PREPARATION AND CHARACTERIZATION OF CuInSe₂-CuAlSe₂, CuInS₂ AND ZnS NANOPOWDER BY MECHANICAL ALLOYING TECHNIQUE

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CuIn_{1-x}Al_xSe₂, CuInS₂ and ZnS chalcogenide semiconductors nano powder were prepared by simple and low cost technique. CuIn_{1-x}Al_xSe₂ with wide composition range 0.2-1.0 were milled for 40-50 min in a stainless steel veal of the ball mill which produces homogeneous nano powder. CuInS₂ was also prepared easily within the same preparation conditions while ZnS took longer time. All the prepared nano powder were characterized and identified by XRD with the aid of data bank ICDDView 2006 showing that the prepared materials structure agree well with those in standard cards. High reactive materials as well as high vapor pressure materials can be prepared by this technique instead of thermal methods. Besides, low cost and shorter time are required. Smaller crystallite sizes were obtained by this technique in the range 10-25 nm and larger particle of 70-100 nm size were obtained.

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1. Introduction

Copper aluminum chalcogenides semiconducting materials have been investigated in recent years as a potential material for realization of blue LEDs, solar cells and other optoelectronic applications. However, the growth of perfect single crystals of CuAlVI₂, [VI =Se, S, Te] compounds are known to be difficult due to the presence of chemically active aluminum in the matrix [1]. For example, preparation of polycrystalline aluminum based materials in evacuated silica ampoule at the melting temperature of the constituent elements makes a corrosion of the silica tube and dangerous reaction takes place beside highly contaminated silicon dioxide in the product. Chalcognides in the tube exhibit high vapor pressure and may be exploded when the tube wall is corroded. There are few reports on the aluminum based chalcogenides and most of them deal with preparation of the thin film form either by co- evaporation of the four elements [2,3], hot wall epitaxy [4], Metal organic vapor phase epitaxy [5], multilayer evaporation of each element followed by annealing and solid state reaction takes place [6] or by selenization of metallic precursors. Electrodeposition and sputtering preparation techniques [7, 8] were used in several reports of CuInGaSe₂ and CuInAlSe₂ thin films. Nanoparticlas of In/Ga based CuInGaSe₂ was prepared by CuInGaSe₂ by solvothermal route [9]. The substitution of the gallium atom by indium

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cause a rise in the band gap which the same behavior in the case of aluminum based CuInAlSe₂. Another case of chalcogenides is the ZnS which also is very important material in powder, film and also nanostructure forms due do its high luminescence and wide band gap semiconductor. The preparation of the polycrystalline nano-powder ZnS is also difficult due to high vapor pressure of sulfur during reaction at high temperature. Chemical routs preparation methods is very important but the purity of the prepared materials may be changed. In a previous works, we succeeded to prepare high purity ZnSe [10], Se_{1-x}S_x, x=0.0-0.4 chalcogenides [11,12] nano powder by mechanochemical process and the conditions were optimized to control the purity and homogeneity of the materials. Their optical, structural and morphological properties were studied. The aim of aim of this work is to prepare these three systems by simple and low cost technique and overcome the high corrosive and active materials such as aluminum.

2. Exprimental

CuIn_{1-x}Al_xSe₂, x=0.2, 0.4, 0.6, 0.8, CuInS₂ and ZnS nano-powder were prepared by mechanical reaction. Granules of size 0.5-1 mm of In and Zn, small copper sheets, Se and S powder of purity 5N "Acros-Organics chemicals" were used for this purposes. The weights of each constituent elements were suggested to form 5 gm of the final sample in the required stiochiometry and compositions. In every preparation, the materials were weighted in 4 digit analytical balance of type "SARTRIUS CP224S" then the materials were loaded in the stainless steal veal of a ball mill of type "Retsch-PM 100 planetary Ball Mill" and adjusted at 300 rpm "continuous mode". The veal was filled and closed under pure nitrogen atmosphere. The 300 rpm speed was chosen before to be less mechanical heating effect and no contamination form stainless steel of the veal, i. e. higher speed contaminates the materials of the samples and veal while lower speed requires longer mechanical reaction time.

X-ray powder diffraction was used to identify and characterize the phase change due to the mechanochemical reaction. XRD powder diffractometer of type "Schimadzu 7000 maxima" was calibrated by Si single crystal for the angular position and the peak width. The measurements were done within the angular range $2\theta = 10-100^{\circ}$ and scanning rate 2 degree/min. A target of CuK $\alpha_1(\lambda=1.5406)$ and Ni filter were used. The powder morphology and homogeneity were imaged and measured by SEM of type "Jeol-JSM-636 OLA" with EDX analysis.

3- Results and discussion

Preparation of CuIn_{1-x}Al_xSe₂ system with different milling time was done in high composition x=1.0 as well as low composition in order to optimize the preparation conditions. Fig.(1) shows the phase change from Cu, Al and Se metallic phases to CuAlSe₂ compound phase. First of all, the granular shape of the constituent materials were changed to thinner pieces and sheets due to deformation then selenium reacts with the surfaces of these sheets and powdered out of these surfaces. This may explain how the mechanical alloying process takes place in a big granule as well as in powder. The powder form is preferred but powdering of some metals such as In, Zn and Sn is difficult. At these milling times, it is observed that the Cu, Al and Se peeks decreases and vanishes due to reaction. At longer milling time crystallizes the materials to a new crystalline phase. The XRD chart shows that the new phase of CuAlSe₂ is completely formed after 35 min. It was identified by "the card ID 00-044-1269 of ICDDview 2006 library" and the CuAlSe₂ tetragonal phase with preferred orientation (112) was resolved. Table (1) shows a comparison between the standard card and the calculated data from the results. The data in the table (1) agrees well with those in the standard card. At lower composition, i.e $CuIn_{0.8}Al_{0.2}Se_2$, it was found that the final new phase requires more milling time for completing the reaction as shown in Fig.(2). This observation introduces the rule of Al reactivity during the milling process. From the high and low composition range experiments, it was concluded that 40 min milling is enough for completing the reaction in both high and low compositions. Further milling time reduces the crystallite size but may contaminate the product as we studied before in Ref. [10]. All compositions between the $CuAlSe_2$ -CuInSe_2 system were prepared as shown in Fig.(3), The calculated d-values of the highest three peaks are shown in table (2). It was concluded that as Al percent increases, the interatomic spacings increase due to smaller ionic radius of aluminum rather than indium.

With Standard							
	Peak 1		Peak 2		Peak 3		
	experimental	Standard	experimental	Standard	experimental	Standard	
2θ	27.76	27.73	46.31	46.23	54.37	54.34	
I/I _o	100 %	100%	38 %	36 %	19 %	26 %	
d	3.211 Å	3.214 Å	1.959 Å	1.962 Å	1.686 Å	1.687 Å	
hkl		(112)		(204)		(312)	

Table (1) the first three maximum diffracted peaks identification for CuAlSe₂ compared with standard

Table (2) Effect of Al/In (composition) on the d (Å)spacing in $CuIn_{1-x}Al_xSe_2$

Х	Peak 1	Peak 2	Peak 3
0.2	3.325	2.035	1.731
0.4	3.291	2.012	1.724
0.6	3.274	2.002	1.717
0.8	3.211	1.955	1.684
1.0	3.211	1.959	1.686



Fig.(1) XRD of the reactant materials and the milled CuAlSe₂



Fig.(2) XRD of CuIn_{0.8}Al_{0.2}Se₂ prepared by mechanical alloy.



Fig.(3) XRD patterns of the final prepared CuIn_{1-x}Al_xSe₂ [x=0.2-1.0]

 $CuInS_2$ is also prepared by this method. The elements were loaded in the veal and attached to the ball mill with the same conditions. The effect of longer milling time was studied, as shown in Fig.(4), there is no effect of increasing the milling time higher than 1 h except peaks broadening

due to decreasing the crystallite size and the internal micro strain. In our previous work in ZnSe nano particles [10] and in this work, it was recommended that milling with longer time increase the impurities of the materials of the veal and balls (stainless steel). In most cases, working with lower milling time minimizes the contamination.



Fig.(4) XRD patterns of CuInS₂ milled at different and longer milling time

In the ZnS case, Fig.(5), the ZnS requires longer milling time due to plastic deformation of Zn grains and transform to thin sheets of ZnS compound. During the formation, ZnS crystallizes into observable crystallographic phases at 60 min, cubic sphalerite and hexagonal wurzite phases. Longer milling timse refine the compound to mainly hexagonal wurzite structure as compared with the standard ICDDview cards [13].



Fig.(5) XRD patterns of ZnS nanopowder prepared at different milling time



Fig.(6. a)



Fig.(6. b)



Fig.(6. c)



Fig.(6. d)

The average crystallite size was calculated from peaks broadening with an approximation of the micro strain. The average crystallite size are in the range 15-25 nm in the lower milling time and decreases to 10 nm for longer milling time. The powder size was also measured by SEM and found to be larger. The smallest powder size is in the range 70-100 nm due to agglomeration of smaller particles or crystallites. Figs. (6- a, b, c and d) show the powder morphology of ZnS as Representative image of the chalcogenide compounds nano powder prepared by mechanical alloying at different magnifications. In figures one can observe that large varieties of powder particle sizes can be observed while, the in-depth view at higher magnifications, the smaller particles agglomerates to form a bigger ones. In this case it is considered that the powder is cohesive enough to agglomerate smaller particles to bigger ones.

4. Conclusions

CuIn_{1-x}Al_xSe₂, x=0.2, 0.4, 0.6, 0.8, 1.0, CuInS₂ and ZnS compound chalcogenide semiconductors were successfully prepared by mechanical alloying technique. The technique and the optimization of the preparation conditions can overcome some problems facing the preparation of such systems by thermal or other methods either due to corrosivity of the constituent materials or high vapor pressure of the chalcogenide during heating process. In this technique, cold preparation of the materials and continuous milling does not determine only the reaction of the constituent materials one with another, but also reduce the powder size to be in the nano scale which is required for many technological applications. Generally milling time in the range 35-40 min is required for CuInAlSe₂ and CuInS₂ preparation and increased more than one hour for ZnS formation. The prepared materials possess high homogeneity as observed from XRD patterns that only one crystallographic phase of the prepared materials was observed in the final step.

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