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Microstructure of Ag_2BI_4 ($\text{B} = \text{Ag}, \text{Cd}$) superionics studied by SEM, impedance spectroscopy and fractal dimension analysis

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Abstract

Two silver ion conducting solid electrolytes, Ag_2HgI_4 and Ag_2CdI_4 , representing a wide class of AgI-based halogenide superionics have been the subjects of study by means of electrical impedance spectroscopy, SEM, porosity measurements and fractal dimension analysis. Even though both materials have been obtained by the same method under strictly identical conditions they were found to exhibit certain differences at the microstructural level. Thus, by the direct measurements of porosity and density it was found that the grain boundaries are better developed in silver mercuric iodide. On the assumption that pore geometry in the materials under study displays fractal character it was shown that the fractal dimension of the pore contours is larger in the case of Ag_2HgI_4 . These results are in agreement with electrical studies which indicated that the grain boundary capacitance in Ag_2CdI_4 is two orders of magnitude smaller than that of the silver mercuric iodide.

1. Introduction

Many superionic compounds including those belonging to the Ag_2BI_4 group ($\text{B} = \text{Pb}, \text{Cd}, \text{Hg}$, etc) are usually obtained by means of ceramic technology [1–4]. As a consequence, they possess a specific microstructure formed by the combination of crystalline grains and intergranular space. The question about the influence of grain volume to intergrain space volume ratio on conductive, thermal and other physical properties of polycrystalline materials attracted significant attention [5, 6] which is now renewed due to the observations of specific features of crystalline grains at the nanoscale [7]. Thus, methods developed in the last ten years allow for obtaining nanostructured superionics which exhibit essentially higher values of electrical (ionic) conductivity [8, 9]. But another, also interesting, aspect is related to the fact that the smaller

the size of crystalline grains is the more developed is the grain boundary structure and, respectively, the pore morphology. Intensive studies of various porous ceramics indicated that the surface morphology in this type of disordered media can often be considered fractal in nature [10, 11]. In this sense it is very interesting to have an insight into the relationship between the parameters of such a fractal structure and the behavior of different physical properties of the material.

In the present paper we provide the consolidated analysis of scanning electron microscopy (SEM), electrical impedance spectroscopy, density/porosity measurement data and fractal dimension calculation results carried out for Ag_2CdI_4 and Ag_2HgI_4 (silver mercuric iodide) compounds. Our aim was to study the distinctions between the microstructure of these superionic materials, being prepared by the same technology and under strictly identical conditions, and to draw correlations

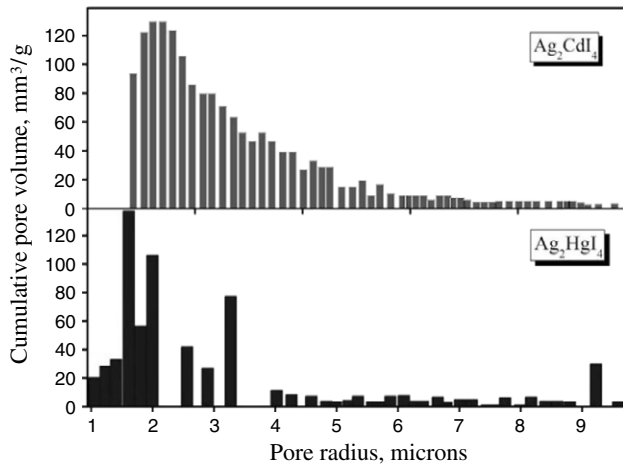


Figure 1. Pore distribution in Ag_2CdI_4 and Ag_2HgI_4 .

between the pore structure, its fractal character and electrical properties.

2. Experimental details

Bulk samples of Ag_2CdI_4 and Ag_2HgI_4 were obtained by means of solid state chemical reactions. More details on the preparation method can be found elsewhere [12]. Electrical impedance spectroscopy was carried out using an automated set-up on the basis of a Schlumberger 1260 amplitude-phase analyzer (for details see [13]). Electrical measurements covered the frequency range $10\text{--}10^6$ Hz and were performed at different temperatures, starting from 300 K up to $T > T_c$, where T_c denotes the superionic phase transition temperature for the respective material (nearly 400 K for Ag_2CdI_4 [14] and ~ 326 K in the case of Ag_2HgI_4 [15]). The perturbation signal magnitude was 0.1 V, that is, small enough to ensure the linear response of the samples. A JSM-T 220A scanning electron microscope was used to obtain 2D images of the porous structure. In order to measure the fractal dimension of the porous surface the classic box-counting algorithm, recently demonstrated to be effective for the analysis of the nanofractal structure of particles [16], was adopted; further peculiarities of the performed calculations are discussed below. Porosity measurements were performed with a Pascal 140 instrument, coupled to the PC for data handling. Since the mercury intrusion technique used in this instrument is destructive, the porosity measurements were the final experiments on the investigated samples.

3. X-ray diffraction, porosity and density

X-ray diffraction study confirmed the formation of tetragonal Ag_2HgI_4 (unit cell parameters $a = 6.33 \text{ \AA}$, $c = 12.62 \text{ \AA}$) and Ag_2CdI_4 (unit cell parameters $a = 6.35 \text{ \AA}$, $c = 12.68 \text{ \AA}$). The values of lattice parameters were used to estimate the x-ray density (ρ_{xr}) of both compounds. Considering that the unit cell volume is $V = a^2c$ and there are two molecules per unit cell we obtained the ρ_{xr} values, listed in table 1. Samples of both materials are porous, hence their real density is expected to be

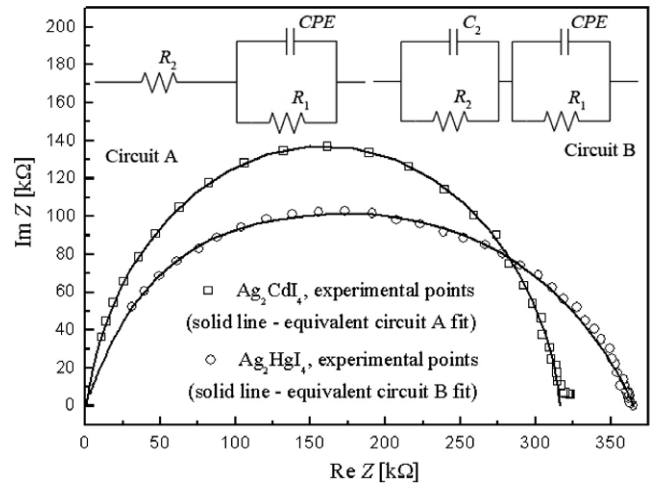


Figure 2. Typical complex impedance plots obtained in the experiment for the low-temperature phases of Ag_2CdI_4 and Ag_2HgI_4 (circles and squares) and fitting curves calculated on the basis of the respective equivalent circuit models.

Table 1. X-ray densities and real densities of the investigated bulk samples of solid electrolytes.

Compound	X-ray density ρ_{xr} (kg m^{-3})	Measured density ρ_{ex} (kg m^{-3})
Ag_2CdI_4	5.605×10^3	4.6×10^3
Ag_2HgI_4	6.097×10^3	3.1×10^3

smaller than that predicted theoretically. This has been proved in the porosity measurements which also allow for estimating the real sample density. The deviation of the experimentally measured density ρ_{ex} from the theoretical one can be clearly seen from table 1. Noticeable differences between ρ_{xr} and ρ_{ex} exist for both materials, being larger in the case of Ag_2HgI_4 .

Possibly the larger deviation of the real density from the theoretically estimated value for Ag_2HgI_4 may be due to the relatively large ($\sim 10 \mu\text{m}$) pores. According to the pore distribution which is shown in figure 1, these larger pores are not observed in Ag_2CdI_4 , but are present in the samples of silver mercuric iodide.

It should also be mentioned that the distribution of pores is much less homogeneous in the case of Ag_2HgI_4 . Large pores and the character of pore distribution might be responsible for the intergrain capacitance. In order to check this we used the most appropriate technique which allows for probing the electrical properties of superionics—electrical impedance spectroscopy [17].

4. Electrical studies

The goal of the electrical studies was in constructing the models of electrical transport, i.e. the equivalent circuits for both materials and estimating the parameters of these circuits, obtaining the quantities characterizing the conduction processes in the investigated compounds. Typical complex impedance spectra (Nyquist plots) recorded for both solid electrolytes at $T < T_c$ are presented in figure 2. Although there

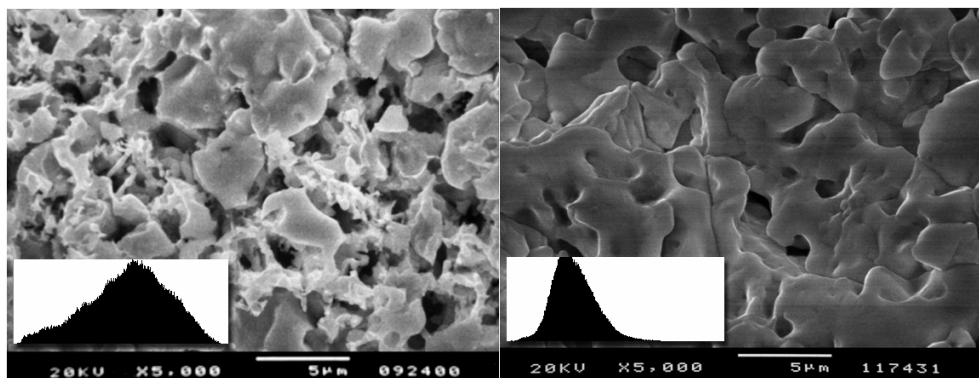


Figure 3. Parts of the cross-sectional micrographs of Ag₂HgI₄ (left) and Ag₂CdI₄ (right) samples (256 gray levels). Insets show the respective histograms.

exist several possible electrical circuits for which one obtains impedance spectra similar to those of the measured objects, not all of them are physically meaningful. Thus, to model the electrical behavior of the samples, additional considerations are needed. In our case, it is reasonable to suggest that the electrical model should consist of two parts, one describing the ionic transport in the bulk and the other being responsible for the conductivity in the intergrain volume. This suggestion has eventually led to the models shown in the upper part of figure 2. An additional factor in favor of the proposed models is concerned with the temperature dependence of the measured spectra: it was verified that, in order to model the experimental spectra recorded at different temperatures (in the same phase of the material), it is enough just to change the parameters of the proposed circuit but there is no need for adding or removing circuit elements.

From the constructed circuits marked as A and B two basic contributions (intergrain and intragrain) to the total ionic conductivity can be separated. The bulk conductivity in both cases is modeled as a parallel connection of the resistor and the constant phase element (CPE). The grain boundary contribution appears as an additional resistance in the case of Ag₂CdI₄ and as the parallel sub-circuit consisting of resistor and capacitor in the case of silver mercuric iodide. Relevant parameters of the equivalent circuits have been analyzed in a different report [18]: here, we would only like to mention that the activation energies for the ionic conductivity of Ag₂CdI₄ and Ag₂HgI₄ estimated on the basis of our temperature measurements are 0.95 eV (temperature range 300–400 K) and 0.56 eV (temperature range 290–320 K), respectively. In this work we restrict ourselves to outlining the grain boundary contribution which essentially distinguishes between the isostructural samples treated identically during the preparation process. As it follows from circuit A, the intergrain capacitance is either absent or negligibly small (of the order 10⁻¹³ F which is smaller than the error of the instrument) in Ag₂CdI₄. This capacity (C_2) in circuit B equals approximately 9 pF at room temperature, which is almost two orders of magnitude smaller than in the previous case. Thus impedance spectroscopy results give another experimental evidence (in addition to the direct porosity measurements) of the specific

features of the pore geometry in each of the investigated materials.

5. SEM and fractal dimension

Further insight into the microstructure was made utilizing scanning electron microscopy. We inspected the surfaces of both Ag₂CdI₄ and Ag₂HgI₄ in the reflected electron beam with an energy of 20 keV. Original cross-sectional SEM images of both samples under study are shown in figure 3. Here, pores are clearly visible as dark areas while the edges of the crystalline grains are essentially bright. It is worth noticing that during the solid state synthesis of Ag₂CdI₄ a small amount of AgI phase is segregated, localizing in the form of clusters at the edges of grains. Contamination of the silver iodide phase may lead to the appearance of darker regions in the micrograph of Ag₂CdI₄. This is reflected in the histogram for this material. Rough estimates of the average pore sizes based on the SEM observations are in agreement with distributions obtained from the porosity measurements.

Geometric irregularities and self-similarity as characteristic features of the pore morphology are often described by fractal dimension parameters. The concept of fractals and possible applications for surface analysis have been developed by Mandelbrot [19, 20]. In later studies it was proved to be a useful tool for the description of pore geometry [21, 22]. Hereafter we present the results of the analysis carried out in the realm of the fractal approach.

First, two square areas (768 × 768 pixels) of the respective micrographs obtained at the same level of magnification have been selected. Then we applied some digital image processing procedures to remove the noise and enhance the quality of the images. Next, in order to detect more clearly pore contours, processed images were transformed into binary ones. The described procedure is depicted in stages in figure 4. The important point here is the transformation from the grayscale image, where each pixel has brightness value P ranging from 0 to 255, to the binary image in which each pixel is either black ($P = 0$) or white ($P = 255$). Inasmuch as the result of such a transformation depends substantially on the brightness threshold (pixels having the brightness value below

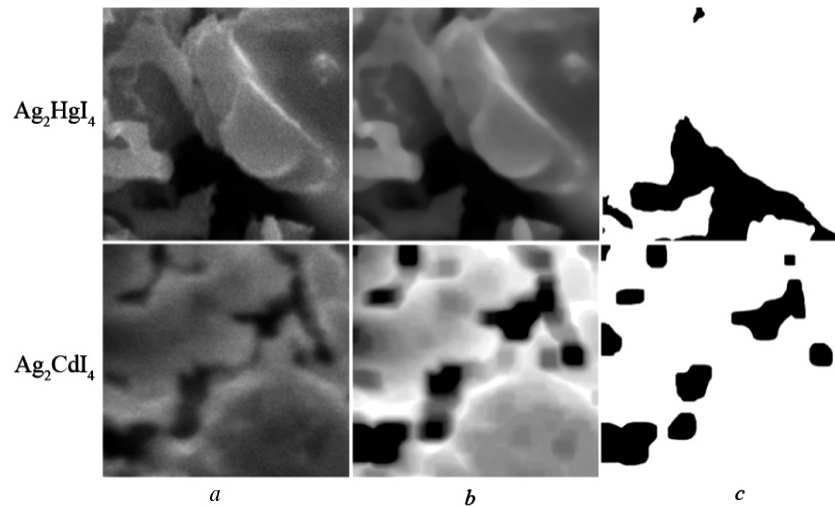


Figure 4. SEM image processing for the detection of pore contours: *a*—input image, *b*—processed image, *c*—binary image (black pixels represent pores).

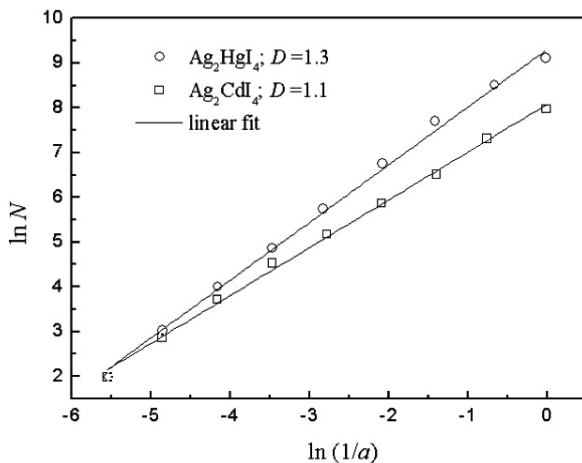


Figure 5. Logarithmic plots for the determination of the fractal dimensions of pore contours.

the threshold limit are changed to black, the rest are considered white), the eventual threshold was adjusted in order to achieve the best visual resemblance between the pore morphology in the binarized images and in the original SEM micrographs.

Finally, we obtained the fractal dimension of both porous structures by means of box-counting as the slope D of the line $\ln N = D \ln(1/a)$, where N denotes the box size and N is the number of boundary pixels, which means pixels which are found on the bulk/pore edge. The respective linear plots are shown in figure 5. It has to be emphasized that D values obtained characterize the contours formed by pores, not by the crystalline grains, therefore the higher level of the intergrain structure evolution in the material should give rise to a larger fractal dimension.

It has been found that there is a clear difference in fractal dimension values for Ag_2HgI_4 (1.3) and Ag_2CdI_4 (1.1). This clarifies that the porous structure is more developed in silver mercuric iodide and the geometry of pores in this material as well as their size can also contribute to the conductivity mechanism.

6. Conclusion

Several complementary techniques have been employed to study microstructural properties of Ag_2HgI_4 and Ag_2CdI_4 superionics obtained by the same synthesis process. By direct and indirect methods it was shown that the level of intergrain porous structure development is higher in the samples of silver mercuric iodide. Electrical equivalent circuits which model the electrical transport in both materials have been constructed using the results of electrical ac measurements. Differences in the equivalent circuits support the inference drawn on the basis of the porosity and density measurements and agree with the calculations of fractal dimension which is larger for the pore contours in Ag_2HgI_4 .

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