



# Recycling of photovoltaic panels by physical operations

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## ABSTRACT

Recycling of polycrystalline silicon, amorphous silicon and CdTe photovoltaic panels was investigated by studying two alternative routes made up of physical operations: two blade rotors crushing followed by thermal treatment and two blade rotors crushing followed by hammer crushing. Size distribution, X-ray diffraction and X-ray fluorescence analysis of obtained products were carried out in order to evaluate their properties as valuable products. Results showed that for all kinds of investigated photovoltaic modules the two blade rotors crushing followed by hammer crushing and eventually by a thermal treatment of  $d > 1$  mm fractions, was the best option aiming to a direct recovery of glass.

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## 1. Introduction

Photovoltaic power generation system is a promising and well-established solution for renewable energy utilization. Nevertheless, as for all human activities, in few years a waste problem related to the large use of solar cell modules is expected [1]. In fact the average lifetime of crystalline silicon photovoltaic module is estimated in 25–30 years because of the deterioration of encapsulant materials and wires.

Currently the dominant photovoltaic (PV) technology uses crystalline silicon (monocrystalline and polycrystalline) as semiconductor, but the thin film photovoltaic modules using cadmium telluride (CdTe), amorphous silicon, Copper–Indium–Gallium–Selenide (CIGS) and Copper–Indium–Selenide (CIS) are recently getting much more importance because of their lower production costs and higher efficiency [2,3].

The necessity of mass recovery from these devices has been shown by different researchers [4–6] and recently even the European Union issued the Guideline 2012/19/EU (replacing the previous 2002/96/EC) in order to fix rules about end of life photovoltaic panels [7]. According to this guideline end of life photovoltaic panels must be considered as electric and electronic equipment waste (WEEE) and specific goals of collecting, recovering and recycling must be achieved within the next years. In particular:

- Minimum collecting rate as average weight of photovoltaic panels is 45% of total devices by 2016 and 65% later.

- Minimum targets as recovery and recycling are respectively 75% of and 65% as average weight by 2015.

Up to now several authors carried out research related to PV panels recycling. Fernandez et al. [8] examined the possibility of silicon solar cells recycling by insulating them into cement-based systems. Chemical studies about silicon recovery from PV panels were also carried out by using acid/alkaline agents as well as organic solvents for EVA degradation and/or dissolution [9,10]. Some authors focused on thin film PV panels. In particular Sasala and co-authors [11] studied the recycling of CdTe modules by both physical and chemical operations. They proposed a pretreatment by water blasting and chemical operations such as leaching, precipitation and electroplating of semiconductors materials.

Berger et al. [12] also studied the recycling of thin film PV panels (CdTe and CIS) by using wet mechanical processes like attrition and flotation as well as dry mechanical methods like vacuum blasting.

In spite of the recent efforts only two full scale processes were developed. In particular the company Deutsche Solar (Solar World) carried out the treatment of crystalline silicon modules [13], whilst First Solar have been recycling CdTe thin film panels by mechanical and chemical operations [14]. However, nowadays, neither technologies were designed for treating together more kinds of photovoltaic panels nor completely automated processes have been developed yet.

This work aimed to provide a further contribution about recycling of PV modules. In particular, in order to achieve the minimum targets of recovery and recycling fixed by the latest European Guideline 2012/19/EU, a recycling process was developed and tested to treat silicon-based (crystalline and amorphous

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Si panels) and CdTe panels, both separately and together. Moreover this goal was accomplished by developing a process easily performable by using simple and conventional technology like those used for the recycling of other electronic wastes such as batteries [15]. This feature would give high flexibility to the recycling plant and then the capability of treating different kinds of electronic wastes.

In the present work two options of recycling processes by physical operations were examined and quantitative/qualitative results in terms of mass recovery and quality of products have been provided.

Novelty aspects are the development of a process of physical pretreatment for the simultaneous recycling of different kinds of PV panels, and its assessment in pilot scale tests.

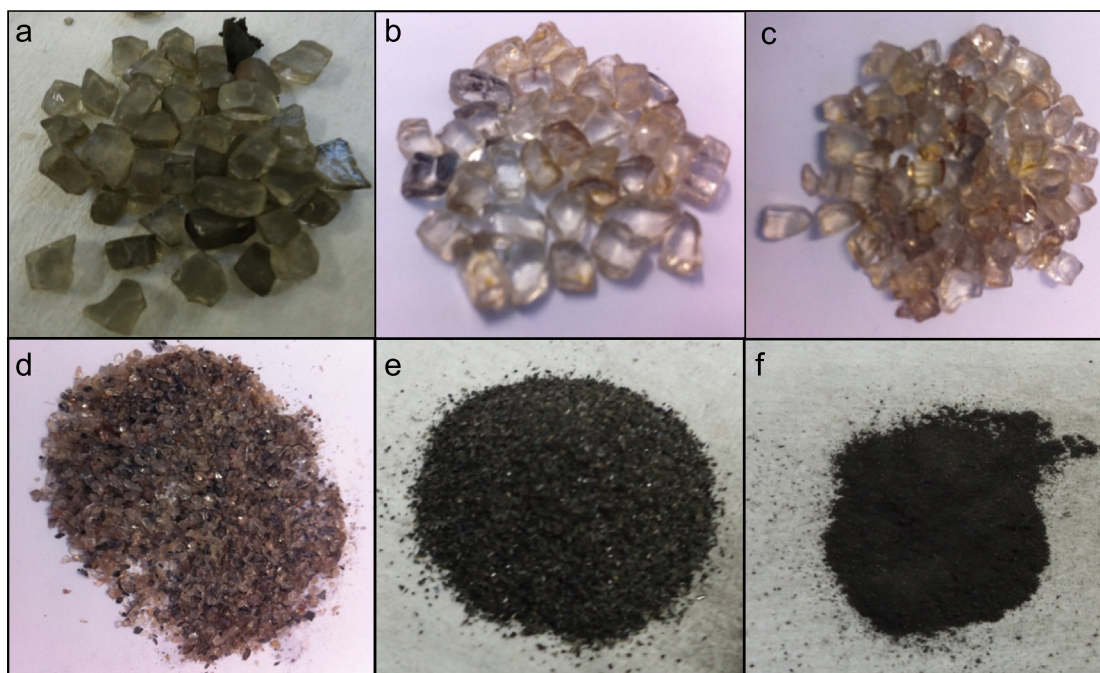
## 2. Materials and methods

The input material used in this work was taken from three different kinds of PV devices: a polycrystalline silicon PV module

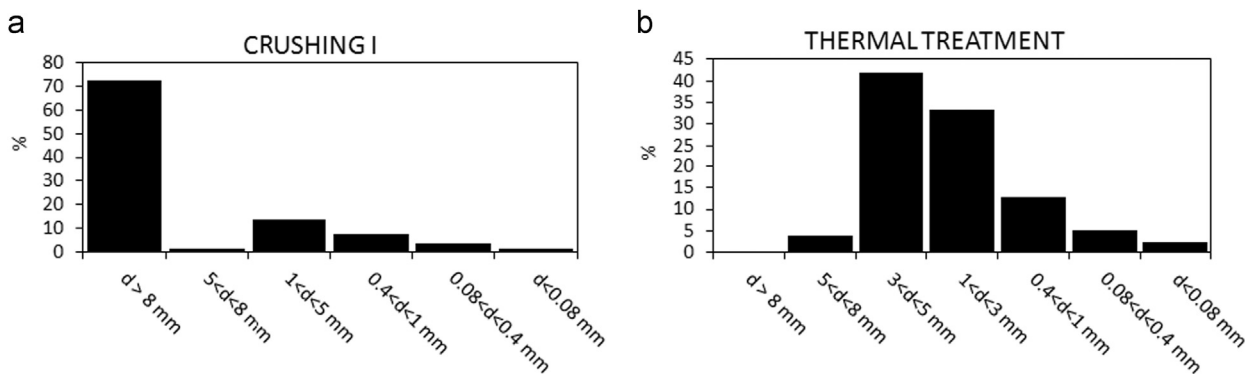
(BYD–230P6–30), an amorphous silicon PV module (Sharp NA-901 WQ) and a CdTe PV module (First Solar FS2). The silicon devices were previously manually disassembled in order to separate the modules from external frames and then, in each test, around 2 kg of photovoltaic modules were used as input materials.

Crushing operations were carried out in a two blade rotors crusher (DR120/360, Slovakia) without any controlling sieve and in a hammer crusher (SK 600, Slovakia) using a 5 mm sieve. Thermal treatment was performed at 650 °C for 1 h in a silite resistance furnace aiming to a complete degradation of cross-linked EVA.

After each operation of size reduction and thermal treatment, a sieving analysis was carried out to evaluate size and products distribution as well as mass fluxes in the process. For this purpose all samples were sieved by using 5 different sieves (8 mm, 5 mm, 1 mm, 0.4 mm, 0.08 mm) and an automatic shaker, then they were weighed. After hammer crushing, sieving was also used as process operation since only fractions  $d > 1$  mm were put together and used as feeding for the following thermal treatment.



**Fig. 1.** Fractions obtained after crushing and thermal treatment of a polycrystalline silicon module (a)  $d > 8$  mm; (b)  $5 < d < 8$  mm; (c)  $1 < d < 5$  mm; (d)  $0.4 < d < 1$  mm; (e)  $0.08 < d < 0.4$  mm; (f)  $d < 0.08$  mm).

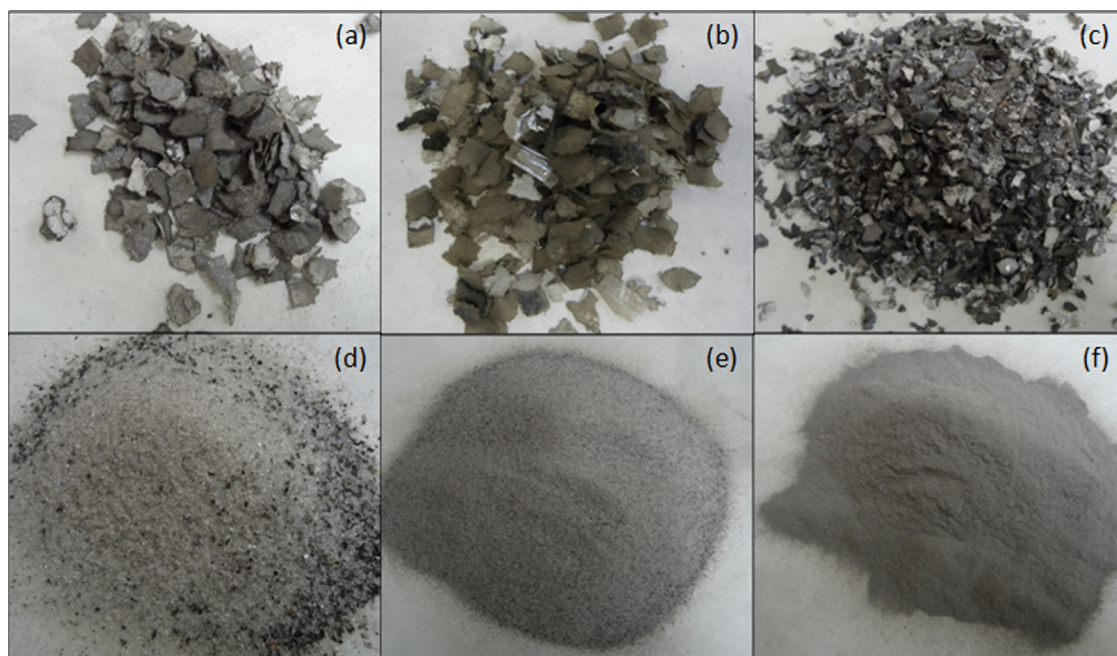


**Fig. 2.** Total size distribution after treatment of polycrystalline silicon module by crushing (a) and thermal treatment (b).

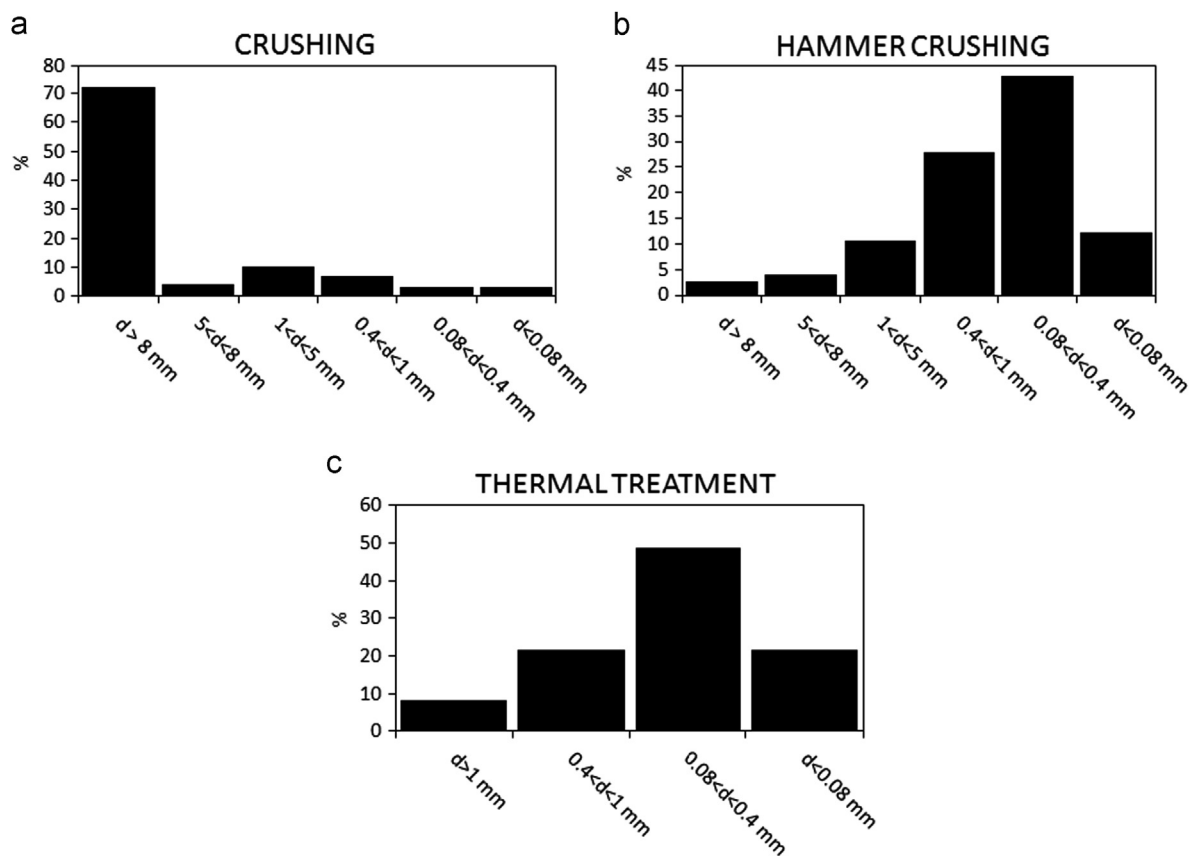
Obtained products ( $d \leq 1$  mm) were analyzed by X-Ray diffraction (PANalytical X'Pert Pro, Co-K $\alpha$  radiation) and X-ray fluorescence (SPECTRO XEPOS Spectrometer).

0.2 g samples of recoverable glass fractions from CdTe panels (1–0.08 mm fractions) were digested using sulfuric acid (9 ml of a 96% solution) (Sigma-Aldrich Reagent Grade) and hydrogen

peroxide (1 ml of a 35%<sub>vol</sub> solution) (Sigma-Aldrich Reagent Grade) at 220 °C in a microwave digester (Milestone Ethos 900 Microwave Digester). Liquid samples were filtrated and analyzed by an Inductively Coupled Plasma Optical Emission Spectrophotometer (Varian Vista-MPX CCD Simultaneous) for the determination of dissolved Cd.



**Fig. 3.** Fractions obtained after crushing and hammer crushing of a polycrystalline silicon module: (a)  $d > 8$  mm; (b)  $5 < d < 8$  mm; (c)  $1 < d < 5$  mm; (d)  $0.4 < d < 1$  mm; (e)  $0.08 < d < 0.4$  mm; and (f)  $d < 0.08$  mm.



**Fig. 4.** Total size distribution after treatment of polycrystalline silicon module by crushing (a) hammer crushing (b) and thermal treatment of fraction with  $d > 1$  mm (c).



### 3. Results and discussion

#### 3.1. Polycrystalline silicon modules

##### 3.1.1. Crushing by two blade rotors crusher and thermal treatment

Crushing operation and thermal treatment of crushed materials resulted into the products shown in Fig. 1 having a size distribution as reported in Fig. 2. After crushing 70% of sample was made by a  $d > 8$  mm (Fig. 2a) still kept together by the EVA polymer. Thermal treatment at 650 °C determined 9% of weight loss because of EVA decomposition and it resulted in a dramatic weight decrease of largest size fractions (Fig. 2b). As it can be seen from Figs. 1 and 2, after thermal treatment, around 85% of products could be directly recovered as  $d > 1$  mm glass (Fig. 1a–c) and around 10% could be recovered as fraction with  $d < 1$  mm (Fig. 1d and e). However the fraction  $0.08 < d < 1$  mm cannot be considered as directly recoverable because, according to XRD results in Fig. 13a, it contains a considerable amount of silicon. Around 2–3% of total input weight was found to be a fine  $d < 0.08$  mm fraction (1f) having a composition as in Table 4. This fraction could be collected separately and eventually valorized by operations for zinc, silicon and/or further glass recovery.

**Table 1**  
Mass balance for polycrystalline silicon photovoltaic modules.

	Crushing–thermal treatment [%] <sup>a</sup>	Crushing–hammer crushing [%] <sup>a</sup>
Direct recovery as glass	70–75	80
Not directly recoverable fraction	15–20	10
Weight loss due to thermal treatment	10	10

<sup>a</sup> Percentage of total initial weight.

##### 3.1.2. Crushing by two blade rotors crusher followed by hammer crushing

Crushing operation and hammer crushing resulted into the products shown in Fig. 3 after crushing around 70% of sample had a  $d > 8$  mm (Fig. 4a) because of EVA being adhered to the glass. However hammer crushing determined the separation between glass, EVA-Tedlar and powder. As it can be seen the EVA cut sheets along with Tedlar were mostly contained in the  $d > 8$  mm and  $5 < d < 8$  mm fractions (Fig. 3a and b) and in a mixture with glass in the  $1 < d < 5$  mm fraction (Fig. 3c). Glass can be also recovered from fractions with  $d < 1$  mm. In particular, for the fraction  $0.08 < d < 1.0$  mm (Fig. 3d and e), the XRD data showed an amorphous pattern (Fig. 13b) meaning that it can be considered as a recoverable glass fraction. Instead, from the XRD pattern in Fig. 13c, it can be seen how the fraction  $d < 0.08$  mm (Fig. 3f) contains silicon and it cannot be considered as clean. Anyway because of the high amount of amorphous glass contained in this fraction, no other phase could be detected by XRD (XRD pattern like in Fig. 13b but not shown here); thus a XRF analysis was also carried out. Results (Table 4) showed a considerable amount of silicon and other elements in the fraction  $d < 0.08$  mm, confirming that it cannot be considered as a recoverable glass and it must be collected separately for a possible valorization by further pyro/hyrometallurgical operations.

These results also suggested the possibility to carry out a thermal treatment to decompose EVA and Tedlar sheets in order to both clean the glass contained in the  $1 < d < 5$  mm fraction and free more fine powder. As listed in Fig. 4c the thermal treatment of  $d > 1$  mm fractions resulted into a further recovery of glass from the residual  $d > 1$  mm fraction and into an enrichment as fine  $d < 0.08$  mm powder. After thermal treatment the total direct mass recovery as glass from fractions  $d > 0.08$  mm was 80–85%.

A summary of results concerning mass recovery from polycrystalline silicon modules is listed in Table 1. As it can be seen the main difference between the two physical routes was found in the different fraction percentages and in their composition. According to the previous results, hammer crushing allows a higher mass



**Fig. 5.** Fractions obtained after crushing and thermal treatment of an amorphous silicon module: (a)  $d > 8$  mm; (b)  $5 < d < 8$  mm; (c)  $1 < d < 5$  mm; (d)  $0.4 < d < 1$  mm; (e)  $0.08 < d < 0.4$  mm; (f)  $d < 0.08$  mm.

recovery because the fractions  $d > 0.08$  mm did not contain impurities in terms of Si, metals and EVA.

### 3.2. Amorphous silicon photovoltaic modules

#### 3.2.1. Crushing by two blade rotors crusher and thermal treatment

Samples obtained after crushing and thermal treatment of amorphous silicon modules are shown in Fig. 5. The crushing operation resulted mainly in a  $d > 8$  mm fraction (Fig. 6a) where glass was still kept together by EVA polymer being adhered to the glass itself. Thermal treatment after crushing determined around 10% of weight loss because of EVA decomposition and it resulted also in a dramatic decrease of sample particle size. In fact, by decomposing EVA, the  $d > 1$  mm fraction was mostly made free (Fig. 6b) and interesting products could be recovered. The 70–75% of total initial mass of sample was recovered as  $1 < d < 5$  mm glass (Fig. 5b and c), whilst an interesting aluminum fraction was

recovered from the  $d > 8$  mm fraction (Fig. 5a). According to the XRD results (Fig. 13d) the glass fraction  $0.08 < d < 1$  mm (Fig. 5d and e), contains also a quite detectable amount of silicon and other oxides not directly due to glass such as  $\text{TiO}_2$  and  $\text{ZnO}$ . Hence this fraction cannot be considered as a directly recoverable clean glass fraction. XRD analysis was also performed on the fraction  $d < 0.08$  mm (Fig. 5f) and results revealed that it contains several oxides (Fig. 13e) such as the titanium, zinc and silicon ones (probably coming from the antireflective material and from the semi conductive layer). However the obtained peaks were low because this fraction contains also a considerable amount of amorphous phase (glass). In fact XRF results (Table 4) showed a high percentage of silicon which must come from amorphous glass since no crystalline silicon was found by XRD. In spite of this high percentage of silicon (glass) the  $d < 8$  mm fraction contains also other metals and it cannot be considered as directly recoverable. It could be eventually valorizable by further pyro/hydrometallurgical operations.

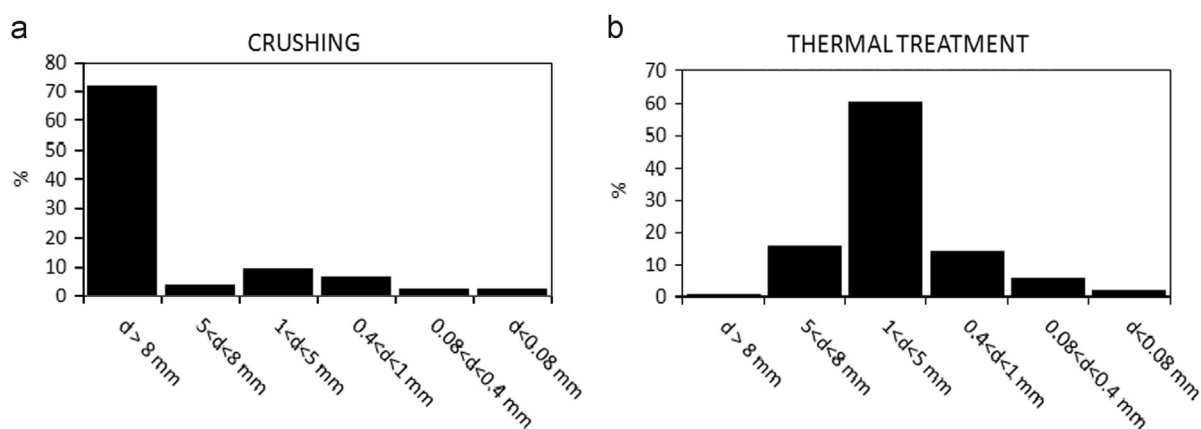


Fig. 6. Total size distribution after treatment of amorphous silicon module by crushing (a) and thermal treatment (b).

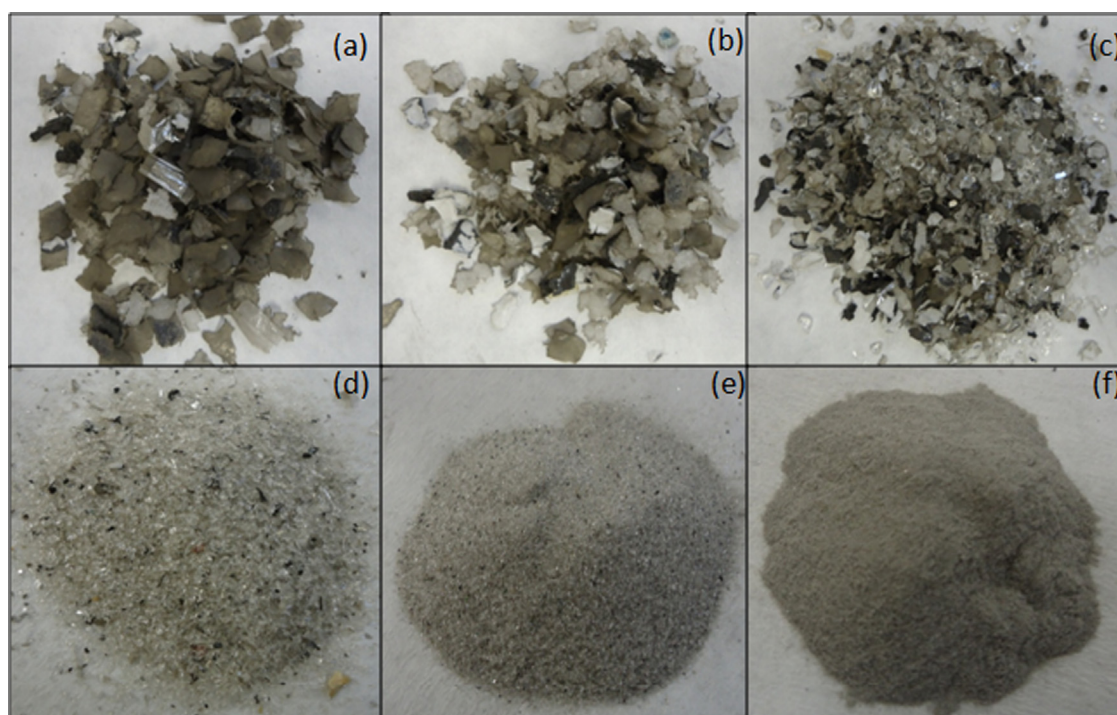


Fig. 7. Fractions obtained after crushing and hammer crushing of amorphous silicon module: (a)  $d > 8$  mm; (b)  $5 < d < 8$  mm; (c)  $1 < d < 5$  mm; (d)  $0.4 < d < 1$  mm; (e)  $0.08 < d < 0.4$  mm; and (f)  $d < 0.08$  mm.

### 3.2.2. Crushing by two blade rotors crusher and hammer crushing

Crushing operation and hammer crushing resulted into the products shown in Fig. 7. Once again, as observed for polycrystalline silicon module, after crushing around a 70% of sample was a  $d > 8$  mm fraction due to the adhesive effect of EVA keeping together glass layers. Hammer crushing determined a sharp size reduction of input sample (Fig. 8) and it lead also to a separation between glass, EVA sheets and finer fractions. As it can be seen the EVA cut sheets were mostly contained in the  $d > 8$  mm and  $5 < d < 8$  mm fractions (Fig. 7a and b), and in a mixture with glass in the  $1 < d < 5$  mm fraction (Fig. 7c). Most of glass was anyway contained in the fraction  $0.08 < d < 1$  mm (Fig. 7d and e). In fact XRD analysis confirmed this fraction being totally amorphous (XRD pattern like in Fig. 13b but not shown here) and then a directly recoverable glass fraction. Regarding the fine fraction  $d < 0.08$  mm (Fig. 7f), once more the percentage obtained by hammer crushing (10%) was higher than that one obtained by crushing and thermal treatment (2–3%). XRD revealed this fraction being basically amorphous (Fig. 13e). However, since some not identifiable peaks were detected in the pattern, a XRF analysis was also performed on the same sample. XRF results showed a not negligible amount of Fe, Zn and Sn. Once more, as a result of a deeper size reduction of glass, the amount of silicon was higher than that one coming from the crushing–thermal treatment route. Perhaps this high content of amorphous silicon due to the glass could be the responsible for “diluting” the eventually detectable peaks.

Anyway this fraction cannot be considered as directly recoverable glass and it should be collected separately for a possible valorization by further pyro/hydrometallurgical operations.

Thermal treatment of  $d > 1$  mm fractions determined the decomposition of EVA sheets and it allowed a cleaning of

$1 < d < 5$  mm glass resulting into a further direct recovery of glass from the residual  $d > 1$  mm fraction.

Therefore by crushing and hammer crushing the amount of recovered glass from amorphous silicon modules was significantly higher because, in spite of some glass lost in the finest powder, cleaner glass fractions ( $0.08 < d < 1$  mm) can be directly recovered (Table 2).

### 3.3. CdTe photovoltaic modules

#### 3.3.1. Crushing by two blade rotors crusher and thermal treatment

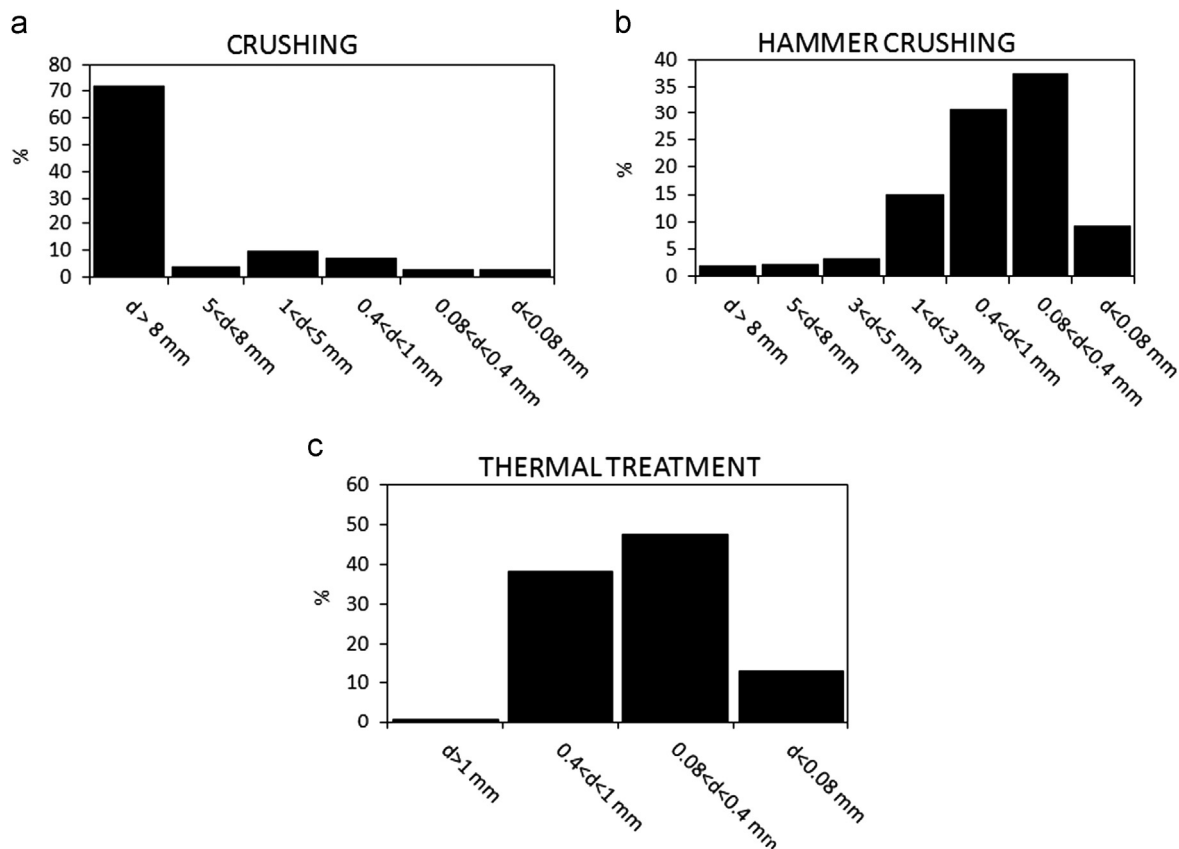
Products obtained by crushing and thermal treatment of CdTe PV modules are shown in Fig. 9. The two blade rotors crushing determined a first size reduction where around 45% of the total initial weight was still present as a large  $d > 8$  mm fraction (Fig. 10a). This percentage was significantly lower than the one obtained for silicon modules because CdTe modules contain only one layer of EVA polymer between the module core and the rear

**Table 2**

Mass balance for amorphous silicon photovoltaic modules.

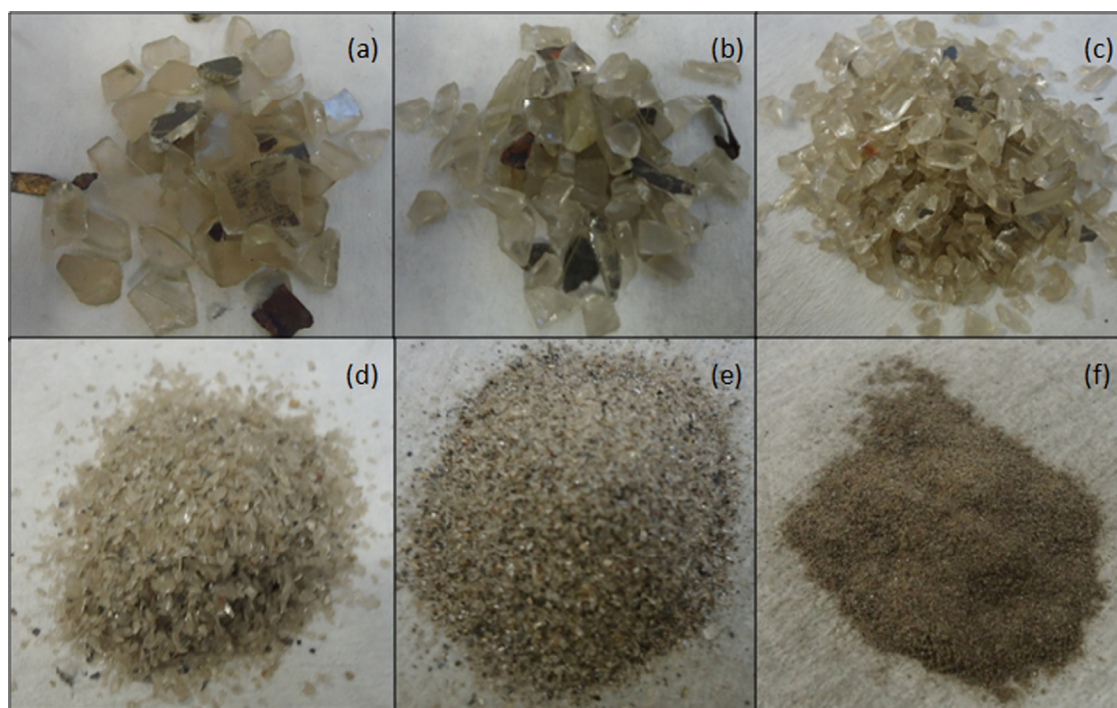
	Crushing–thermal treatment [%] <sup>a</sup>	Crushing–hammer crushing [%] <sup>a</sup>
Direct recovery as glass	70	80–85
Direct recovery as aluminum	2	–
Not directly recoverable fraction	15–20	5–10
Weight loss due to thermal treatment	9–10	10–11

<sup>a</sup> Percentage of total initial weight.

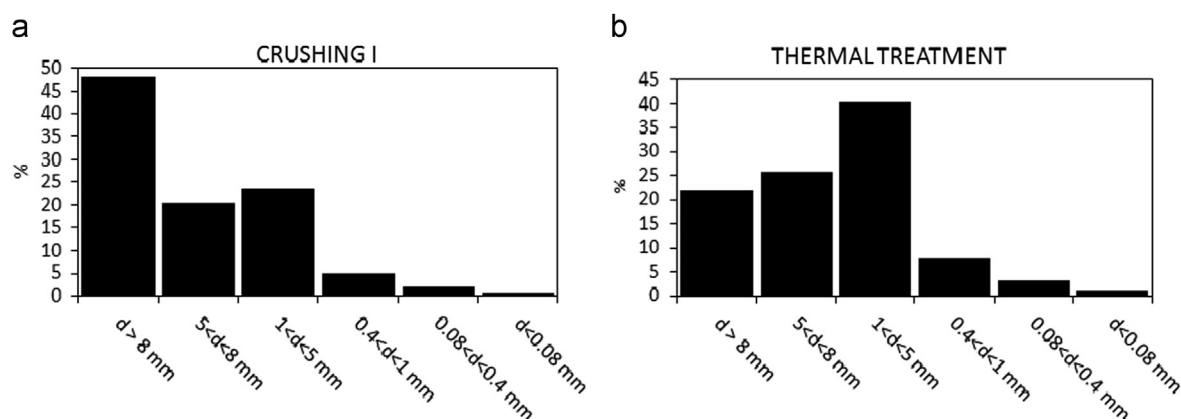


**Fig. 8.** Total size distribution after treatment of amorphous silicon module by crushing (a) hammer crushing (b) and thermal treatment of fraction with  $d > 1$  mm (c).





**Fig. 9.** Fractions obtained after crushing and thermal treatment of CdTe module: (a)  $d > 8$  mm; (b)  $5 < d < 8$  mm; (c)  $1 < d < 5$  mm; (d)  $0.4 < d < 1$  mm; (e)  $0.08 < d < 0.4$  mm; and (f)  $d < 0.08$  mm.



**Fig. 10.** SIZE distribution after treatment of CdTe module by crushing (a) and thermal treatment (b).

glass. This makes easier the size reduction of the front glass resulting in a lower percentage of  $d > 8$  mm fraction. For the same reason the thermal treatment determined around 4–5% of weight loss instead of the previous 9–10%. Moreover, as it can be seen in Fig. 10a and b, after thermal treatment the largest  $d > 8$  mm fraction decreased of around 25% in weight just because only the rear glass pieces were kept together by the EVA polymer and no further size reduction could be seen for front glass pieces. Observing the obtained products (Fig. 9), it can be noted that only the intermediate fractions  $0.08 < d < 5$  mm (Fig. 9c and d) can be considered as a directly recoverable clean glass because the larger fractions  $d > 5$  mm (Fig. 9a and b) still contained CdTe layers. According to XRD data (Fig. 13f), the fractions  $0.08 < d < 1$  mm (Fig. 9e and f) cannot be considered as a directly recoverable glass because it contains compounds not due to glass such as  $\text{TiO}_2$ , ZnO and aluminum.

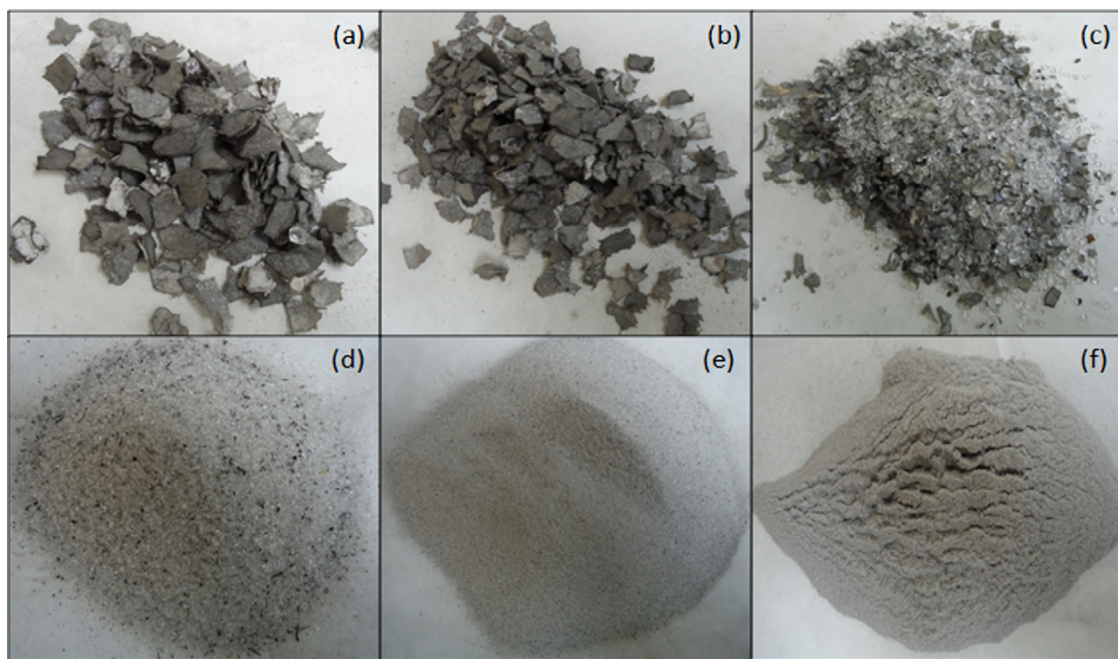
XRD results for the finest  $d < 0.08$  mm fraction (Fig. 9f) showed a clearly amorphous pattern (XRD pattern like in Fig. 13b but not shown here) but once more it must be taken into account that a high amount of an amorphous finest glass can provoke a “dilution”

of crystalline compounds. XRF analysis of the same sample (Table 4) revealed several elements such as silicon, other elements contained in glasses (Mg, Ca, etc.), cadmium and tellurium. Hence neither this fraction can be considered as recovered but it could be collected for a possible valorization by further pyro/hydrometallurgical operations.

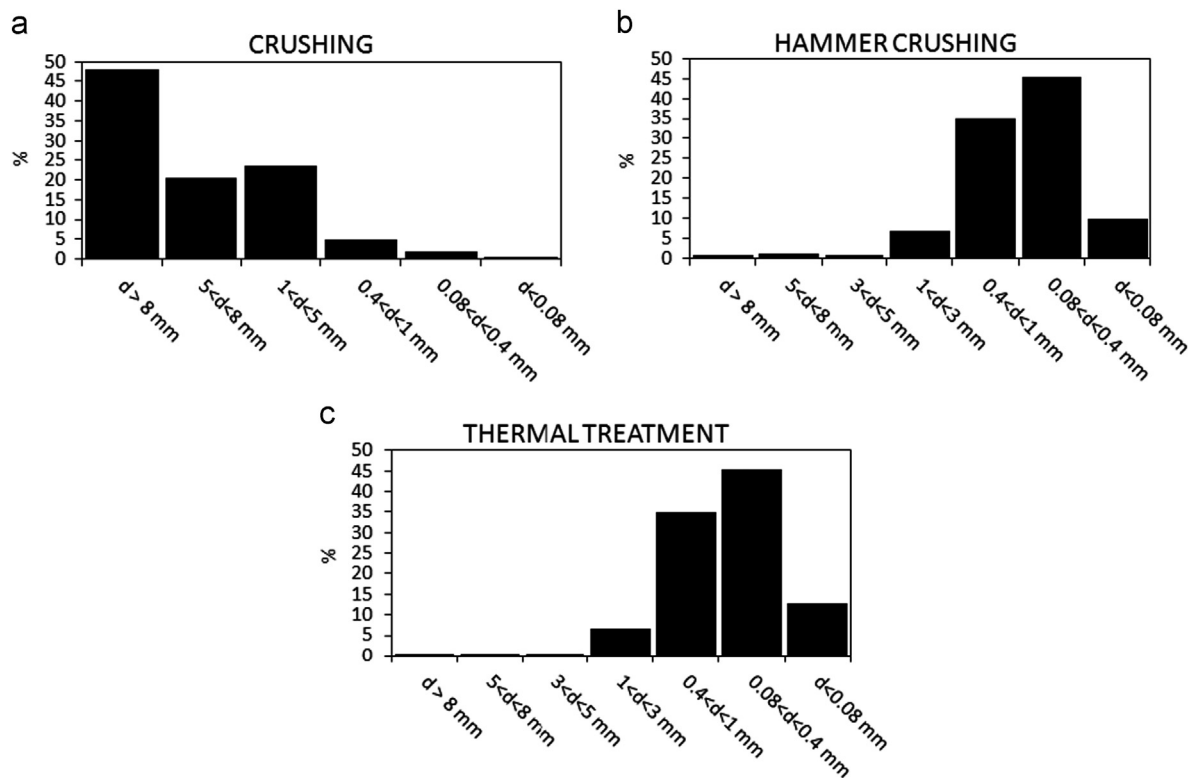
### 3.3.2. Crushing by two blade rotors crusher and hammer crushing

Hammer crushing after two blade rotors crushing resulted into the products shown in Fig. 11. As can be seen from Fig. 12a and b, hammer crushing suddenly shifted the sample size distribution to lower values.

Fractions obtained by this route were a glass fraction  $0.08 < d < 1$  mm (Fig. 11d and e), a fine fraction  $d < 0.08$  mm (Fig. 11f) and a lighter and largest fraction made up of EVA sheets (Fig. 11a and b) even in mixture with glass (Fig. 11c). These fractions  $d > 1$  mm were a lower percentage of those obtained by hammer crushing of silicon modules probably just as consequence of a single EVA layer in CdTe modules. A further thermal treatment of  $d > 1$  mm fraction was also carried out and it determined once



**Fig. 11.** Fractions obtained after crushing and hammer crushing of CdTe module (a)  $d > 8$  mm; (b)  $5 < d < 8$  mm; (c)  $1 < d < 5$  mm; (d)  $0.4 < d < 1$  mm; (e)  $0.08 < d < 0.4$  mm; (f)  $d < 0.08$  mm.



**Fig. 12.** Size distribution after treatment of CdTe module by crushing (a) hammer crushing (b) and thermal treatment of fractions with  $d > 1$  mm (c).

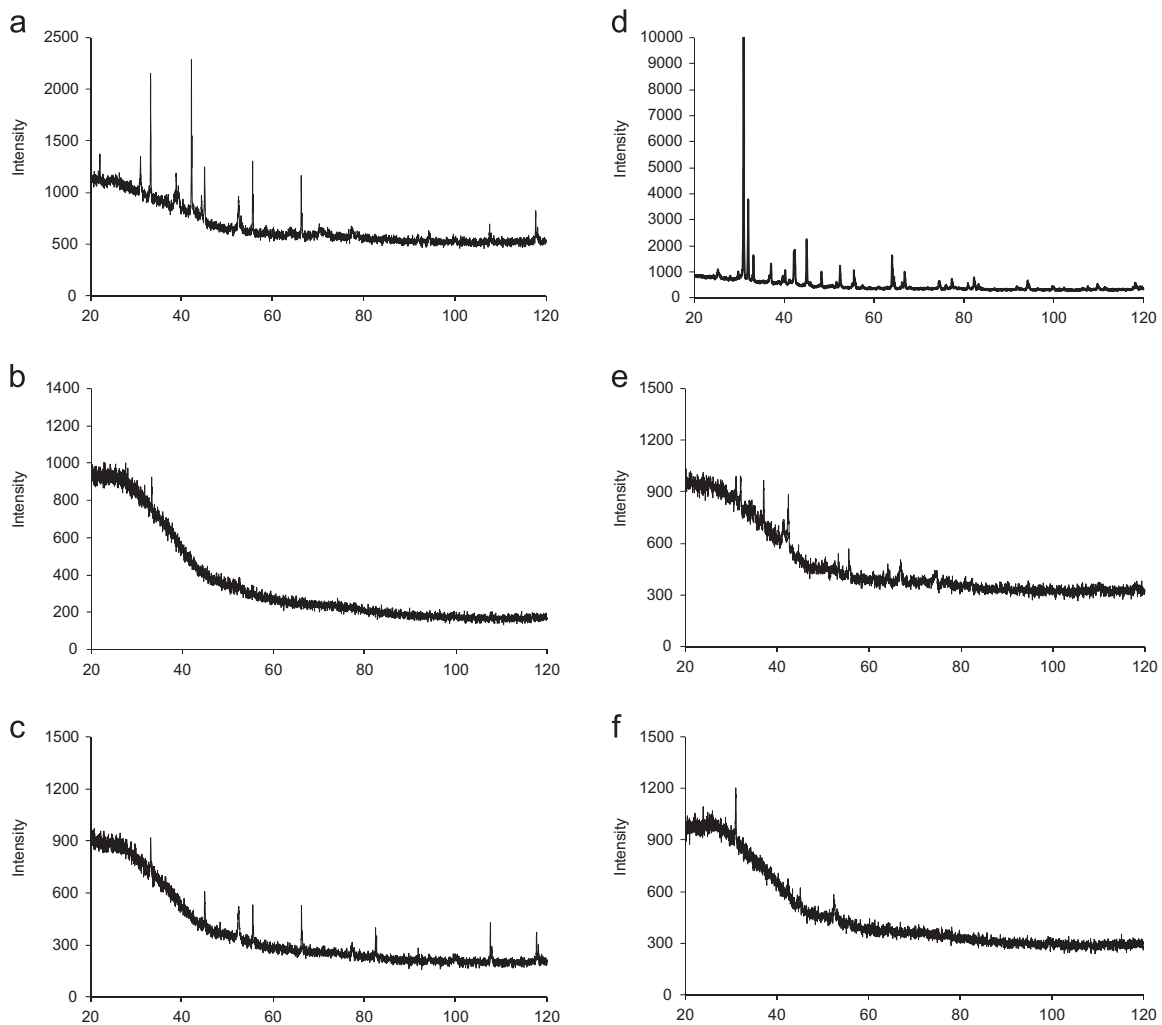
more around 5% of weight loss resulting into a clean  $d > 1$  glass fraction and into a further enrichment as a  $d < 1$  mm fraction (Fig. 12c). XRD analysis revealed the  $0.08 < d < 1$  mm fraction being clearly amorphous (XRD pattern like in Fig. 13b but not shown here), meaning it can be directly recovered as clean glass.

XRF results (Table 4) showed a high percentage of amorphous silicon (not detected by XRD) in the fraction  $d < 0.08$  mm as a result of a deeper size reduction of glass pieces due to hammer

crushing. The same sample contained also other elements such as cadmium and tellurium from the CdTe layers, and other metals probably due to mixed oxides in the glass.

As a results of this physical route, around 80–85% of the total initial weight could be recovered as valuable glass ( $d > 0.08$  mm) whilst around 10% was collected as finer  $d < 0.08$  mm sample (composition in Table 4) for a possible valorization by further pyro/hydrometallurgical operations.





**Fig. 13.** XRD pattern of obtained products: p-Si  $0.08 < d < 1$  mm after crushing plus thermal treatment (a), p-Si  $0.08 < d < 1$  mm after crushing plus hammer crushing (b), p-Si  $0.08 < d < 1$  mm after crushing plus hammer crushing (c), a-Si  $0.08 < d < 1$  mm after crushing plus thermal treatment (d), a-Si  $0.08 < d < 1$  mm after crushing plus thermal treatment (e), CdTe  $0.08 < d < 1$  mm after crushing plus thermal treatment (f).

**Table 3**

Mass balance for CdTe photovoltaic modules.

	Crushing—thermal treatment [%] <sup>a</sup>	Crushing—hammer crushing [%] <sup>a</sup>
Direct recovery as glass	50	80–85
Not directly recoverable fraction	45	10
Weight loss due to thermal treatment	5	5

<sup>a</sup> Percentage of total initial weight.

Mineralization tests on recoverable glass fractions showed Cd content of about 0.1 mg/g corresponding to 0.01% of Cd. Then a partial reduction of Cd in recoverable fraction was attained. Further improvement could be achieved by physical treatment of glass in order to remove impurities particles (dark fragments in Fig. 11d) exploiting density differences (by flotation, pneumatic separation or vibrant table).

A summary of results for CdTe photovoltaic modules is listed in Table 3. As for based-silicon modules the hammer crushing route allowed a higher direct mass recovery as glass from fractions  $d > 0.08$  mm.

#### 4. Conclusions

A physical recycling of silicon based and CdTe photovoltaic modules has been investigated by studying two different routes: crushing by two rotors crushing followed by thermal treatment and crushing by two rotors crushing followed by hammer crushing and by a possible thermal treatment of larger fractions.

Obtained results suggested that, in order to obtain the highest mass recovery, for all the three kinds of PV modules, the treatment route involving the crushing by two rotors crusher plus hammer crushing was the best option. In particular, in order to achieve the highest mass recovery, the three kinds of PV modules could be processed even together by a processing scheme as follows:

- (1) crushing by two blade rotors crusher;
- (2) hammer crushing;
- (3) thermal treatment (650 °C) of fractions larger than 1 mm; and
- (4) sieving by a  $d=0.08$  mm sieve

By these operations around 85%<sub>w</sub> of the total panels weight can be recovered as glass from fractions  $d > 0.08$  mm satisfying the European Guidelines minimum target as mass recovery, whilst the

**Table 4**XRF results: metal composition of fractions  $d < 0.08$  mm.

PV	Route	Mg (%)	Al (%)	Si (%)	Ca (%)	Mn (%)	Fe (%)	Ti (%)	Zn (%)	Sn (%)	Cd (%)	Te (%)
p-Si	CR-HC	1.64	1.42	31.7	5.59	0.59	1.51	0.06	0.34	0.08	< 0.01	< 0.01
p-Si	CR-TT	0.90	4.7	25.3	3.88	2.17	1.67	1.65	2.13	0.48	< 0.01	< 0.01
a-Si	CR-HC	1.94	< 0.01	28.4	5.04	0.37	2.63	0.03	0.24	0.1	0.015	0.016
a-Si	CR-TT	1.48	0.5	24.6	4.3	3.06	1.62	0.62	2.07	0.21	< 0.01	< 0.01
CdTe	CR-HC	2.02	< 0.01	31.2	5.5	0.22	1.35	0.02	0.11	0.05	0.05	0.05
CdTe	CR-TT	1.68	< 0.01	27.7	4.8	1.94	1.52	0.03	1.13	0.07	0.16	0.2

CR-HC=crushing by two rotors crushing and hammer crushing.

CR-TT=Crushing by two rotors crushing and thermal treatment.

fraction  $d < 0.08$  mm can be collected and eventually treated for a further silicon/cadmium/tellurium/zinc recovery.

As for thermal treatment experimental results reported in this work, they showed about 10% of weight loss for Si panels and 5% for CdTe panels according to the presence of a single EVA layer in CdTe and a double layer in Si panels. Emissions from thermal treatment are mainly those due to EVA decomposition which according to literature data occurred following a two stage process consisting first in deacetylation with acetic acid release [16] and then in random-chain scissions giving mainly propane, propene, ethane, ethene, butane, hexane-1, butane-1 [17]. Hence, in a hypothetical recycling plant, a condensation unit could be added to the thermal treatment equipment in order to recover these secondary raw materials which could be used as integration feed in heat production.

The degree of glass-EVA separation in recovered glass fractions is the main determinant of the value of the recovered glass. Glass needs to be completely clean of polymeric material in order to be used as cullets in soda-lime glass manufacturing of flat glass, otherwise only reuse in glass fiber is possible with reduced revenues. Glass-EVA separation was determined by thermogravimetric analyses (TGA) of recoverable glass fractions obtained for the three types of panels (crystalline and amorphous silicon-based panels and CdTe panel). TGA results (not reported here) showed no thermal transition nearby the EVA combustion temperature (650 °C). It means the glass fractions are clean enough to be reused as cullets in soda-lime glass manufacturing.

Experimental results reported in this work are then particularly significant also in comparison with the only automated process actually used for photovoltaic panels recycling, i.e. the First Solar process declaring 90% glass recovery. In the here proposed process a similar amount of glass with the same purity can be recovered (80–85%). On the other hand First solar process is primary used for the recycling of CdTe panels by combining a dry section (shredding and hammer mill) and a wet section with acid-reducing leaching of the whole mass of ground material [16]. More advantageously the here proposed process route allows for the treatment of different kinds of panels (not only CdTe but also crystalline and amorphous silicon) by using a unique process line made up of conventional physical operations, generally available even for small and medium enterprises working on waste recycling. Moreover, in the here proposed process scheme, only fractions larger than 1 mm (10–20%<sub>w</sub>) are treated by thermal treatment and only fractions smaller than 0.08 mm (less than 10%<sub>w</sub>) could be further

treated in a hydrometallurgical section for eventual metal recovery. This implies a significant reduction of energy and chemicals consumption as well as a reduction of equipment size.

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