Ag₂CdI₄: Synthesis, characterization and investigation the strain lattice and grain size

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Abstract

In this work the Ag₂CdI₄ nanostructures have been synthesized via a solid state reaction from reaction of AgI and CdI₂ as precursors. The effect of the mole ratio of precursors, time and temperature of reaction have been optimized to achieve the best product on morphology and purity. Nanostructures have been characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman (FT-IR) techniques, X-ray energy dispersive spectroscopy (EDS) and Ultraviolet spectroscopy (UV-vis). The XRD patterns of nanostructures have been used to estimate the grain sizes and strain lattice. Grain size of nanostructures are in range of 5 – 17 nm and the strain of lattice are changed in range of 0.0024 – 0.014. The band gap of this nanostructures has been estimated by DRS spectrum about 5.4 eV. Raman spectroscopy has been confirmed the XRD results and show that the Ag₂CdI₄ nanostructures have been synthesized. SEM and TEM images have been used for investigation of morphology of product. Results show that the best morphology and purity have been achieved in 12 h and 200 °C in 1:1 mole ratio of precursors.

Keywords: Nanostructures; Solid state; Ag₂CdI₄; Electron microscopy.

1. Introduction

In recent years super ionic conductors containing silver have attracted a lot of attention because of their application in solid state batteries as solid electrolytes [1, 2]. Because of the phenomena that the transformation of luminescence center changes by concentration of silver ion, these crystals are in first of interest [3-5]. The silver mobility properties of crystals show a local irradiation that confirmed by both experimental and computational efforts.

A_2BI_4 (A= Ag, Cu; B = Hg, Cd) are considered as a type of solid electrolytes that show phase transition at moderate temperatures [7]. Recently Ag_2CdI_4 is synthesized as a super ionic conductor with silver ion. The conductivity value of Ag_2CdI_4 is about 10^{-7} ($\Omega.cm^{-1}$) at room temperature, the phase transition occur in $80^\circ C$ and the conductivity value in this temperature is 10^{-3} ($\Omega.cm^{-1}$) [8]. By the combination of inter grainy space and crystalline grains the microstructures formed consequently. In recent years a lot of researches focused on influence of inter grain space volume on thermal, conductivity and physical properties of these crystals [9-10]. When the crystalline grains have nano size, new futures observed in super ionic crystals [11]. Therefore in last ten years, different methods developed to produce super ionic nanostructures with high value of ionic conductivity [12-14]. By decreasing the size of super ionic crystals increase the grain boundaries and pores in morphologies of nanostructures [15]. In this work we synthesized the Ag_2CdI_4 nanostructures by a simple solid state method in low temperature and investigated the grain size, morphology and the strain of lattice.

2. Experimental

2.1. Materials

All the chemicals such as Lithium iodide (LiI), Silver nitrate ($AgNO_3$), Cadmium nitrate ($Cd(NO_3)_2$) were of analytical grade and were purchased from Merck Company (pro-analysis) and used without further purification.

2.2. Physical measurements

XRD patterns were recorded from a diffractometer of Philips Company with X'PertPro filtered by Cu K α radiation ($\lambda = 1.54\text{\AA}$). Microscopic morphology of products was achieved by a LEO 1455VP scanning electron microscope. Prior to taking images, the samples were coated by a very thin layer of Pt to make the sample surface conductor and prevent charge accumulation, and obtaining a better contrast.

2.3. Synthesis of precursors

2.3.1. Synthesis of AgI

The AgI precursor have been achieved by a co-precipitation method from LiI and AgNO₃. For synthesis of AgI stoichiometry amount of AgNO₃ and LiI were dissolved in separate Beakers in distilled water and one of the solutions were added to other solutions. The results solution were remained to crystalize the AgI precipitate.

2.3.2. Synthesis of CdI₂

The preparation approaches and crystalize method for CdI₂ is similar to AgI preparation.in this method Cd(NO₃)₂ were used as Cd precursors.

2.3.3. Synthesis of Ag₂CdI₄

For preparation of Ag₂CdI₄, AgI and CdI₂ were mixed together with a curtained ratio and grinned in mortar for 2h and the result powder were heated at a relatively low temperature (200 °C) in the air. An average temperature increase of 30°C is recorded every minute, before the temperature reached 200 °C, and after keeping the thermal treatment at 200°C for defined time, it was authorized to cool naturally in the room temperature. Different effective parameters on synthetic approaches changed and the results of these changes investigated. These reaction condition listed in [Table 1](#).

3. Results and discussion

3.1. XRD patterns: Strain lattice and grain size

Figure 1a shows the XRD patterns of AgI and CdI₂ precursors. XRD pattern show that the AgI precursor have been made up from AgI with the literature values of JCPDS No. 01-0503 and JCPDS No. 09-0374 without any purification. The XRD pattern of CdI₂ that shown in Figure 1b illustrates the product has hexagonal structure with the literature value of JCPDS No. 02-1200 without any purifications.

In Figure 2a the XRD patterns of Sample No 1 that synthesizes in 200 °C for 24 h and the mole ration of AgI : CdI₂ is 1:1. Product have been made up from Ag₂CdI₄ and a low amount of AgI and CdI₂ remained in product. The Ag₂CdI₄ have been crystalized in tow structures by literature values of JCPDS No. 37-1092 and 36-1112. X-ray diffraction measurements were carried out in a Philips X'Pert High Score diffractometer using Cu K α (λ = 1.5405 Å) radiation over 20–140 °C. To adjust the shift of zero angle, the silicon crystal was used as a standard sample. The crystallite size and lattice strain were estimated using the Williamson-Hall method [16]:

$$\beta_s \cos \theta = \frac{k\lambda}{d} + 2\varepsilon \sin \theta$$

Where β_s is the full-width at half-maximum of the diffraction peak, θ is the diffraction angle, λ is the X-ray wavelength, d is the crystallite size, and ε is the lattice strain. β_s can be given as:

$$\beta_s^2 = \beta_e^2 - \beta_i^2$$

Where β_i is the width at half-maximum of the Si powder peaks used for calibration and β_e is the evaluated width. Thus, it is clear that when we plot $\beta_s \cos \theta$ against $\sin \theta$ we get a straight line with slope (ε) and intercept $K\lambda/d$. The crystallite size (d) can be calculated from $K\lambda/d$ (K and λ are determinate) and lattice strain is slop line (ε) [17]. The grain size for Ag₂CdI₄ by literature value JCPDS No. 37-1092 has been estimated about 5.5 nm and this size for Ag₂CdI₄ by literature value JCPDS No. 36-1112 has been estimated about 86 nm. The strain lattice for 5.5 nm crystals is about 0.0114 and the strain lattice for 86 nm crystals is about 0.0172 (Figure 2b, c).

Because of presence the precursors in product the mole ratio of product have been changed and the product have been synthesized in tow mole ratio of AgI:CdI₂. Figure 3a, b show the XRD patterns of Sample No 2 and

Sample No. 3 that synthesized in presence of different mole ratio of precursors. In these conditions the amount of precursors in product are very high and amount of Ag_2CdI_4 is very low. Therefore the best mole ratio for preparation of Ag_2CdI_4 is 1:1 in 200 °C and 24 h.

Figure 4 shows the XRD pattern of Sample No. 4 that prepared from AgI and CdI_2 with the mole ratio of 1:1 in 150 °C for 24 h. product has been made up from Ag_2CdI_4 and CdI_2 . The grain size and strain of lattice for Ag_2CdI_4 in this structure are 17.5 nm and 0.0024 respectively. The grain size of this Ag_2CdI_4 with literature value of 37-1092 that synthesized in 150 °C in comparison with other product in 200 °C have been increased and the best temperature for preparation of Ag_2CdI_4 is 200 °C.

For preparation of Ag_2CdI_4 as pure phase in product have been optimized the time of reaction and the lower time 18 h and 12 h were examined in reaction. Figure 5a shows the XRD patterns of product in the mole ratio of 1:1 in 18 h. in this condition product have been made up from AgI and Ag_2CdI_4 and CdI_2 have been eliminated from product. The grain size in this condition has been estimated about 8.2 nm and the strain lattice in this condition are about 0.0024 (Figure 5b). Figure 5c shows the XRD pattern of sample No 6 that synthesized in 200 °C for 12 h, this product is pure and made up from Ag_2CdI_4 in two different phase by JCPDS No. 37-1092 and 47-0870, Ag_2CdI_4 by JCPDS No. 37-1092 is major product. The grain size for major and minor product have been estimated 11.6 and 3.8 nm respectively and the strain lattice for these phases are about 0.0043 and 0.0175 respectively (Figure 5 d, e). Table 2 show the grain size and strain lattice of different samples by JCPDS No. 37-1092.

3.2. SEM and TEM images: morphology

Figure 6 illustrates the SEM images of products. Figure 6a has been shown the SEM images of Sample No 1. Product has been made up from nanoparticles but a low amount of bigger nanostructures have been seen in product images. In Figure 6b and 6c the images of product that synthesized in different mole ratio of precursors. The morphology of product in these conditions are not suitable and not regular. The morphology of

sample No 4 that prepared in 150 °C have been shown in [Figure 6d](#). Product in this condition have not regular morphology and are agglomerate structures. [Figure 6e](#) shows the morphology of product in 18 h. As-prepared nanostructures have nanoparticles morphology but a low amount of irregular nanostructures have been seen in SEM images. In [Figure 6f](#) has been shown the SEM images of Sample No 6 that achieved in 12 h. as-prepared Ag_2CdI_4 in this condition are very small nanoparticles that arrayed in very regular structures.

[Figure 7](#) has been shown the TEM images of Sample No 1. Nanoparticles that synthesized in this condition have about 30 nm diameters. The product has not regular shape and the morphology of product are not suitable.

[Figure 8](#) illustrates the TEM images of optimized product (Sample No. 6). As-prepared Ag_2CdI_4 nanoparticles in this condition has about 15 nm diameters and array in regular nanostructures.

3.3. *DES spectrum: purity*

Chemical purity of as-prepared Ag_2CdI_4 nanoparticles (sample No 1 and sample No 6) has been investigated by Electron Diffraction X-ray spectroscopy (EDS). [Figure 9a](#) and [9b](#) shows the product involved Ag, Cd, I and O. Additional amount of O is caused because of surface oxidation of product in atmosphere [\[18\]](#).

3.4. *Optical property: DRS spectrum*

The optical absorption spectrum of Ag_2CdI_4 nanoparticles represents in [Figure. 10a](#). The DRS spectrum was used to further access their quality and electronic structure information. It demonstrates a major absorption peaks about 220 nm and different low intensity absorption peaks in 300 – 400 nm. The absorption that occurred in 226 nm is due to the fundamental absorption within the band gap of this material. The others absorption bands have been attributed to the impurities or vacancies [\[19-20\]](#). The optical band gap of Ag_2CdI_4 has been evaluated using the optical density (OD) vs. energy (E) plot ([Figure 10b](#)). The value of band gap energy for this nanoparticle is ~ 5.4 eV [\[21\]](#).

3.5. *Raman spectrum*

Figure 11 shows the Raman spectrum of sample No 6. The characteristic absorption of as-prepared Ag_2CdI_4 have been occurred in $10\text{ cm}^{-1} - 110\text{ cm}^{-1}$. The vibrational modes of Ag_2CdI_4 have been assigned by considering the nanostructures as vibration modes of AgI and $(\text{CdI}_4)^{2-}$. The band at 119 cm^{-1} can be allocated to the symmetric stretching of $(\text{CdI}_4)^{2-}$ that are in good agreement with other tetrahedral compound with $(\text{CdI}_4)^{2-}$ [22]. The range of $70 - 110\text{ cm}^{-1}$ consists of two bands at the positions 76 cm^{-1} and 95 cm^{-1} , these bands are assigned to symmetric stretching modes of AgI [23]. The bands at 37 cm^{-1} and 52 cm^{-1} can be assigned to Cd-I deformation type bands. The band at 16 cm^{-1} is assigned to the E symmetry of Ag^+ translational mode [24].

4. Conclusion

Ag_2CdI_4 nanostructures have been made up from reaction of CdI_2 and AgI_2 in solid states reaction. The XRD patterns of nanostructures have been used to estimate the grain sizes and strain lattice. Grain size of nanostructures are in range of $5 - 17\text{ nm}$ and the strain of lattice are changed in range of $0.0024 - 0.014$. The band gap of this nanostructures has been estimated by DRS spectrum about 5.4 eV . Raman spectroscopy has been confirmed the XRD results and show that the Ag_2CdI_4 nanostructures have been synthesized.

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Figure and Table Captions

Table 1. Different reaction condition for solid state preparation of Ag_2CdI_4

Table 2. Grain size and strain lattice of product

Figure 1. XRD patterns of (a) AgI (b) CdI_2

Figure 2. (a) XRD pattern (b,c) Williamson-Hal diagram of Sample No. 1

Figure 3. XRD pattern of sample No (a) 3 (b) 4

Figure 4. (a) XRD pattern (b) Williamson-Hal diagram of Sample No. 4

Figure 5. (a) XRD pattern (b) Williamson-Hal diagram of Sample No. 5 (C) XRD pattern (d,e) Williamson-Hal diagram of Sample No. 6

Figure 6. SEM images of sample No (a) 1 (b) 2 (c) 3 (d) 4 (e) 5 (f) 6

Figure 7. TEM image of Sample No 1

Figure 8. TEM image of Sample No 1

Figure 9. EDS spectrum of Sample No (a) 1 (b) 2

Figure 10. (a) DRS spectrum and (b) optical density ($(\alpha h\nu)^2$) vs. energy (E) plot of Sample No 6

Figure 11. Raman spectrum of Sample No 6

Table 1.

Sample. No	Precursors Ratio	Time	Temperature
1	$\text{AgI} + \text{CdI}_2$	24 h	200 °C
2	$2\text{AgI} + \text{CdI}_2$	24 h	200 °C
3	$\text{AgI} + 2\text{CdI}_2$	24 h	200 °C
4	$\text{AgI} + \text{CdI}_2$	24h	150 °C
5	$\text{AgI} + \text{CdI}_2$	18 h	200°C
6	$\text{AgI} + \text{CdI}_2$	12 h	200 °C

Table 2

Sample No	Grain Size (nm)	Strain Lattice
1	5.5	0.014
4	17.5	0.0024
5	8.2	0.0024
6	11.6	0.0043

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11