Structure and properties of rapidly quenched ionic conductors belonging to AgI-Ag$_2$MoO$_4$ family

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Abstract. AgI-Ag$_2$MoO$_4$ materials were obtained by rapid quenching method. Their structures were investigated by X-ray spectroscopy and Scanning Electron Microscopy (SEM). Additionally the compressibility of the amorphous samples was investigated. A relation between electrical and mechanical properties was suggested. It was also found that short range order of amorphous samples changes with composition.

1. Introduction

Materials described by formulae AgI-Ag$_2$MoO$_4$ belong to class of solid states referred as superionic conductors. Superionic conductors are solid bodies which exhibit electrical conductivity comparable to fluid electrolytes and semiconductors [1,2]. The main difference between ionic conductors and semiconductors is that electrical conductivity in ionic conductors is a result of ion movements while in semiconductors electrical conductivity is a result of electron drift. Because ions have a meaningful volume materials which show high ionic conductivity must have special structure. Special structure means that so called conducting channels must be present. While confirmation of their existence in crystalline materials seems relatively simple by x-ray measurements in case of amorphous ones such tasks become more complicated. AgI-Ag$_2$MoO$_4$ materials are a member of a wider group referred as an oxide based ionic conductors [3,4]. Such materials can be obtained by rapid quenching from liquid phase. As a result of such process homogenous glass or two face system with crystalline precipitates can be obtained. So far most research concentrated on glassy materials [5,6]. This is caused by the fact that glassy material have the highest conductivity and have the bigger application potential. However in order to understand properties of glassy materials knowledge of properties of materials with precipitates can be useful. Even when considering glassy material there are still important interesting properties which should be studied. So far mainly electrical properties of this materials were investigated but to understand the conduction mechanism in this material also mechanical properties should be taken into account. The aim of this work is to present some wider spectrum of investigated materials and find correlation between their mechanical and electrical properties. The materials of the discussed family differ by the percentage of AgI so the general formula can be written as xAgI-(1-x)(Ag$_2$MoO$_4$).
2. Experimental Details
As a starting material AgI, Ag₂O MoO₃ provided by Sigmaaldrich were used. Suitable amounts of raw materials were grinded in an agate mortar, placed in a ceramic crucible, and heated up to 800 °C for 1 hour than they were rapidly quenched between two metal plates. Structure was analyzed by SEM microscopy, X-ray diffraction. Compressibility was measured by special high pressure technique described in [7].

3. Results and Discussions
Results of SEM observation of fractures of investigated materials are presented on figure 1. One can see that in case of small value of x<0.4 (Figure 1A) the structure of the material is very complicated. Apart from glassy component it contains octahedral microcrystalline precipitates. This small crystals are linked together forming a columnar structure. Another interesting feature of this structure is the presence of empty space – pores. Presence of such pores is responsible for the lowered conductivity of the described material. In order to get some information about nature of the crystalline precipitates X-ray scattering were done. X-ray pattern show presence of many peaks which was the proof that precipitates have crystalline structure with low symmetry [8]. It was found that precipitates were build of Ag₂MoO₄ crystals. For materials with medium concentration of AgI 0.4<x<0.8 homogenous structures without pores or precipitates were found (figure 1B). Structure of samples with high amounts of AgI is presented on figure 1C. In this structures precipitations are observed, but there are no voids. In order to elucidate internal structure of homogenous phase pair distribution function was measured for samples for which x=0.6; x=0.7 and x=0.8. Results are presented on figure 2 and in table 1. On analysis of the data presented there one can conclude that short range arrangement are changing on the dependence of AgI concentration expressed by the x value. The most sharp with three visible maxima seems to be the pair distribution function obtained for x=0.6. In the case of sample of x=0.8 the third peak is weakly visible. One should stress that with increasing AgI content position distances between the maximums increases and the positions are becoming similar to positions of peaks for the high ionic conducting phase of αAgI. One should conclude that with increase of AgI interatomic distances are becoming bigger and the structure more irregular. Changes of interatomic distances should also influence the mechanical properties of the investigated materials. In order to check whether such situation takes place we have measured Compression modulus of elasticity of amorphous samples. Results of measurements are presented on figure 3.
Figure 1. SEM observation of AgI-Ag$_2$MoO$_4$ materials A) 0.3AgI-0.7Ag$_2$MoO$_4$ B) 0.8AgI-0.2Ag$_2$MoO$_4$ C) 0.95AgI-0.05Ag$_2$MoO$_4$.

Figure 2. Pair distribution function measured for x=0.6; x=0.7; x=0.8

| x    | First maximum | Second maximum | Third maximum | Distance between first and second maximum | Distance between first and third maximum | Relation between peak high h2/h1 |
|------|---------------|----------------|--------------|------------------------------------------|-----------------------------------------|-------------------------------|
| 0.6  | 2.945         | 3.74           | 6.38         | 0.79                                     | 3.435                                   | 0.83                          |
| 0.7  | 2.91          | 3.77           | 6.44         | 0.86                                     | 3.53                                    | 0.58                          |
| 0.8  | 2.883         | 4.26           | 6.74         | 1.37                                     | 3.857                                   | 0.42                          |
| $\alpha$-cubic | 2.82          | 4.60           | 5.40         | 1.78                                     | 2.58                                    | 1.03                          |

Table 1. Characteristic feature of pair distribution function obtained for samples with different x, h1 - the high of first maximum, h2 - the high of second maximum.
As one can see the compression modulus of elasticity (compressibility) increases with AgI content. It is known that materials with higher inter-atomic distances have bigger compression modulus of elasticity. Using this relation one can also drive conclusion about the relation between compressibility and conductivity. One the most important parameter which describes ionic conductivity is an activation energy - $E_a$. According to free volume theory [8] $E_a$ is a measure of the energy which a movable atom needs to push aside its neighbors. The bigger the inter-atomic distance is the lower $E_a$. Such relation is perfectly fulfilled in amorphous materials belonging to AgI-Ag$_2$MoO$_4$ family. So materials with big compression modulus of elasticity usually have high ionic conductivity. In work described here also materials with big amount of AgI were studied $x>0.9$. The structure of such materials loses its homogeneity (Figure 1C). One can distinguish presence of glassy phase and some precipitates. X-ray investigation showed that this precipitates are formed of so called $\beta$ AgI which is electrically isolating both for ions and electrons. The presence of such precipitates blocks channels of conductivity which leads to rapid decrease in conductivity [9].

4. Conclusions
Properties of AgI-Ag$_2$MoO$_4$ pseudo binary system were investigated. It was found that investigated materials show at least three different types of structure depending on AgI content. Short range order of amorphous samples were also investigated. It was found that with increase of AgI the structure becomes more disordered. Compressibility investigation allowed to find relation between compressibility and activation energy. It was found that increase of compression modulus of elasticity is usually accompanied by decrease of activation energy. This findings are in agreement with free volume theory.

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