Perspective ion-conducting materials based on complex tungstates

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S G Dorzhieva[1], B G Bazarov[1], A K Subanakov[1] and J G Bazarova[1]

[1] Baikal Institute of Nature Management SB RAS, Ulan-Ude, 670047, Russia

E-mail: bsesegma@mail.ru

Abstract. Novel electrolytes based on complex tungstates with general formula Cs*R*Ti$_{0.5}$(WO$_4$)$_3$ (*R*= Al, Cr) were investigated. X-ray diffraction results show that the single-phase samples can be formed by ceramic technology at 1023 K. Dielectric measurement results indicate that the conductivity of CsCrTi$_{0.5}$(WO$_4$)$_3$ can reach 0.0011 S cm^{-1} at 1023 K. The activation energy of the compound calculated according to the Arrhenius plots are 0.4–0.6 eV for T > 873 K. Impedance spectra of the ceramic samples at different temperatures are characterized the high frequency semicircle and a straight line at low frequencies, which is typical for ion-conducting materials. Cs*R*Ti$_{0.5}$(WO$_4$)$_3$ (*R*= Al, Cr) ceramic materials correspond to a new strategy to design novel electrolytes for various applications.

1. Introduction

The rapid development of electronic technologies determines the growing interest of researchers to batteries with high power density and environmental safety. Typical ionic batteries based on liquid electrolytes do not meet these requirements due to high flammability and possible leakage. Solid state ion batteries have better safety due replacing the liquid with solid solutions. Tungstates were widely studied for potential applications in many areas, such as luminescence, optical spectroscopy, catalysis [1-8]. Nowadays, these compounds are attracted renewed attention because of their high conductivity. A wide variety of electrical conduction properties of complex alkali tungstates have been explored [9–12]. In this work, the temperature and frequency dependences of dielectric parameters, thermal characteristics of newly-synthesized triple Cs*R*Ti$_{0.5}$(WO$_4$)$_3$ (*R* = Al, Cr) tungstates were determined.

2. Models and Methods

The Cs*R*Ti$_{0.5}$(WO$_4$)$_3$ (*R*= Al, Cr) tungstates were synthesized via a solid state reaction method. The used starting materials were Cs$_2$CO$_3$, Al$_2$(WO$_4$)$_3$, Fe(NO$_3$)$_3$·9H$_2$O Cr$_2$O$_3$, TiO$_2$ and WO$_3$ (all of chemical grade). Starting simple tungstate Cs$_2$WO$_4$ were obtained by gradual annealing of stoichiometric mixtures of Cs$_2$CO$_3$ and WO$_3$ at 673–773 K. For the synthesis, industrial aluminum tungstate was used. X-ray powder diffraction (XRD) measurements were performed on a Bruker D8 Advance diffractometer with Eva software package (CuKα radiation, secondary monochromator, 2θ range 8–100°).

Differential scanning calorimetry (DSC) was carried out on a NETZSCH STA 449 C (Jupiter) thermal analyzer (sample mass ~ 20 mg, argon atmosphere, platinum crucibles, heating and cooling rate – 10 K/min). The temperature and frequency dependences of the dielectric parameters of Cs*R*Ti$_{0.5}$(WO$_4$)$_3$ (*R*= Al, Cr) ceramic samples were studied in the temperature range 473–1023 K using impedance meter «Z-1500J» in heating and cooling modes (2 K/min) at frequency in the 1 Hz–1 MHz range. Tablets for measurements were prepared by pressing of powder phase under pressure of 10 MPa and applying platinum electrodes by burning platinum paste.

3. Results and Discussion

Polycrystalline powders $CsRTi_{0.5}(WO_4)_3$ (R= Al, Cr) were prepared by a conventional solid state method from a stoichiometric mixture of tungstates, nitrates and oxides at 673–1023 K. Stepwise annealing of the reagents with homogenization of the mixture every 50 K was carried out for 200–300 hours. The final temperature for the synthesis of tungstates was 1023 K. According to XRD powder data, the diffractograms do not contain the lines of the starting compounds, possible double tungstates and polytungstates (Figure 1). The single phase of the obtained samples was established. The powder diffraction data were preliminarily assigned to hexagonal system.

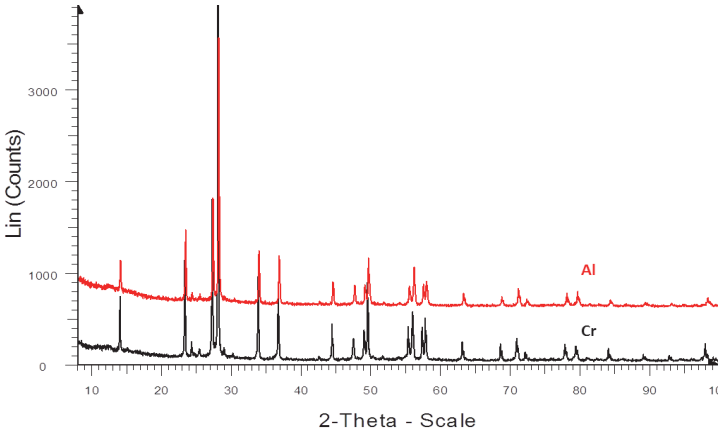

Figure 1. XRD patterns of $CsRTi_{0.5}(WO_4)_3$ (R= Al, Cr) tungstates.

The DSC curves recorded for polycrystalline powders of $CsRTi_{0.5}(WO_4)_3$ (R= Al, Cr) are shown in Figure 2. The endothermic peaks at 1302 and 1380 K corresponds to the melting points of $CsAlTi_{0.5}(WO_4)_3$ and $CsCrTi_{0.5}(WO_4)_3$, respectively. The melting temperature increases with increasing the ionic radius of the trivalent element.

The investigations revealed that $CsCrTi_{0.5}(WO_4)_3$ shows interesting dielectric behavior. Figures 3a, b shows Arrhenius plots of conductivity log σ (1/T) in heating and cooling modes. At low temperatures (T < 800 K) the conductivity log σ (1/T) depends on frequency. At high temperature region heating and cooling plots are well represented by straight lines, that demonstrating thermally activated process of conduction. The thermally dependences of conductivity undergoes a jump by approximately 4–5 orders of magnitude with an activation energy Ea = 0.4–0.6 eV at high temperatures.

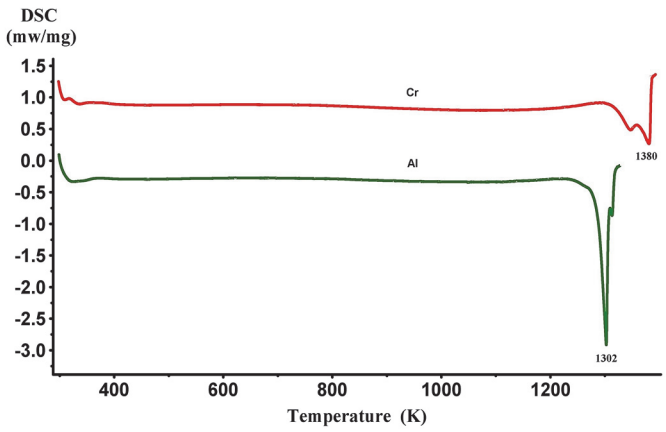

Figure 2. DSC-curves of $CsRTi_{0.5}(WO_4)_3$ (R = Al, Cr).

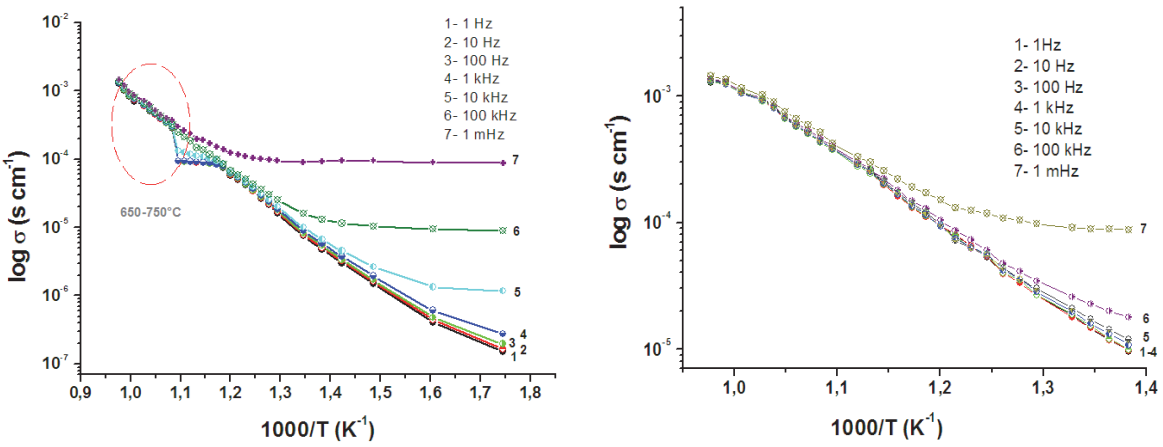

Figure 3. The temperature dependences of conductivity for $CsCrTi_{0.5}(WO_4)_3$ in heating (*a*) and cooling (*b*) modes at different frequencies.

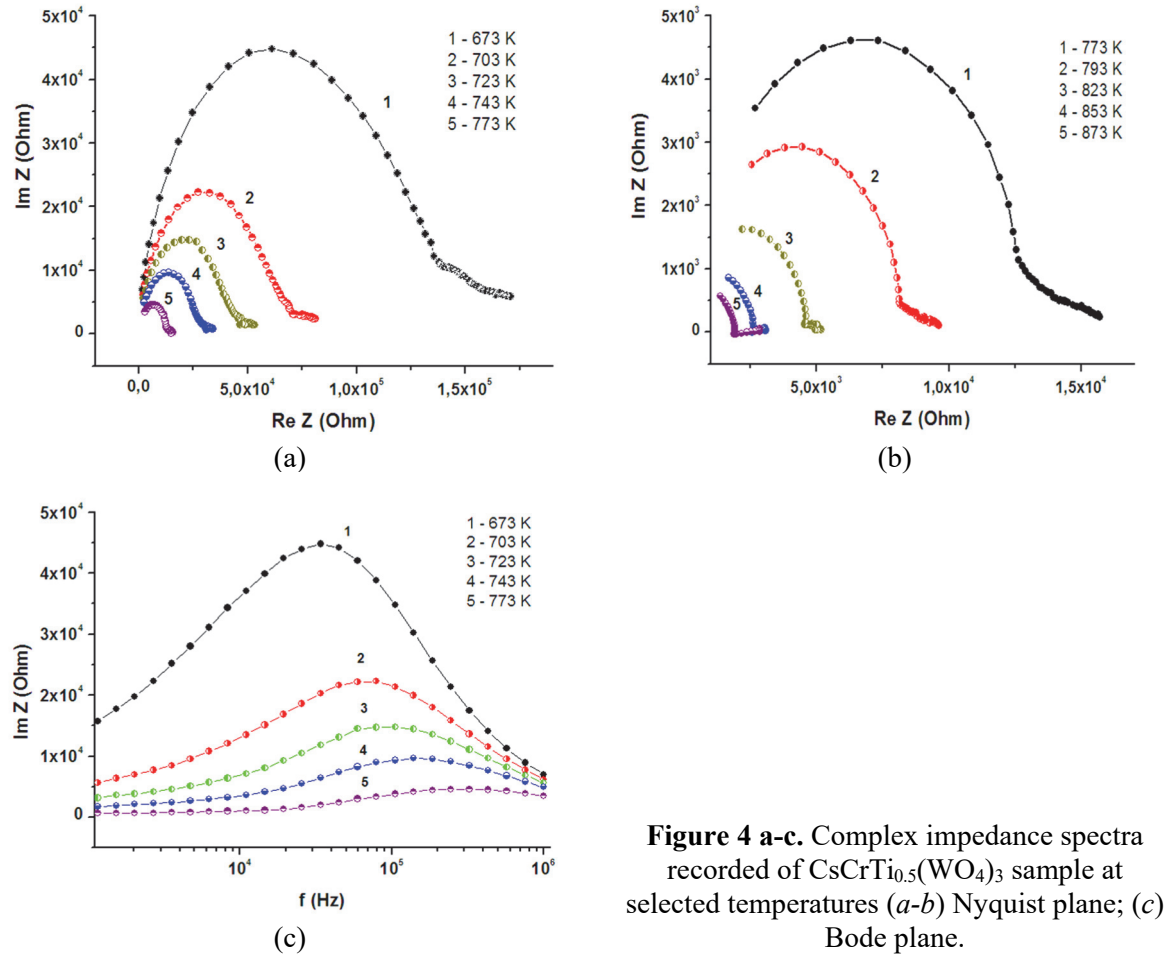

Figure 4 a-c. Complex impedance spectra recorded of $CsCrTi_{0.5}(WO_4)_3$ sample at selected temperatures (*a-b*) Nyquist plane; (*c*) Bode plane.

The Nyquist plots for $CsCrTi_{0.5}(WO_4)_3$ sample at different temperatures are shown in Figure 4 a-b. In Figure 4a, the impedance responses are similar, which consist of a semicircle at high frequency region and a sloping line at low frequency region. The high frequency semicircle decreases with increasing temperature (Figure 4 b).

Figure 4 c shows the frequency dependences of the imaginary part of the complex resistance *Im Z* at different temperatures. The measurements were performed in the frequency range f = 1 Hz to 1 MHz. It can be seen, that as the temperature increases, the *Im Z (f)* curves monotonically shift downward, the resistance value changes from ~ 10^4 Ohm to 100 Ohm. The maximum on the dependence *Im Z (f)* initially decreases in magnitude, and then almost disappears at T = 773 K. At the same time, the maximum is shifted to higher frequencies.

4. Conclusion

In this work, a new cesium-titanium tungstates $CsRTi_{0.5}(WO_4)_3$ (*R*= Al, Cr) were synthesized by solid state reaction. The electrical conductivity is rather high, $0.11*10^{-2}$ $S \cdot cm^{-1}$ at high temperature region (973–1023 K) and the Arrhenius energy activation is 0.4–0.6 eV. In high frequency domain, the impedance diagrams show typical semicircle. The nature of the temperature and frequency curves of dielectric parameters, obtained values of conductivity and energy activation reveal that the prevailing ionic conductivity of $CsCrTi_{0.5}(WO_4)_3$ compound is probably ensured by cations. The *Ea* values obtained in this study approach those reported for ceramics [13–16] and correspond to thermally activated conductors. The present results suggest that the synthesized tungstates studied here are potentially attractive for high temperature dielectric materials engineering.

Acknowledgments

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