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Microstructure and conductivity evolution in Bi_2CuO_4–Bi_2O_3 and Bi_2MoO_6–$Bi_2Mo_2O_9$ oxide composites nearby eutectic temperatures

Nikolay V. Lyskov,*[a] Yuri G. Metlin,[b] Daria V. Vinogradova[b] and Yuri D. Tretyakov[a,b]

[a] *Department of Materials Science, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation.*
Fax: +7 095 939 0998; e-mail: lyskov@inorg.chem.msu.ru
[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation*

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The enhance of electrical conductivity at the eutectic temperature was attended with a thermally reversible microstructural change of composites, expressed by redistribution of an eutectic liquid between triple grain junctions (at cooling) and grain boundaries (at heating).

Inorganic materials with mixed ionic and electronic conductivity are of interest because of their applications in non-polluting electrochemical devices, membranes for oxygen separation and conversion of methane in syngas.[1–3] The combining of two phases, one of which has electronic conductivity, while the other is an ionic conductor, is an advantageous approach. Our research is concerned with Bi_2CuO_4–Bi_2O_3 and Bi_2MoO_6–$Bi_2Mo_2O_9$ ceramic composites. At the eutectic temperature, these compounds form composite structures consisted of grains (with electron-ionic conductivity) and liquid channels (with high ionic conductivity) located at the grain boundaries. In this work, the microstructure evolution and the electrical conductivity of composites were examined in order to reveal the processes that take place nearby the eutectic temperature.

The Bi_2CuO_4 + (12 and 23) mol% Bi_2O_3 and Bi_2MoO_6 + (8 and 22) mol% MoO_3 composites were prepared from Bi_2CuO_4, Bi_2O_3, Bi_2MoO_6 and MoO_3 powders using a conventional ceramic technique. Bi_2CuO_4 and Bi_2MoO_6 were synthesised by solid-state reactions using Bi_2O_3, MoO_3 and CuO (reactive grade) as initial reagents. The sintering was carried out for 30 h in air at 700 °C for Bi_2CuO_4 and at 600 °C for Bi_2MoO_6. The formation of single-phase Bi_2CuO_4 and Bi_2MoO_6 powders was confirmed by X-ray powder diffraction. Then, the powders of Bi_2CuO_4 and Bi_2MoO_6 were mechanically mixed with Bi_2O_3 and MoO_3 and thoroughly reground in an agate mortar in acetone for 1 h. In order to increase the density of composite ceramics, polyvinyl alcohol was added to the oxide mixtures. After that, the mixtures were compacted into rectangular bars (4×10×2 mm) at a uniaxial pressure of about 3000 kg cm^{-2}. The sintering of Bi_2CuO_4–Bi_2O_3 and Bi_2MoO_6–$Bi_2Mo_2O_9$ composites was carried out in air for 10 h at 700 and 630 °C, respectively. The densities of the Bi_2CuO_4 + (12 and 23) mol% Bi_2O_3 composites were 6.60 and 6.90 g cm^{-3}, respectively, whereas the densities of Bi_2MoO_6 + (8 and 22) mol% MoO_3 were 6.00 g cm^{-3} and 5.82 g cm^{-3}, respectively.

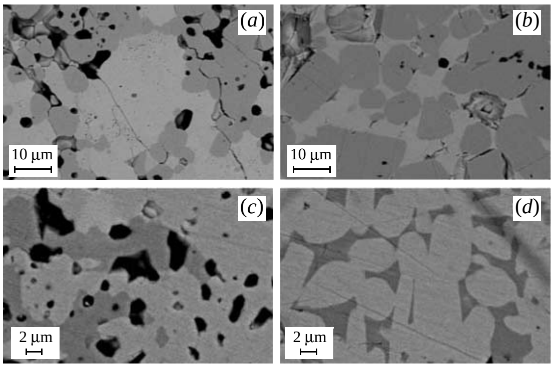

Figure 1 SEM micrographs of a Bi_2CuO_4 + 23 mol% Bi_2O_3 composite after quenching from (*a*) 770 and (*b*) 775 °C (dark, light and black areas correspond to Bi_2CuO_4, Bi_2O_3 and pores, respectively) and a Bi_2MoO_6 + 22 mol% MoO_3 composite after quenching from (*c*) 670 and (*d*) 690 °C (light, dark and black areas correspond to Bi_2MoO_6, $Bi_2Mo_2O_9$ and pores, respectively).

To study the microstructure evolution in Bi_2CuO_4–Bi_2O_3 and Bi_2MoO_6–$Bi_2Mo_2O_9$ systems nearby the eutectic temperatures (770[4] and 682 °C,[5] respectively), the ceramic samples were rapidly heated to temperatures below and above the eutectic point and immediately quenched in air. The polished cross-sections of ceramic composites were studied by scanning electron microscopy (LEO Supra 50VP). The microstructure of Bi_2CuO_4–Bi_2O_3 composites quenched from temperatures below the eutectic point is characterised by a random distribution of Bi_2O_3 over the ceramic bulk. However, another situation was observed in the samples quenched from temperatures slightly above the eutectic temperature. Bi_2O_3 is localised at triple grain junctions and some grain boundaries of Bi_2CuO_4. Figure 1(*a*),(*b*) shows the SEM micrographs, which illustrate the redistribution of Bi_2O_3 in the Bi_2CuO_4–Bi_2O_3 composite. A similar situation was observed in the Bi_2MoO_6–$Bi_2Mo_2O_9$ system, where a $Bi_2Mo_2O_9$ phase redistributes over the composite [Figure 1(*c*),(*d*)]. This evolution in the location of a minor phase is most likely caused by grain boundaries wetting and liquid channel structure formation.

The conductivity *vs*. temperature measurements of Bi_2CuO_4–Bi_2O_3 and Bi_2MoO_6–$Bi_2Mo_2O_9$ composites were performed by a four-point DC technique and two-point AC impedance

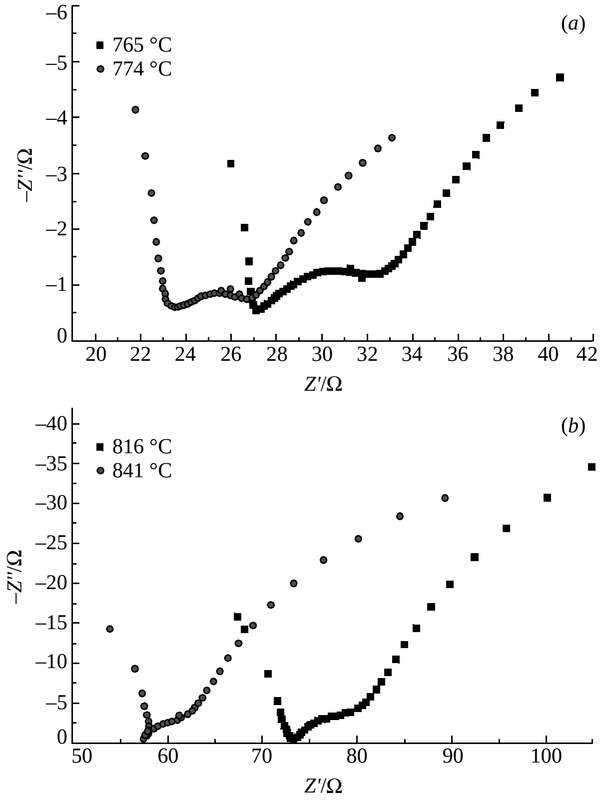

Figure 2 Impedance spectra of (*a*) Bi_2CuO_4 + 23 mol% Bi_2O_3 and (*b*) Bi_2MoO_6 + 22 mol% MoO_3 composites.

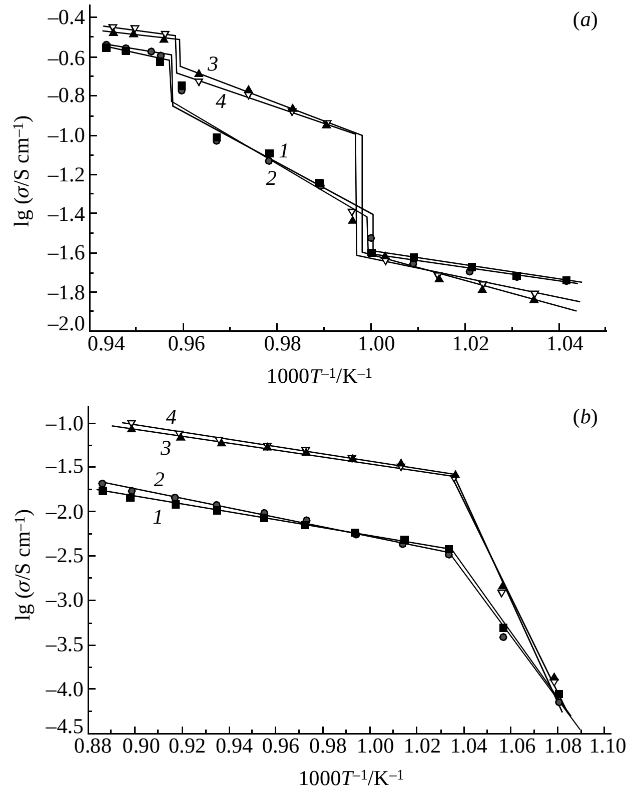

Figure 3 Total conductivity of Bi_2CuO_4–Bi_2O_3 and Bi_2MoO_6–$Bi_2Mo_2O_9$ composites obtained by (*1*, *3*) a four-point DC technique and (*2*, *4*) two-point AC impedance spectroscopy: (*a*) Bi_2CuO_4 + 12 mol% Bi_2O_3 (*1*, *2*) and Bi_2CuO_4 + 23 mol% Bi_2O_3 (*3*, *4*) composites; (*b*) Bi_2MoO_6 + 8 mol% MoO_3 (*1*, *2*) and Bi_2MoO_6 + 22 mol% MoO_3 (*3*, *4*).

spectroscopy in air using the rectangular bars of samples. The DC measurements were carried out on a Solatron SI 1287 potentiostate/galvanostate in a potentiostatic mode. The AC impedance measurements were made using a Solatron SI 1255B frequency response analyser in the frequency range 1 Hz–1 MHz at a signal voltage of 100 mV.

To study the conductivity, the impedance spectra of Bi_2CuO_4–Bi_2O_3 and Bi_2MoO_6–$Bi_2Mo_2O_9$ composites were measured as a function of frequency, and the results were plotted on a complex plane (Figure 2). We found that the spectra exhibit three semicircles. The high frequency semicircle is attributed to the grain interior. It overlaps with the grain boundary semicircle in the mid-frequency range. Finally, the beginning of the third semicircle attributed to the Pt electrode signal becomes visible at the low frequency end.

The results of electrical conductivity measurements in Bi_2CuO_4–Bi_2O_3 and Bi_2MoO_6–$Bi_2Mo_2O_9$ composites are shown in Figure 3. In order to demonstrate that the conductivity variations cannot be attributed to possible chemical reactions, we present one plot with the conductivity–time relationships for Bi_2CuO_4 + 23 mol% Bi_2O_3 at 773 °C and Bi_2MoO_6 + 22 mol% MoO_3 at 714 °C (Figure 4). One can see that the conductivity variations are negligible, and they cannot be a result of possible chemical reactions with other materials (*e.g.*, crucibles, holders for conductivity measurements, *etc*.).

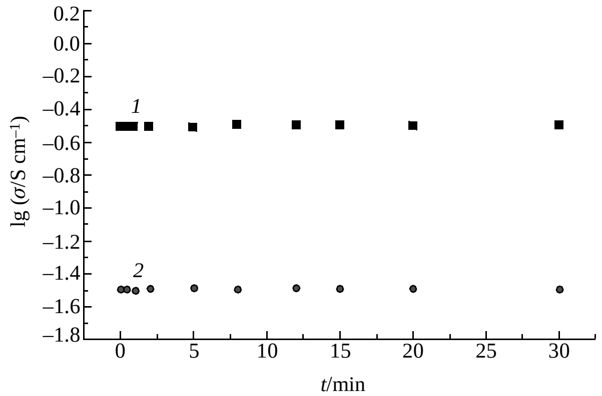

Figure 4 Conductivity *vs*. time for (*1*) Bi_2CuO_4 + 23 mol% Bi_2O_3 at 773 °C and (*2*) Bi_2MoO_6 + 22 mol% MoO_3 at 714 °C (four-point DC technique).

The data obtained by a four-point DC technique and two-point AC impedance spectroscopy are in good agreement with each other. The temperature dependence of conductivity exhibits a thermally activated behaviour. The conductivities of Bi_2CuO_4–Bi_2O_3 composites [Figure 3(*a*)] in the temperature range 690–730 °C are similar because the main contribution to the total conductivity is given by the electronic conductivity of Bi_2CuO_4.[6] In the temperature range 730–770 °C, where δ-Bi_2O_3 modification exists, the contribution of oxygen-ion conductivity to the total conductivity becomes considerable,[7] and the conductivity of composites increases. Finally, in the temperature range 770–790 °C, the conductivity increases due to eutectic liquid occurrence and liquid channel structure formation. The two jumps on the curve of conductivity *vs*. temperature at about 730 and 770 °C can be explained as described below. The first is caused by the α→δ Bi_2O_3 polymorphic transition accompanied by a sharp increase in the oxygen ion conductivity.[7] The second is caused by grain boundary wetting by an eutectic liquid.

The conductivity of Bi_2MoO_6–$Bi_2Mo_2O_9$ composites [Figure 3(*b*)] above the eutectic point (682 °C) is several times higher than the conductivity of solid-state composites before liquid channel structure formation. This is caused by liquid phase formation, as well as by the appearance of high-temperature γ-Bi_2MoO_6 modification, which has a high oxygen-ion conductivity.[8] The enhanced conductivity of the composite with a higher MoO_3 content resulted from a larger amount of liquid phase at the eutectic temperature.

Thus, the conductivity jump observed in Bi_2CuO_4–Bi_2O_3 and break in Bi_2MoO_6–$Bi_2Mo_2O_9$ composite at the eutectic temperature supports the processes of grain boundary wetting and liquid channel structure formation. These processes are advantageous and enhance the electrical conductivity of materials with mixed electron-ionic conductivity.

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