised phases are in good agreement with the published earlier (Table 1) [6].
Figure 1: XRD patterns Gd₂(WO₄)₃, Ho₂(WO₄)₃.

![XRD patterns for Gd₂(WO₄)₃ and Ho₂(WO₄)₃](image)

Table 1: The unit cell parameters of Ln₂(WO₄)₃ (Ln = Gd, Ho).

<table>
<thead>
<tr>
<th>Substance</th>
<th>Unit cell parameters (lit.) [6]</th>
<th>Unit cell parameters (exp.)</th>
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<td></td>
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Figure 2: TGA and DSC results for Ln₂(WO₄)₃.

![TGA and DSC results for Ln₂(WO₄)₃](image)

3.2. Thermogravimetric Analysis and DSC Ln₂(WO₄)₃ Research

TG and DSC data are presented in Fig. 2. TG analysis showed no change in the weight of the Gd₂(WO₄)₃ samples in the entire temperature range under study. Mass loss at 150°C for tungstate holmium associated with dehydration due to its hygroscopicity. Endothermic effect at 1172°C on the DSC curve of Gd₂(WO₄)₃ and 926°C on the DSC curve of Ho₂(WO₄)₃ can be interpreted as the phase transformation from low-temperature defect scheelite Eu₂(WO₄)₃ structure to the high-temperature Sc₂(WO₄)₃ type structure [6].

3.3. Electrical Conductivity and Transference Numbers of Ln₂(WO₄)₃

The resistance of Ln₂(WO₄)₃ samples was measured by impedance spectroscopy. The temperature dependences of the conductivity of the Ln₂(WO₄)₃ are shown in Fig. 3. The jump in conductivity Ho₂(WO₄)₃ at 850°C is probably due to the phase transition, the nature of which is not yet clear.

Conductivity value of both phases is almost identical (Fig. 3) below 850°C, due to close radii values of Ln³⁺ (Gd³⁺ - 0.1193 nm, Ho³⁺ - 0.1155 nm) [7] and due to the same phase structure. But above 850°C Ho₂(WO₄)₃ conductivity is 7-8 times higher than for Gd₂(WO₄)₃.
Figure 3: Temperature dependence of conductivity for Ln₂(WO₄)₃.

Figure 4: Oxygen pressure dependence of conductivity for Ln₂(WO₄)₃.

Gd₂(WO₄)₃. This fact can probably be explained by the Ho₂(WO₄)₃ phase transition at 850°C.

The conductivity isotherms of Ln₂(WO₄)₃ versus oxygen partial pressure are shown in Fig. 4. The fact of independence of the value of total conductivity with oxygen pressure may confirm the ionic conductivity in Ho₂(WO₄)₃ and Gd₂(WO₄)₃ within the temperature range 700-940°C. The conductivity isotherm of Gd₂(WO₄)₃ measured by EMF method is close to 1. This fact is in a good agreement with the independence of the Gd₂(WO₄)₃ electrical conductivity of the Pₒ₂ (Fig. 4).

3.4. The Nature of Mobile Carriers in Ln₂(WO₄)₃ (Tubandt method)

To clarify the type of charge carriers for Ln₂(WO₄)₃, Tubandt experiments were carried out in a two-section cell at 850°C. Mass loss of the cathode section and growth of the anode section weight were found (Fig. 5).

Reproducible mass reduction of the cathode section proved that negative ions were responsible for the charge transfer. Since the transfer of oxygen ions cannot lead to a change in mass of the samples, the experimentally observed change in mass of cathode and anode sections are due to the [WO₄]²⁻ transfer. If this supposition is correct, then a phase enriched by lanthanide and a phase enriched by tungsten should appear in the cathode space and in the anode space, respectively. The XRD results of the cathode and anode areas of Ho₂(WO₄)₃ briquettes are shown in Fig. 6. Indeed, XRD
pattern of the Ho₂(WO₄)₃ cathode briquette surface with was in contact with the Pt(−) electrode reveals an appearance of a phase enriched by holmium (Ho₆WO₁₂). At the same time, a phase enriched by tungsten (WO₃) was identified on the surface of the anode briquette Ho₂(WO₄)₃ in contact with the Pt(+) electrode.

Possible electrode reactions that can occur in the cathode and anode sections are:

\[ (-)3Ho_2(WO_4)_3 + 4O_2 + 16e^- = Ho_6WO_{12} + 8WO_4^{2-} \]  \hspace{1cm} \text{(4)}

\[ (+)WO_4^{2-} = WO_3 + \frac{1}{2}O_2 + 2e^- \]  \hspace{1cm} \text{(5)}

By using the Faraday’s law and assuming that the amount of mass loss of the cathode section \( \Delta m^{(-)} \) is correspondent to the WO₃ mass related to the migration of \([WO_4]^{2-}\) ions, the \([WO_4]^{2-}\) ion transference number was calculated according to the formula:

\[ t_{WO_4^{2-}} = \frac{\Delta m^{(-)}}{M_{WO_3}} \cdot z_{WO_4^{2-}} \cdot \frac{F}{Q}, \]  \hspace{1cm} \text{(6)}

where \( M_{WO_3} \) is WO₃ molar mass (g/mol), \( z = 2 \), \( Q \) is the amount of electricity passed through the system (C), \( F \) is Faraday’s constant.

The molar mass of WO₃ \( M_{WO_3} \) (instead of \( M_{WO_4^{2-}} \)) was used in the formula, because according to the equation of reaction (4), the mass loss of the cathode section caused by the disappearing of tungsten oxide is the following:

\[ \Delta m^{(-)} = m(WO_4^{2-}) - m(\frac{1}{2}O_2) \]  \hspace{1cm} \text{(7)}

The transference numbers of tungstate ion calculated according to the Eq. (6) are about 4% for gadolinium tungstate and 11% for holmium tungstate.
The obtained results indicate that [WO$_4^{2-}$] makes no significant contribution to the charge transfer in the studied systems; therefore, the particles that do not affect the mass change play a predominant role. Thus, one can conclude that oxygen ions can serve as mobile species, i.e., $t (O^{2-}) >> t (WO_4^{2-})$.

This result is quite unexpected, because the contribution of tungstate ion in the electric transport for isostructural divalent metal tungstates (CaWO$_4$, SrWO$_4$, BaWO$_4$) according to the data [2], is much higher, and varies from 20 to 50%. The insignificant contribution of [WO$_4^{2-}$] transfer to the electrotransport of Ho$_2$(WO$_4$)$_3$ and Gd$_2$(WO$_4$)$_3$ with the defect scheelite structure (as compared with the divalent metal tungstates) can be due to the fact that structural vacancies V$_{Ln}$ open channels for the O$^{2-}$ migration that increase the contribution of oxygen conductivity.

4. Conclusion

Thus, the set of the experimental results suggests that O$^{2-}$ ions are the main charge carriers in the tungstates Ln$_2$(WO$_4$)$_3$ (Ln = Ho, Gd). Together with that, a minor (under 11%) contribution of polyanions [WO$_4^{2-}$] into the ion transport was detected.

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References