International Journal of Electrical and Electronic Science
2018; 5(1): 14-32
http://www.aascit.org/journal/ijees
ISSN: 2375-2998

AASCIT American Association for Science and Technology

Studying Characteristics of Radiation Shielding Glass Made of Glass of Cathode Ray Tubes and Heavy Metal Oxides

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Citation

Abdullah Mohammad Shehada, Mohammad Hassan Kharita, Serag Yousef. Studying Characteristics of Radiation Shielding Glass Made of Glass of Cathode Ray Tubes and Heavy Metal Oxides. *International Journal of Electrical and Electronic Science.* Vol. 5, No. 1, 2018, pp. 14-32.

Received: February 27, 2018; **Accepted**: March 26, 2018; **Published**: May 9, 2018

Abstract: The purpose of the research in this paper is to produce a radiation shielding glass by recycling glass of cathode ray tubes (CRTs) which come from used computers and TV sets and adding some heavy metal oxides as lead oxide (PbO) to increase the density, and using some other oxides such as potassium oxide (K_2O) as a modifier for the resulted glasses. Because of, the glass of cathode ray tubes (CRTs) contains some heavy oxides. Where the part Funnel contains about 20% of lead oxide (PbO) while the part Panel contains about 10% of barium oxide (BaO) and the same percent for strontium oxide (SrO). So these glasses can be used as a radiation shielding glass for nuclear and radiation applications. In this paper, the glasses of cathode ray tubes (CRTs) have been used as powdered glass to make new samples with lead oxide (PbO) and potassium oxide (K_2O). Then, the optical and radiation properties of these samples have been investigated. The effects of 1% added of cerium oxide (CeO_2) on the radiation resistant and optical spectra differences have been measured. In addition, this research has environmental benefits that appear in reducing the toxic heavy metals that included in CRT glasses such as lead, barium, strontium and other metals. This paper discuses a new an approach to recycle the CRT glass. The glass transition temperatures (T_g) and the structure of these samples have been investigated by using the differential temperature analysis (DTA) and X-Ray diffraction (XRD) respectively. The optical transmission spectra have been studied, and the transmission studied by using UV-Visible spectrometer and the optical transmission reached to about 85% in the visible spectrum range. Then, attenuation coefficients have been measured for photons emitted by Co^{60}. After that, the optical transmission before and after irradiation have been investigated. The results appeared that these spectra varying by radiation doses and related to the type of used glass in these samples. Where the transmission decreased about 20% to 50% in the beginning of the spectrum range from 400 nm to 600 nm at exposure doses that reached to 5 kGy and high dose rate which was 1 kGy/h. These spectra were not varying in some samples that contain the glass panel. These results agree with similar studies [1], where the density reached to 5.2g.cm^{-3} and the refractive index equal to 1.8, and the value of transmission closed to 85%.

Keywords: Cathode Ray Tubes (CRT's), Radiation Shielding Glass, Recycling, Gamma Attenuation, UV-Visible Spectrometer, Differential Temperature Analysis, Radiation Dose

1. Introduction

The hot cells in nuclear laboratories and isotopes laboratories need vision and observation tools to dealing with isotopes. For this reason, observation cameras or indirect observation systems are used. In addition, the transmittance windows are used for direct using. The glass in these windows that varying in forms and densities used to be the most used material for these applications. The radiation shielding glasses are major tools in these fields to observe

works behind radiation shields especially in high and medium doses in hot cells.

The characteristics of glasses that used as shielding materials varying, such as the density that take the values from 2.3 to 3.6g.cm^{-3} and maybe reach to 6.2g.cm^{-3} in some cases. Where shielding properties of materials against ionizing radiations depend on density and proportion with it generally. As usual, layers of glasses that stable of irradiation putting on the hot side of shielding glass to stop the reduction of transmission that occurs to irradiated glass.

The cerium oxide (CeO_2) is adding by ratios between 1-2% to shielding glasses that have densities between 3.2 to 3.6g.cm^{-3}, since the density increase the added ratio of cerium oxide should be decreasing. Last studies indicated that the stability of transmission of glass against irradiation by gamma rays increases by increasing of cerium oxide until this ratio reaches to 2.5%. Therefore, after this ratio, stability of glass does not depend on ratios of cerium oxide [1-2-3-4].

2. Materials

The amount of waste electrical and electronic equipment (WEEE) or e-waste generated in the world is growing rapidly (Figure 1). The content of hazardous components in electrical and electronic equipment (EEE) is a major concern during the waste management phase. Ideally, the materials in electronic products should be re-used when the products reach the end of their lifetime.

In the European Union (EU), WEEE represents about 7.5 million tons each year, where computer monitors and TV sets containing cathode-ray tubes (CRTs) represent about 80% of the total electronic waste [5].

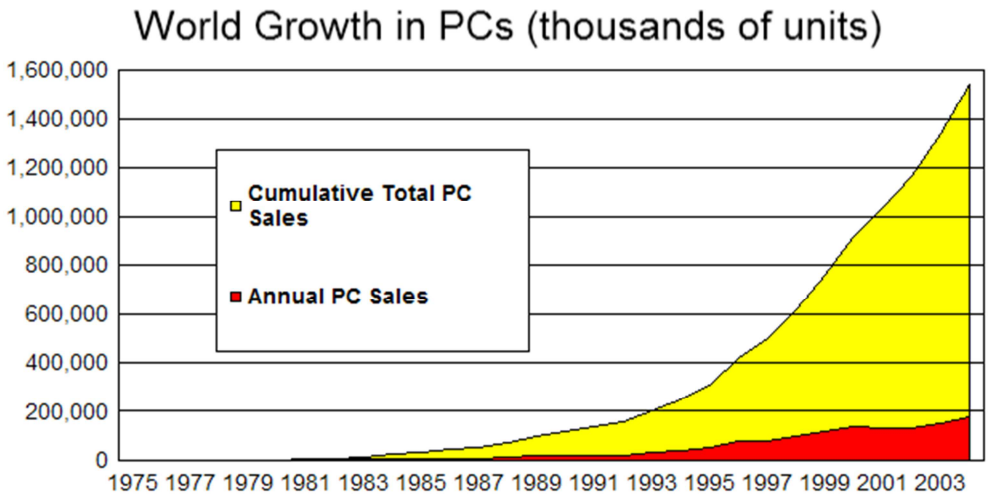

Figure 1. *This figure showing the exponential increases of personal computers In the world [6].*

The Figure 2 Showing the annual energy spending and costing of production a personal computer. In addition, the pollution with a huge amounts of CO_2 gas which released to the atmosphere.

In addition to amounts of CO_2 gas which accompaniment to the production, which emitted to the atmosphere [7].

EfficientProducts.org: US Operational Energy Cost per Computer per Year

Computer Type	Annual Energy Use (kWh)	Electricity Cost (USD)*	CO2 Emissions (lbs.)**	US PCs in Use (millions)	US Total Annual Energy Use (gWh)	US Total Annual CO2 Emissions (millions of lbs)
Desktop	200 - 400	$16 - $32	268 - 536	150	30,000 - 60,000	40,230 - 80,460
Laptop	80 - 140	$6 - $11	107 - 188	50	4,000 - 7,000	5,364 - 9,387
Server	1500	$120,00	2012	10	15,000	20,115

Figure 2. *The spending energy and the costing of production of personal computers per year.*

These huge amounts of toxic wastes effect on the environment and the human especially lead metal that produced by these industries (the total amount of lead metal in 315 million of personal computers that became exhausted between 1997 and 2004 in the united states is about 600 000 tons. Also this amount of personal computers contain about 151.2 tons of metal gold and 1786.1 tons of metal silver almost [8, 9]). These statistics are indicate to the potential importance of recycling these products such as the huge reducing of released CO_2 gas and the reduction spending energies which be needed for the production from the raw materials. In addition, the valuable metals from these PC's can be separated (in these days, these metals are separating by ratio 99% of efficiency).

The three kinds of glass constituting the CRT of the monitor contain hazardous and heavy elements (lead, strontium, antimony, barium, europium, selenium etc...) and weigh between 50% and 85% of the total weight of a

computer monitor or a television set. Currently, collected monitors are dismantled and treated, and the CRT glass generally ends up in a special landfill licensed for hazardous waste. Hence, in Europe almost 90% of the end of life (EOL) electronic goods is disposed of in landfills [5].

As the lead content in these waste products represents as much as 80% of the toxic metals in discard electronics, CRTs represent a clear potential pollution danger to the environment.

To investigate the potential applications of waste CRT glass, characterizations of these materials need to be carried out. Several studies have been carried out to investigate how the waste CRT glass could be re-used [8], but it differs from this paper and its new application on CRT glass.

There are two kinds of cathode-ray tubes: black & white (or monochrome) and color. These two types of CRTs are made of different glass, as shown in Figure 2. The neck

(1 wt%) and funnel (33 wt%) glass constitute the back part of the CRT (hidden inside the monitor or TV set). The front part, usually known as the panel (66 wt%), is made of a barium–strontium glass that has been free of lead since 1995, and is very homogeneous and thick. These three components are usually joined together with a solder glass called frit, which is 85% lead. The neck glass is a lead-rich silicate glass containing more than 25 wt% PbO, which envelopes the electron gun. The lead content of funnel glass is lower than that of neck glass (20 wt% of PbO). The addition of lead to this glass is essential for absorbing the UV and X-ray radiation produced by the electron gun in CRTs; lead is used in funnel and neck glass for this purpose because of its low cost. In the panel glass of color CRTs, however, barium and strontium are used instead of lead, because this glass needs to be colorless. Lead silicate glass is brown whereas barium–strontium silicate glass is transparent under X-ray radiation (i.e. when electrons hit the panel). Lead is only used in the panel glass of black & white CRTs [5].

In the case of color CRT glass, the funnel and screen glass have different densities. Higher densities were obtained for the funnel color glass, i.e. higher than those were of color panels and black & white glass. Color panel glass contains approximately

10 wt% barium oxide and 8.5 wt% strontium oxide, whereas color funnel glass contains approximately 22 wt% lead oxide. The higher density of color CRT funnel glass is because of its lead content. However, the glass densities of the various kinds of glass are quite similar. Indeed, the average densities of color funnel, color panel, and black & white CRT glass are 3.00, 2.80 and 2.70 g/cm^3, respectively, i.e. higher than ‘‘classic’’ window glass (about 2.50 g/cm^3), due to their heavy metal content [5].

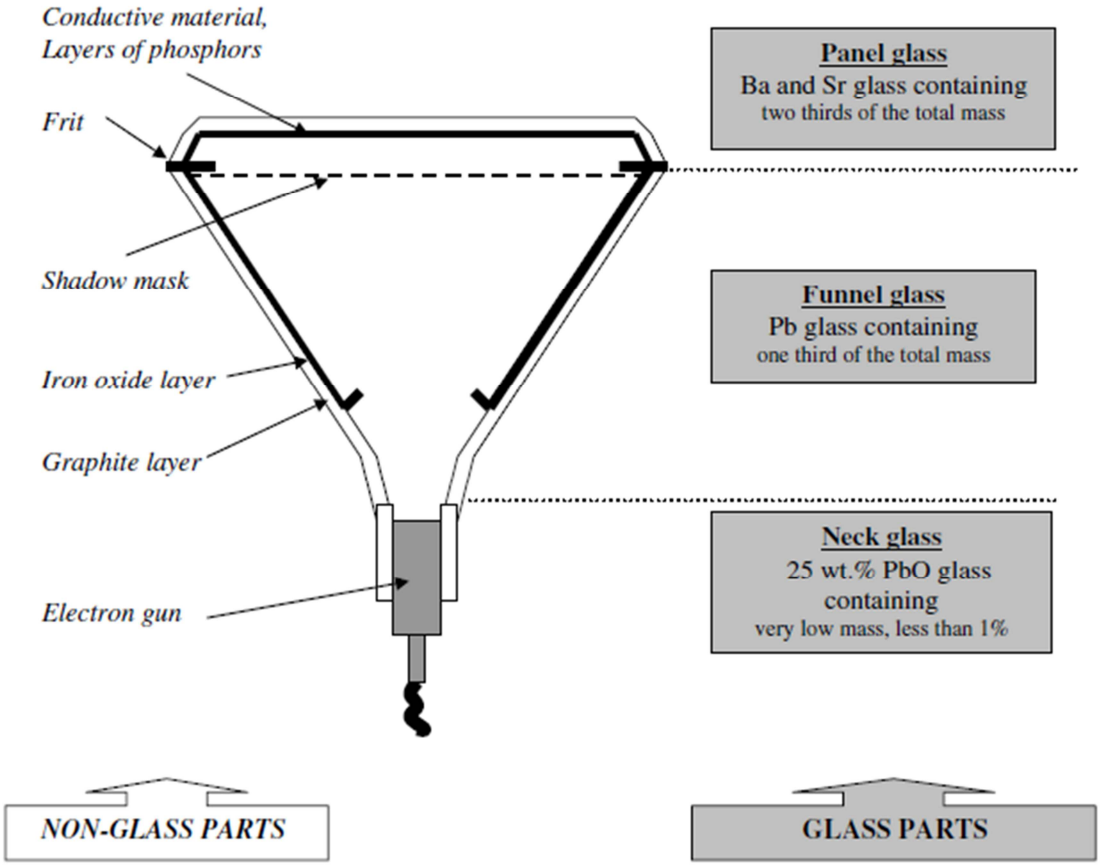

Figure 3. *Showing the glass parts and non glass parts of the Cathode ray tube (CRT) [5].*

The ratios of metal oxides in the CRT’s parts are varying from part to part and from type to type and depend on if the used CRT come from color or non-color monitor as showing in the Figure 4:

Oxide	SiO_2	PbO	K_2O	Na_2O	Al_2O_3	CaO	MgO	BaO	SrO	Sb_2O_3	Fe_2O_3	TiO_2	As_2O_3	ZnO	ZrO_2	Others
Color panel																
Min. conc.	60.00	0.00	6.00	7.80	2.00	0.00	0.00	9.00	6.00	0.25	0.07	0.40	0.00	0.00	0.00	8.48
Max. conc.	63.00	3.00	7.50	9.00	3.50	2.00	1.00	11.00	10.00	0.50	0.12	0.60	0.20	0.60	2.50	0.00
Standard conc.	62.00	0.00	7.50	8.00	2.20	0.50	0.20	10.00	8.50	0.35	0.08	0.50	0.02	0.30	1.50	0.00
HITASHI	58.86	0.00	7.33	7.57	2.21	1.10	0.21	9.30	8.19	0.61	0.04	0.36	0.00	0.01	2.47	1.73
MATSUSHITA	59.74	0.00	7.57	7.16	2.06	0.07	0.00	10.06	8.68	0.65	0.07	0.37	0.01	0.52	1.58	1.48
SAMSUNG	59.51	0.04	7.57	7.19	2.10	0.31	0.06	9.57	8.75	0.59	0.06	0.37	0.01	0.39	1.80	1.68
SONY	59.21	0.01	7.64	7.14	2.07	0.07	0.01	9.93	8.81	0.57	0.07	0.36	0.01	0.51	1.57	2.02
TOSHIBA	60.21	0.00	7.71	6.89	2.05	0.01	0.01	8.99	9.31	0.53	0.07	0.39	0.00	0.52	1.56	1.74
Average values	59.51	0.01	7.56	7.19	2.10	0.31	0.06	9.57	8.70	0.59	0.10	0.37	0.01	0.39	1.80	1.73
Color funnel																
Min. conc.	52.00	19.00	7.50	6.00	3.50	2.00	1.20	0.00	0.00	0.10	0.05	0.00	0.00	0.00	0.00	8.65
Max. conc.	56.00	23.00	8.50	8.00	5.00	4.00	2.00	2.00	1.00	0.30	0.07	0.10	0.10	0.10	0.00	0.00
Standard conc.	52.00	22.00	7.80	6.80	4.00	3.80	1.80	1.00	0.50	0.25	0.06	0.05	0.01	0.00	0.00	0.00
HITASHI	43.37	21.32	6.72	5.08	3.95	2.99	1.58	0.09	0.36	0.88	0.06	0.03	0.00	0.00	0.04	13.53
MATSUSHITA	50.19	23.32	7.30	5.71	3.62	3.78	1.67	0.53	0.69	0.55	0.07	0.05	0.00	0.04	0.09	2.39
SAMSUNG	52.94	23.39	7.74	5.67	2.10	3.53	2.40	0.10	0.47	0.40	0.08	0.03	0.00	0.03	0.04	1.07
SONY	50.51	22.51	7.32	5.64	3.38	3.80	1.83	1.03	1.04	0.53	0.12	0.09	0.00	0.06	0.19	1.96
TOSHIBA	51.85	24.12	7.46	5.54	3.35	3.70	1.77	0.04	0.39	0.48	0.07	0.05	0.00	0.01	0.06	1.09
Average values	49.77	22.90	7.31	5.53	3.28	3.56	1.85	0.36	0.60	0.57	0.10	0.05	0.00	0.03	0.08	4.01
Black & white (panel and funnel)																
Min. conc.	64.00	2.80	6.00	6.50	3.00	0.00	0.00	9.00	0.00	0.30	0.05	0.10	0.00	0.00	0.00	8.25
Max. conc.	66.00	4.40	7.50	8.00	5.00	1.00	0.00	12.00	2.00	0.60	0.20	0.20	0.30	0.10	0.50	0.00
Standard conc.	65.00	4.00	7.00	7.00	3.00	0.50	0.00	11.00	1.00	0.45	0.12	0.15	0.01	0.05	0.25	0.47
Funnel CLINTON Corp.	63.55	3.47	6.24	6.90	3.08	0.03	0.01	12.74	1.15	0.75	0.06	0.00	0.01	0.01	0.01	2.00
Panel CLINTON Corp.	63.88	3.42	6.28	7.00	3.10	0.02	0.01	12.85	1.15	0.74	0.06	0.01	0.00	0.00	0.03	1.46

Figure 4. *Ratios of oxides in any types of CRT's [5].*

Usual Methods of recycling the glass of CRT's:

1. recycling the glass of CRTs to produce new CRTs, but in this case all parts of CRT should be separated because the mixture of parts panel and funnel will contain lead oxide (PbO) which is not suitable for new panels, where the color of panel will be changing under X-rays [5].
2. The glass of CRTs can be used in the ceramics products, building materials and with the cement. This glass is useful to make the foam glass [5].

3. Experimental

3.1. Preparing the CRTs Glasses

Firstly, the type of CRT glass has been chosen for the experiments, HITACHI Corporation makes the chosen CRT. Then, the parts of this CRT have been separated (Funnel, Panel, Neck and Frit). After that, these parts cleaned from the phosphorus layers that coating the entire side of Panel, and the iron oxide and graphite layers that coating the part funnel.

Table 1. *Ratios of oxides of CRT parts analyzed by SEM-EDX.*

Oxides	Panel	Funnel	Mixture	Neck
B_2O_3	7.53	6.90	6.21	5.37
Na_2O	6.78	5.86	6.15	1.58
MgO	0.07	1.71	0.76	0.18
Al_2O_3	1.98	4.89	2.74	2.45
SiO_2	54.72	45.92	52.20	43.21
K_2O	5.65	6.08	6.59	7.11
CaO	0.94	3.47	1.55	1.30
SrO	9.48	1.47	6.89	2.27
ZrO_2	2.44	0.82	2.04	0.37
Sb_2O_3	0.25	0.06	0.14	0.69
BaO	7.88	0.00	5.70	0.42
CeO_2	0.41	0.42	0.37	0.44
PbO	0.00	20.03	6.50	33.15
SnO	0.00	0.06	0.62	0.11
TiO_2	0.33	0.47	0.43	*0.21*

3.2. Preparing the Mixtures of Samples

The program of samples has been divided to two steps:

The first step: preparing the samples to have the ratios: 50%, 60% and 70% of lead oxide (PbO) and adding the potassium oxide (K_2O) to some (not all) samples to investigate the effects of this oxide on the resulted samples. In addition, the potassium oxide is needed to decrease the melting temperature. These ratios of lead oxide applied to the parts: Funnel and Panel in addition to the mixture of parts; Panel, Funnel and Neck as follow: Mixture (Mix) = 65% Panel + 34% Funnel+ 1% Neck, because these ratios of parts is almost the same ratios of them in the total CRT. The second step: in this step the samples that have 60% of lead oxide have been chosen to be added to 1% of cerium oxide (CeO_2). The cerium oxide added to investigate effects of this oxide on the irradiation resistance and discoloring of glasses samples under high doses of gamma radiation.

Table 2. *Weights of added components of mixtures for samples.*

The sample	Weights of added glasses (g)			Weights of added raw materials (g)		
	Funnel	Panel	Mix	Pb_3O_4	K_2CO_3	CeO_2
The first step of samples						
GF1	80	-	-	132.9	-	-
GF2	100	-	-	99	-	-
GF3	120	-	-	70.5	-	-
GF4	80	-	-	149.2	10	-
GF5	100	-	-	125.2	25	-
GF6	120	-	-	87.9	25	-
GP1	-	80	-	191.1	-	-
GP2	-	100	-	153.6	-	-
GP3	-	120	-	122.9	-	-
GP4	-	80	-	231.8	25	-
GP5	-	100	-	179.7	25	-
GP6	-	120	-	140.3	25	-
GM1	-	-	80	170.5	-	-
GM2	-	-	100	134.3	-	-
GM3	-	-	120	104.3	-	-
GM5	-	-	100	160.4	25	-
GM6	-	-	120	121.8	25	-
The second step of samples						
GFCe	100	-	-	102.1	-	2
GPCe	-	100	-	157.4	-	2.5
GMCe	-	-	100	137.8	-	2.3

While the weigh ratios of components are as follow:

Table 3. *Ratios of added components of mixtures.*

The sample	Ratios of added glasses (%)			Ratios of added Oxides (%)		
	Funnel	Panel	Mix	PbO	K_2O	CeO_2
The first step of samples						
GF1	38.1	-	-	61.9	-	-
GF2	50.8	-	-	49.2	-	-
GF3	63.5	-	-	36.5	-	-
GF4	34.4	-	-	62.7	2.9	-
GF5	41.8	-	-	51.1	7.1	-
GF6	53.8	-	-	38.5	7.7	-
GP1	-	30	-	70	-	-
GP2	-	40	-	60	-	-
GP3	-	50	-	50	-	-
GP4	-	24.7	-	70	5.3	-
GP5	-	34.2	-	60	5.8	-
GP6	-	43.8	-	50	6.2	-
GM1	-	-	32.5	67.5	-	-
GM2	-	-	43.3	56.7	-	-
GM3	-	-	54.1	45.9	-	-
GM5	-	-	36.5	57.2	6.3	-
GM6	-	-	46.9	46.5	6.6	-
The second step of samples						
GFCe	49.6	-	-	49.4	-	1
GPCe	-	39	-	60	-	1
GMCe	-	-	42.2	56.8	-	1

4. Results and Discussion

4.1. Thermal Methods and Glass Transition Temperatures of Samples (T_g)

The glass transition temperatures measured by using the differential temperature analysis (DTA). The figure 5, showing the curve of differential temperature analysis (DTA) and glass transition temperature for the sample (GF3) as appearing in the table 4. This table also showing the melting and annealing temperatures and the periods of melting and annealing operations (where the annealing rate was about 23°C/h).

Table 4. *Melting and annealing temperatures and the periods of them. In addition to glass transition temperatures of all samples (T_g).*

The sample	Ratio of PbO (%)	Glass transition temperature (Tg)	Melting temperature Tm (°C)	Time of stability on Tm (minutes)	Annealing temperature Tan (°C)	Time of stability on Tan (minutes)
GF1	70	413.6	1100	150	390	120
GF2	60	431.8	1130	90	390	120
GF3	50	457.0	1200	90	410	30
GF4	70	396.3	1100	150	390	120
GF5	60	390.7	1090	90	390	180
GF6	50	418.2	1150	90	410	45
GP1	70	431.8	1070	90	370	135
GP2	60	431.0	1130	30	410	75
GP3	50	455.6	1200	90	410	30
GP4	70	432.2	1070	30	365	30
GP5	60	417.0	1090	30	375	30
GP6	50	425.8	1190	5	395	15

The sample	Ratio of PbO (%)	Glass transition temperature (Tg)	Melting temperature Tm (°C)	Time of stability on Tm (minutes)	Annealing temperature Tan (°C)	Time of stability on Tan (minutes)
GM1	70	372.8	1070	30	375	75
GM2	60	427.8	1130	30	410	75
GM3	50	454.2	1200	90	410	30
GM5	60	409.3	1090	30	375	30
GM6	50	423.7	1150	60	370	90
Mix	7.6	542.6	1380	5	25	0
GFCe	60	438.8	1160	5	395	30
GPCe	60	417.6	1160	5	395	30
GMCe	60	432.6	1160	5	395	*30*

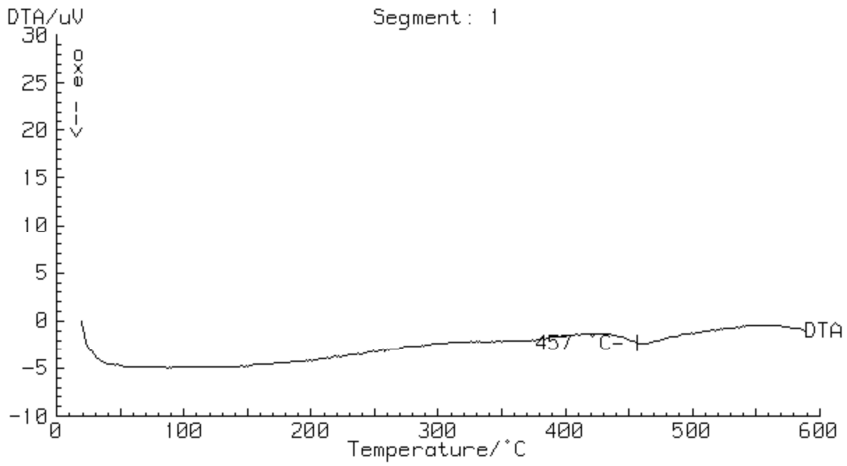

Figure 5. *The differential temperature analysis (DTA) curve and glass transition temperature for the sample (GF3).*

Some remarks for the melting and annealing temperatures and the homogenates of resulted samples:

- All resulted samples were very clear and homogenous and have a little number of cords and bubbles where were very small. Some of these samples were very well and do not have any kinds of cords or bubbles as samples: GM2 and GF6.

GF6

Figure 6. *The GF6 sample.*

GM2

Figure *7. The GM2 sample.*

- Many degrees of colors have been observed that varying by ratio of added oxides especially lead oxide (PbO) and potassium oxide (K_2O). Where the yellow color appears when lead oxide added to the mixtures and this color increases at high ratios of lead oxide.

- The decreasing of melting temperatures have been remarked when lead oxide added to the mixtures, also the same case occurs when potassium oxide added too. Melting temperatures also decreases when the glass of CRT added in high ratios to the mixtures that appeared in the comparison between some samples. These results agree with many papers investigated these effects of added glasses [10], where 2% added glass decrease the melting temperatures about 350°C and that depends on types of added glasses.

- These samples appeared that the CRT glass could be added to the mixtures by ratios between 30% to 60% to produce a radiation shielding glass.

- One of investigated results that the potassium oxide can be added by limited ratios. If it added to the mixtures over these limits, so it may produce non-glasses samples (as happened to the sample (GM4), or it may have a swarthy color (swarthy green color) when it added by high ratio with lead oxide in the mixtures such as the sample (GM1):

GM1

Figure 8. *The GM1 sample.*

- In many cases, the swarthy colors can be disappeared when these samples re-melting at the same temperature or higher temperature or more period of time for melting and annealing operations.
- In some cases, many defects of resulted glass appeared such as very small cords and bubbles (this is a major case in the glass industry). These defects could return to non-homogeneous melting or mixtures.
- The dimensions of resulted samples are between 2 to 5 cm in width and no more than 1 cm of thickness.

4.2. Chemical and Physical Characteristics of Samples

4.2.1. The Chemical Composition

The tables 5, 6 and 7 contain the ratios of oxides of all samples.

Table 5. *Ratios of oxides of the group GF.*

Oxides	GF1	GF2	GF3	GF4	GF5	GF6
B_2O_3	2.63	3.51	4.38	2.07	2.88	3.71
Na_2O	2.24	2.98	3.73	1.76	2.45	3.16
MgO	0.65	0.87	1.09	0.51	0.71	0.92
Al_2O_3	1.87	2.49	3.11	1.47	2.04	2.63
SiO_2	17.51	23.35	29.18	13.78	19.19	24.72
K_2O	2.32	3.09	3.87	8.22	9.66	10.92
CaO	1.32	1.76	2.20	1.04	1.45	1.87
SrO	0.56	0.75	0.93	0.44	0.61	0.79
ZrO_2	0.31	0.42	0.52	0.25	0.34	0.44
Sb_2O_3	0.02	0.03	0.04	0.02	0.03	0.03
BaO	0.00	0.00	0.00	0.00	0.00	0.00
CeO_2	0.16	0.21	0.27	0.13	0.17	0.22
PbO	69.50	59.34	49.18	69.61	59.46	49.30
SnO	0.02	0.03	0.04	0.02	0.02	0.03
TiO_2	0.18	0.24	0.30	0.14	0.20	0.25
P_2O_5	0.00	0.00	0.00	0.00	0.00	0.00
Bi_2O_3	0.00	0.00	0.00	0.00	0.00	0.00
As_2O_3	0.00	0.00	0.00	0.00	0.00	0.00

Table 6. *Ratios of oxides of the group GP.*

Oxides	GP1	GP2	GP3	GP4	GP5	GP6
B_2O_3	2.26	3.01	3.76	1.86	2.57	3.30
Na_2O	2.03	2.71	3.39	1.68	2.32	2.97
MgO	0.02	0.03	0.03	0.02	0.02	0.03
Al_2O_3	0.60	0.79	0.99	0.49	0.68	0.87
SiO_2	16.42	21.89	27.36	13.54	18.71	23.96
K_2O	1.70	2.26	2.82	6.67	7.76	8.69
CaO	0.28	0.37	0.47	0.23	0.32	0.41
SrO	2.85	3.79	4.74	2.35	3.24	4.15
ZrO_2	0.73	0.98	1.22	0.60	0.84	1.07
Sb_2O_3	0.08	0.10	0.12	0.06	0.09	0.11
BaO	2.36	3.15	3.94	1.95	2.69	3.45
CeO_2	0.12	0.16	0.20	0.10	0.14	0.18
PbO	70.00	60.00	50.01	70.00	59.99	50.00
SnO	0.00	0.00	0.00	0.00	0.00	0.00
TiO_2	0.10	0.13	0.17	0.08	0.11	0.15
P_2O_5	0.00	0.00	0.00	0.00	0.00	0.00
Bi_2O_3	0.00	0.00	0.00	0.00	0.00	0.00
As_2O_3	0.00	0.00	0.00	0.00	0.00	0.00

Table 7. *Ratios of oxides of the group GM and samples that have 1% of CeO_2.*

Oxides	GM1	GM2	GM3	GM4	GM5	GM6	GFCe	GPCe	GMCe
B_2O_3	2.02	2.69	3.36	1.64	2.27	2.91	3.42	2.94	2.62
Na_2O	1.99	2.66	3.32	1.62	2.25	2.88	2.91	2.65	2.59
MgO	0.25	0.33	0.41	0.20	0.28	0.36	0.85	0.03	0.32
Al_2O_3	0.89	1.19	1.48	0.72	1.00	1.28	2.43	0.77	1.16
SiO_2	16.94	22.58	28.23	13.77	19.07	24.47	22.76	21.36	22.04
K_2O	2.14	2.85	3.56	7.36	8.63	9.74	3.02	2.20	2.78
CaO	0.50	0.67	0.84	0.41	0.57	0.73	1.72	0.37	0.66
SrO	2.24	2.98	3.73	1.82	2.52	3.23	0.73	3.70	2.91
ZrO_2	0.66	0.88	1.10	0.54	0.75	0.96	0.41	0.95	0.86

Oxides	GM1	GM2	GM3	GM4	GM5	GM6	GFCe	GPCe	GMCe
Sb_2O_3	0.05	0.06	0.08	0.04	0.05	0.07	0.03	0.10	0.06
BaO	1.85	2.47	3.08	1.50	2.08	2.67	0.00	3.08	2.41
CeO_2	0.12	0.16	0.20	0.10	0.14	0.17	1.20	1.14	1.13
PbO	69.66	59.55	49.43	69.72	59.61	49.51	59.36	60.00	59.56
SnO	0.20	0.27	0.34	0.16	0.23	0.29	0.03	0.00	0.26
TiO_2	0.14	0.19	0.23	0.11	0.16	0.20	0.23	0.13	0.18
P_2O_5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Bi_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
As_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

4.2.2. The Density and Refractive Index

The densities of samples have been measured by using Archimedean method in medium of water at lab temperature (about 25°C). The refractive indexes measured by using laser source (wavelength between 630 – 680 nm).

Table 8. *Densities and refractive indexes of samples.*

The sample	Ratio of PbO (%)	Density ($g.cm^{-3}$) (± 0.01)	Refractive index N_d at (655 ± 25 nm) (± 3.5%)	Thickness of sample after polishing (mm) (± 0.05 mm)
GF1	70	5.26	1.906	5.10
GF2	60	4.72	1.807	2.80
GF3	50	4.11	1.790	5.60
GF4	70	5.12	1.813	5.70
GF5	60	4.55	1.746	6.05
GF6	50	4.07	1.734	6.35
GP1	70	4.79	1.827	6.30
GP2	60	4.92	1.880	6.35
GP3	50	4.41	1.760	4.60
GP4	70	5.28	1.908	6.40
GP5	60	4.61	1.842	3.25
GP6	50	4.24	1.700	6.35
GM1	70	5.38	1.833	6.25
GM2	60	4.97	1.807	6.35
GM3	50	4.36	1.689	4.10
GM5	60	4.61	1.856	6.40
GM6	50	4.19	1.743	5.80
Mix	7.6	2.88	1.505	4.10

From the table 8, the density increases when the ratios of lead oxide increases, and that is reasonable result because the high density of added lead oxide (About $9.35 g.cm^{-3}$). This result appears in the figure 9:

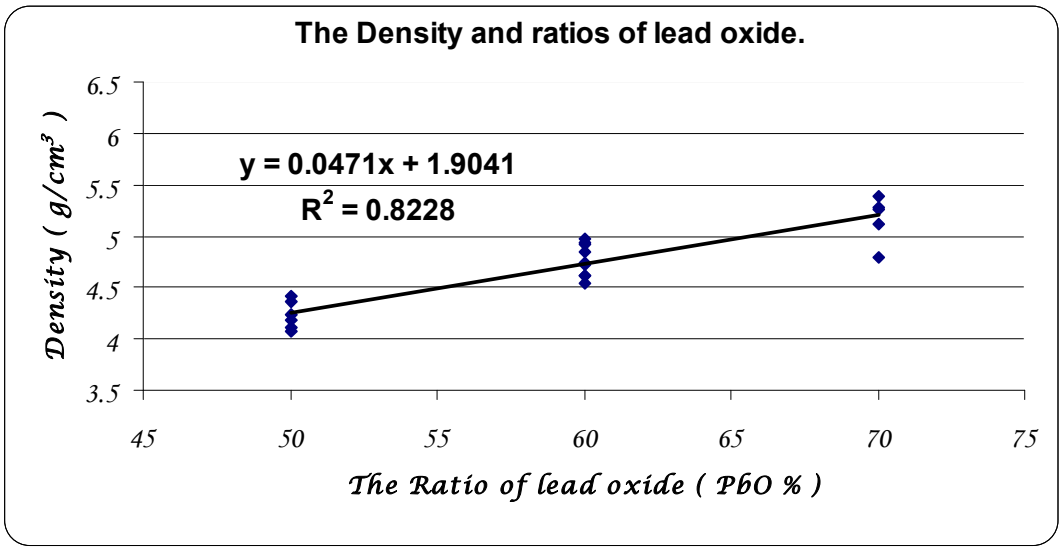

Figure 9. *Increasing densities by increasing ratios of lead oxide.*

At ratios: 50%, 60% and 70% of lead oxide and looking to tables 7, 8, 9, and 10, the decreasing of density to $0.5 g.cm^{-3}$ can be found when the ratio of potassium oxide (K_2O) increases about 7-8% (in the same time the silicon oxide decreases about 7-

8%).

The refractive index also increases by increasing of density as showing in the figure 10:

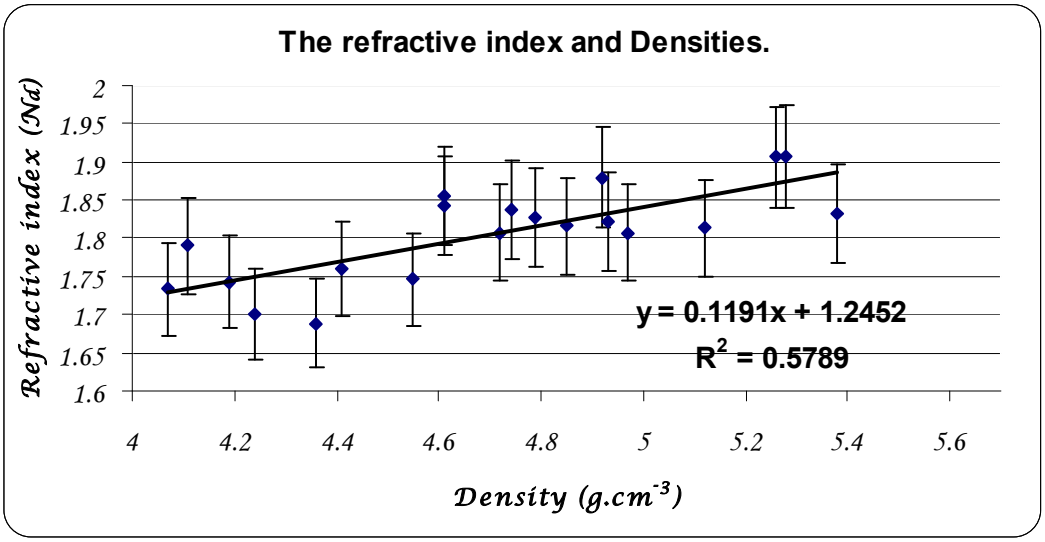

Figure 10. *The increasing of refractive index and densities.*

4.2.3. Linear Attenuation Coefficients, Half and Tenth Value Layers and the Lead Equivalent

The linear attenuation coefficients were measured by using Co^{60} as radiation source. This isotope has two energies: 1.173 MeV and 1.332 MeV, and the detector were at the distance 1 m from the source. Also the linear attenuation coefficients were calculated for other energies by using the code XCOM (this program is used to calculate the attenuation coefficients for photons that have energies between 1 keV to 100 GeV by entering the ratios of compositions of the materials in the program) [11]. The empirical results were very close to the theoretical results as listed in the table 9:

Table 9. *Attenuation coefficients experimentally and theoretically (XCOM code).*

The sample	Density (g.cm^{-3})	Experimental attenuation coefficients (cm^{-1})		Theoretical attenuation coefficients by using the code XCOM (cm^{-1})			
		At energy Co-60 (keV)		At energies (keV)			
				X-Ray	Cs-137	Co-60	
		1332.5	1173.24	100	661.6	1173.24	1332.5
GF1	5.26	0.32		19.18	0.52	0.32	0.29
GF2	4.72	0.22		14.86	0.45	0.28	0.26
GF3	4.11	0.23		10.84	0.38	0.25	0.23
GF4	5.12	0.32		18.70	0.50	0.31	0.28
GF5	4.55	0.27		14.33	0.43	0.27	0.25
GF6	4.07	0.22		10.78	0.37	0.24	0.23
GP1	4.79	0.31		17.87	0.47	0.29	0.27
GP2	4.92	0.30		16.00	0.47	0.29	0.27
GP3	4.41	0.23		12.26	0.41	0.26	0.24
GP4	5.28	0.28		19.66	0.52	0.32	0.29
GP5	4.61	0.29		14.96	0.44	0.28	0.25
GP6	4.24	0.25		11.71	0.39	0.25	0.23
GM1	5.38	0.32		19.93	0.53	0.33	0.30
GM2	4.97	0.29		15.99	0.47	0.30	0.27
GM3	4.36	0.26		11.91	0.40	0.26	0.24
GM5	4.61	0.28		14.82	0.44	0.28	0.26
GM6	4.19	0.24		11.43	0.39	0.25	0.23
Mix	2.88	0.17		1.92	0.23	0.17	0.16
GFCe	4.74	0.30		15.01	0.45	0.29	0.26
GPCe	4.93	0.32		16.12	0.47	0.29	0.27
GMCe	4.85	0.30		15.68	0.46	0.29	0.27
Pb	11.342	0.66		62.94	1.25	0.70	0.64

The attenuation coefficients increase (as expected) when the density increases as showing in the figure 11:

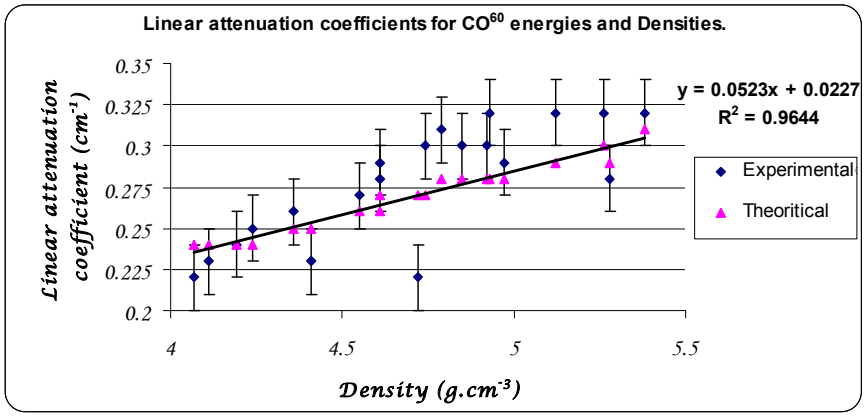

Figure 11. *Increasing of attenuation coefficients by increasing of densities.*

Calculation the half and tenth value layers:

Table 10. *The half value and tenth value layers, in addition to the lead equivalent.*

The sample	Half value layers at isotope's energies (cm)		Tenth value layers at isotope's energies (cm)		The lead equivalent for 1 cm thickness of each sample at isotope's energies (cm)	
	Co-60	Cs-137	Co-60	Cs-137	Co-60	Cs-137
GF1	2.24	1.33	7.43	4.43	0.47	0.45
GF2	2.57	1.54	8.53	5.12	0.41	0.39
GF3	2.89	1.82	9.59	6.06	0.36	0.33
GF4	2.31	1.39	7.68	4.61	0.45	0.43
GF5	2.67	1.61	8.86	5.35	0.39	0.37
GF6	3.01	1.87	10.01	6.22	0.35	0.32
GP1	2.48	1.47	8.22	4.90	0.42	0.41
GP2	2.48	1.47	8.22	4.90	0.42	0.41
GP3	2.77	1.69	9.21	5.62	0.38	0.36
GP4	2.24	1.33	7.43	4.43	0.47	0.45
GP5	2.57	1.58	8.53	5.23	0.41	0.38
GP6	2.89	1.78	9.59	5.90	0.36	0.34
GM1	2.17	1.31	7.20	4.34	0.48	0.46
GM2	2.39	1.47	7.94	4.90	0.44	0.41
GM3	2.77	1.73	9.21	5.76	0.38	0.35
GM5	0.03	1.58	0.09	5.23	0.41	0.38
GM6	2.89	1.78	9.59	5.90	0.36	0.34

4.2.4. The Glasses Structure of Samples

The structure of samples has been studied by using the X-ray diffraction (XRD) and results were all produced samples were a glass (amorphous structure). The figure 12 appears the XRD curve of sample GP4:

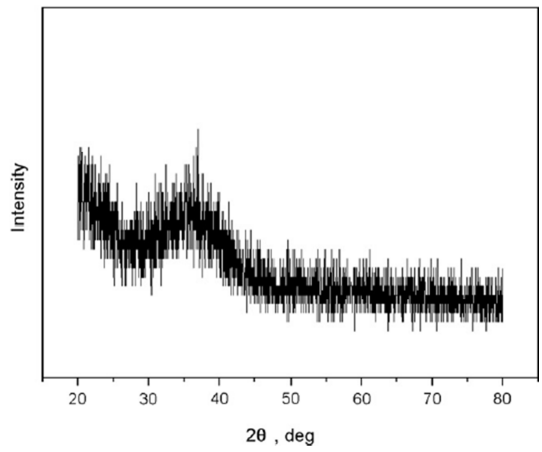

Figure 12. *The XRD curve of sample GP4.*

4.2.5. The Optical Transmission Spectra Before and After Irradiation, and the Effects of Added Cerium Oxide on Irradiation Resistance and Discoloring of Samples

i. The Transmission Spectra Before Irradiation

The transmission spectra are taken for thickness 1 cm of samples. The transmission spectra can be calculated when the transmission and the absorbance are known at determined thickness, then by using Beer-Lambert equation [12]:

$I = I_0 . (1 - R)^2 .\exp(-\mu.d)$ (where the transmission is $T = I / I_0$) so the transmission spectra at any thickness can be calculated by using the following equation:

$T_2 = T_1.\exp(\mu. (d_1 - d_2))$, where T_2 is the optical transmission at 1 cm and $d_2 = 1$ cm.

- The transmission spectra of GF samples:

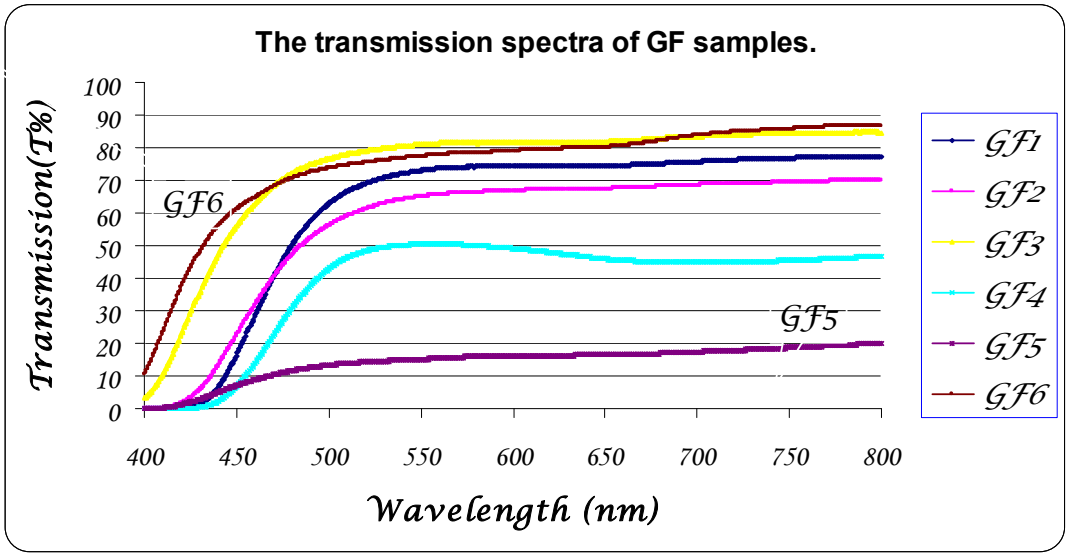

Figure 13. *The transmission spectra of GF samples.*

The best two curves of transmission of these samples are the curves for samples GF3 and GF6, where the transmission can close to 80% at most of the wavelength range. These two samples have 50% of lead oxide (PbO) and the sample GF3 contain about 4% of K_2O while the sample GF6 have about 11% of it. The curves of these two samples are very close to each other. Therefore, that indicate the increasing of potassium oxide (K_2O) was not suitable to increase the transmission (although two samples produced under the same thermal program such as the melting and annealing temperature).

By comparison between samples GF1, GF4 and GF2, GF5 where each pair have the same ratio of lead oxide 70% and 60% respectively. Moreover, the samples in each pair produced under the same thermal conditions but it have different ratios of K_2O. So, the samples that have high ratios of K_2O more than 7-8% and have ratios of lead oxide more than 50% the result would be more decreasing of optical transmission. Where the transmission of sample GF2 decreased from 70% to about 20% (GF5).

- The transmission spectra of GP samples:

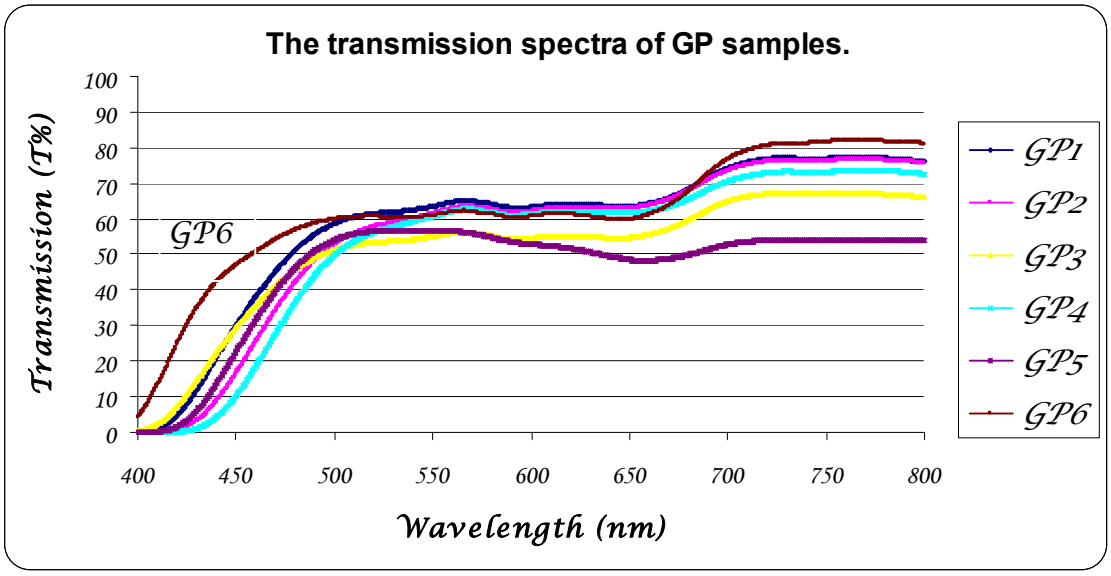

Figure 14. *The transmission spectra of GP samples.*

The best transmission curve is for sample GP6 that consist of 50% PbO + 9 K_2O + …etc, and it is better than sample GP3 that contain the same ratio of PbO but it contain about 3% of K_2O. Therefore, in this case the potassium oxide play positive role to improve the transmission opposite of other samples. Where all curves are close to others although the variation of lead oxide that reaches to 20% and that maybe relates to the strontium oxide (SrO) and barium oxide (BaO) with ratio about 4% of each one in these samples.

- The transmission spectra of GM samples:

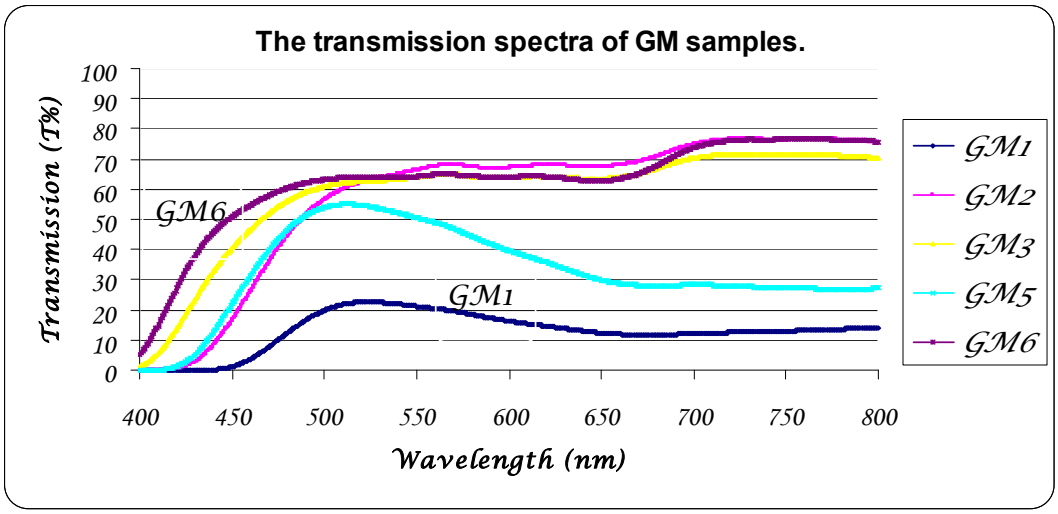

Figure 15. *The transmission spectra of GM samples.*

The sample that has the best transmission curve is the sample GM6, where it is better than sample GM3 with little difference after adding the K_2O. The sample GM1 has very weak optical transmission reaches to 10%. Since the potassium oxide decreasing the transmission when it adds to the mixtures that have high ratio of lead oxide (PbO) (more than 50%) as found from the last figures, so the expectation for the sample GM4 is to be having more weakly transmission than the sample GM1 (that have originally very weak transmission). Therefore, the GM4 will be non-glass samples and this result is what is found in these experiments.

ii. The Transmission Spectra After Irradiation, and Studying the Effects of Added Cerium Oxide on Irradiation Resistance and Discoloring of Samples

The glasses were irradiated by using the source Co^{60} to three doses: 1 kGy, 3 kGy and 5 kGy where the dose rate is 1 kGy/h, and then the optical transmission was studied after about 16 hours. Three samples have been chosen that have 60% of lead oxide (PbO) to add 1% of cerium oxide to them. Then, the transmission spectra were studied before and after adding the cerium oxide to investigate effects of it on the stability of transmission spectra under irradiation conditions.

First: the transmission spectra of sample GF2:

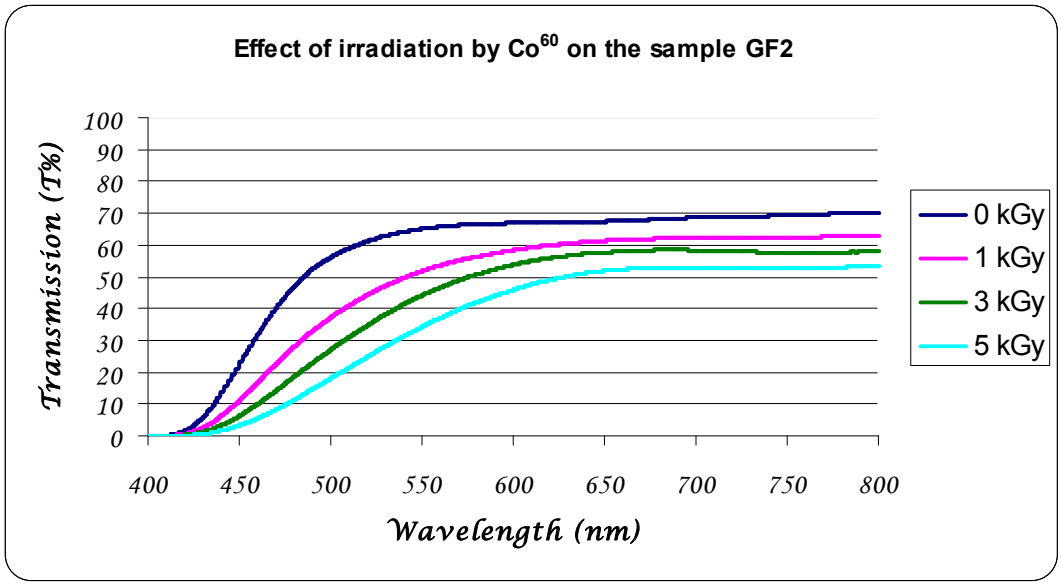

Figure 16. *The effect of irradiation on transmission spectra of sample GF2.*

The transmission decreases by increasing doses of gamma radiation from 70% to 50% in the wavelength 650 nm to 800 nm. Less decreasing occurs at the beginning of wavelength range by comparison between curves in two cases of doses: 0 kGy and 5 kGy.

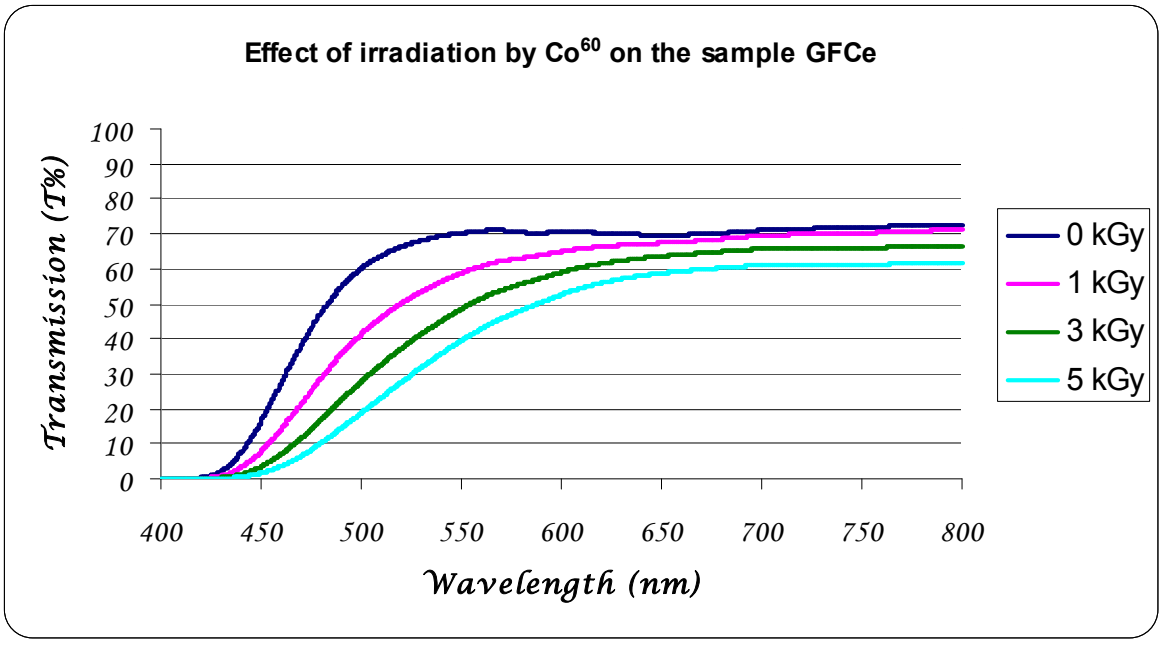

Figure 17. *The effect of irradiation on transmission spectra of sample GFCe (GF2 + 1% of CeO_2).*

The added cerium oxide improved the transmission spectra and made the sample more resistance of irradiation. So, the transmission improved 10% almost at most of the wavelength range (550 nm to 800 nm) but it didn't improve the transmission at smallest wavelengths, by the comparison between samples in two cases 0 kGy and 5 kGy.

These results clearly appear by the figure 18 as follow:

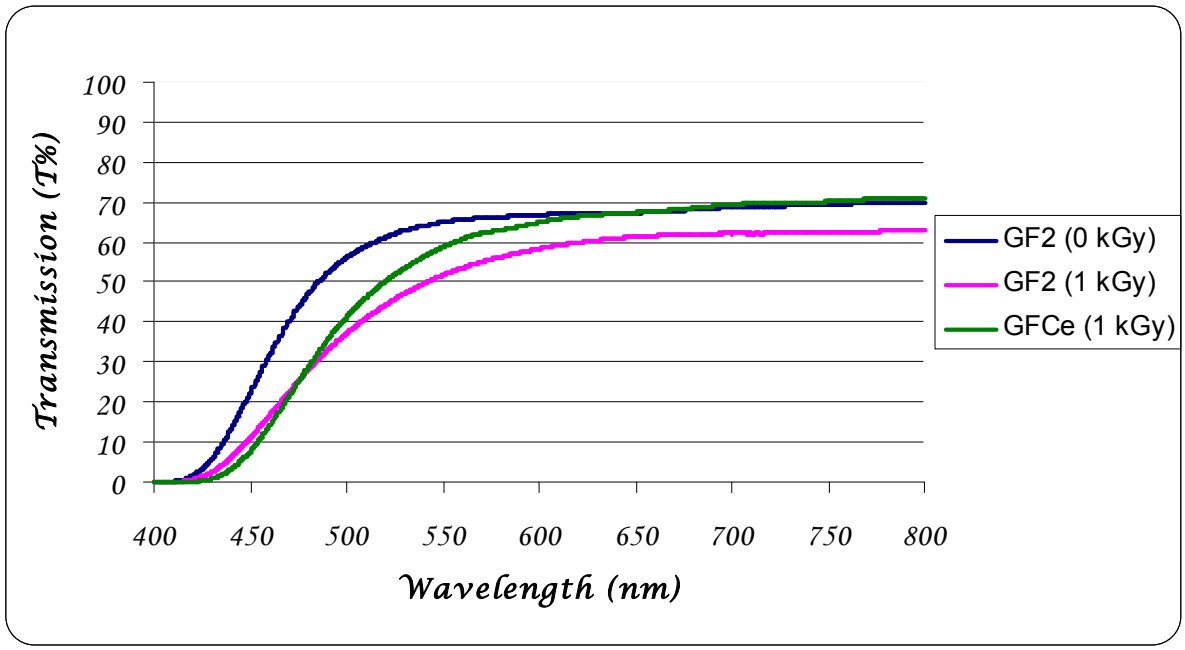

Figure 18. *The effect of added 1% CeO_2 to the sample GF2 at the radiation dose 1 kGy.*

The figure 19, showing the difference of irradiation effect on the sample GF2 before and after adding 1% CeO_2 by increasing doses at the wavelength 589 nm:

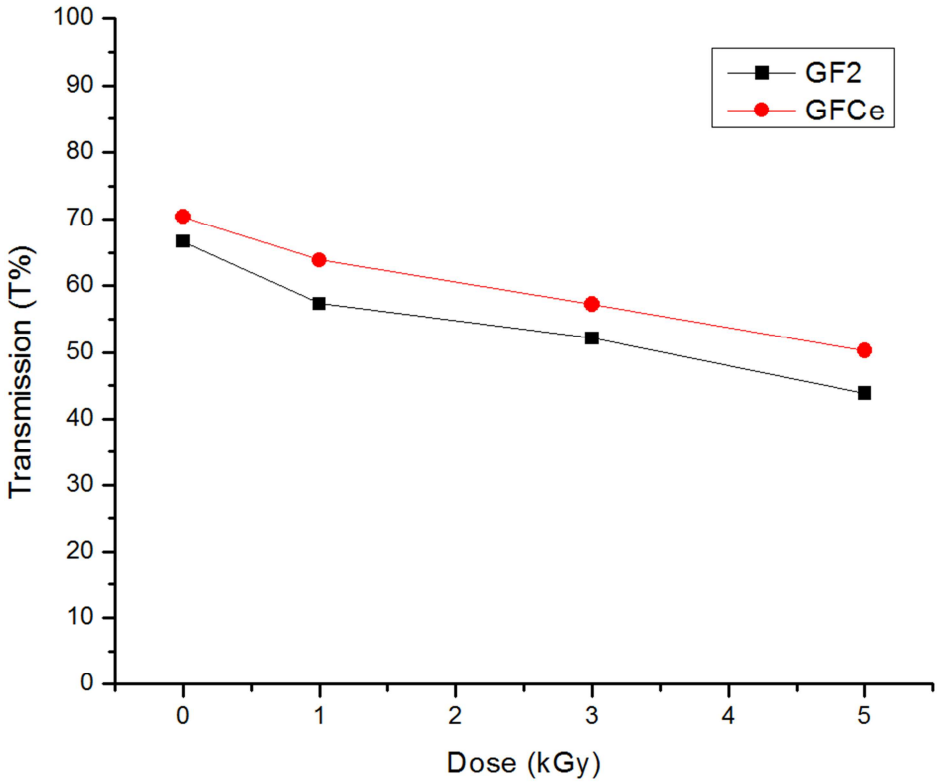

Figure 19. *The difference of irradiation effect on the sample GF2 before and after adding 1% CeO_2 by increasing doses at the wavelength 589 nm.*

The added cerium oxide with 1% to the sample GF2 improved the transmission and the irradiation resistance. In addition, this oxide improved the transmission about 5% even before the irradiation.

Second**:** the transmission spectra of sample GP2:

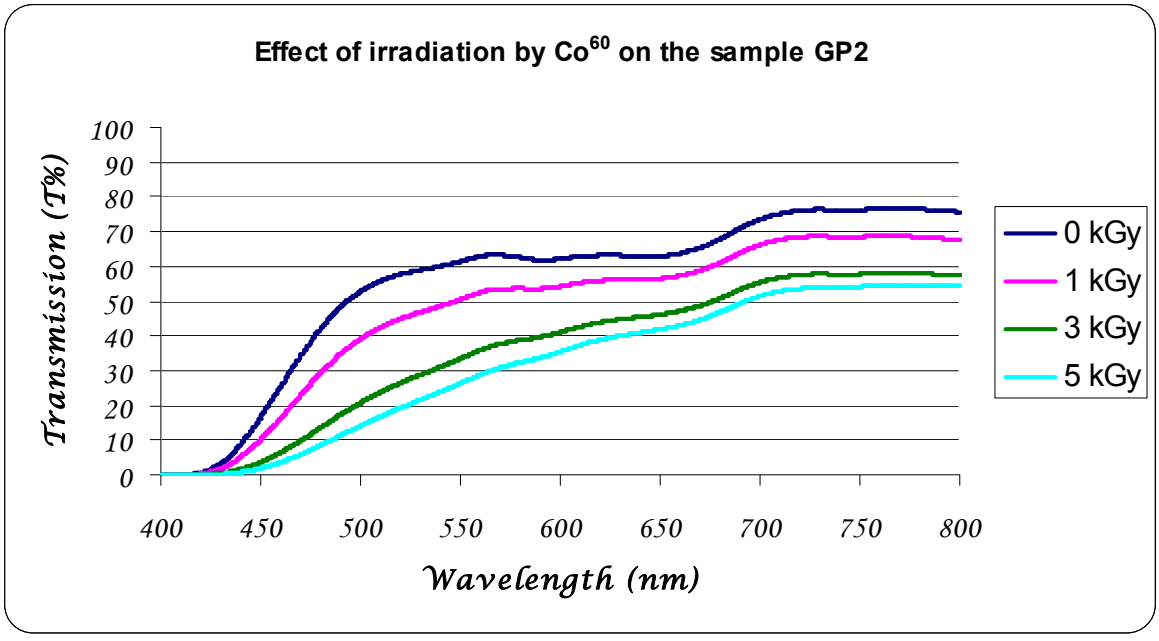

Figure 20. *The effect of irradiation on the transmission spectra of sample GP2.*

The decreasing of transmission by increasing doses can be observed in this case also, where it decreases about 20% from the wavelength 650 nm to 800 nm, and more decreasing occurs at the shorter wavelengths, by the comparison between two cases 0 kGy and 5 kGy.

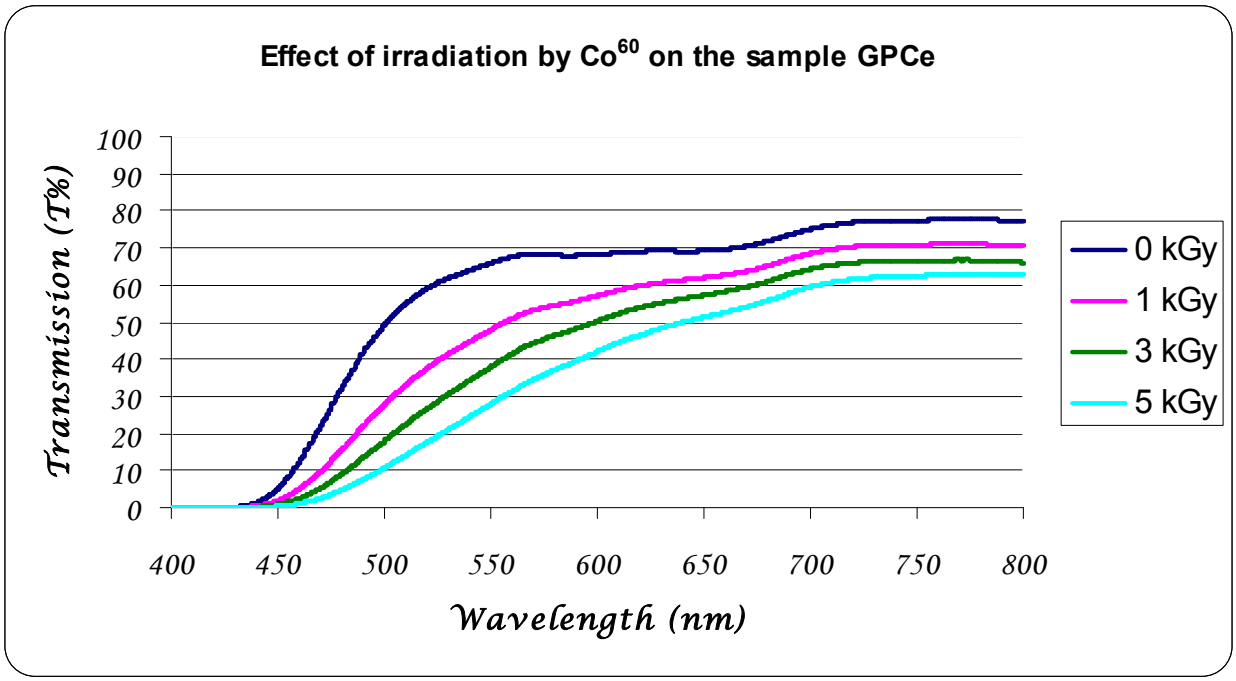

Figure 21. *The effect of irradiation on transmission spectra of sample GPCe (GP2 + 1% of CeO_2).*

In this case, the transmission spectra did not improve clearly by adding the cerium oxide with ratio 1%. Where the transmission did not improve so much in the wavelength range between 570 nm to 800 nm almost. While in the shorter wavelength, the transmission decreased about 10% when the cerium oxide added. This result appears clearly by the figure 22:

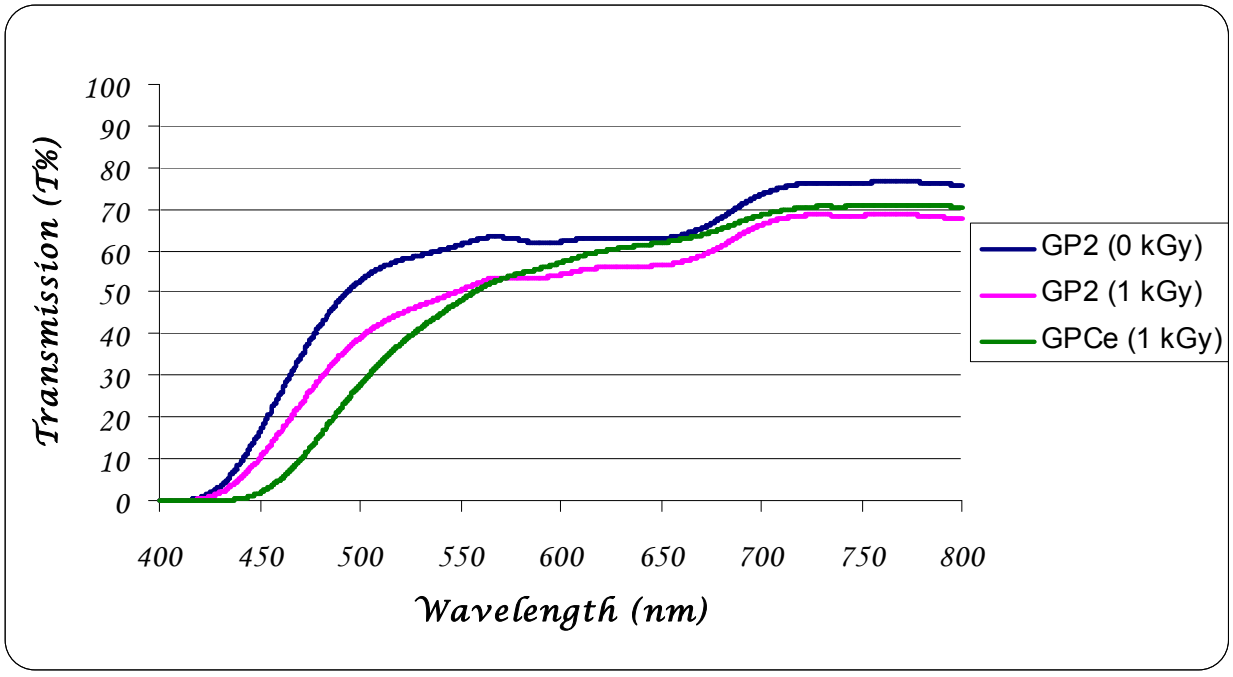

Figure 22. *The effect of added 1% CeO_2 to the sample GP2 at the radiation dose 1 kGy.*

The figure 23, showing the difference of irradiation effect on the sample GP2 before and after adding 1% CeO_2 by increasing doses at the wavelength 589 nm:

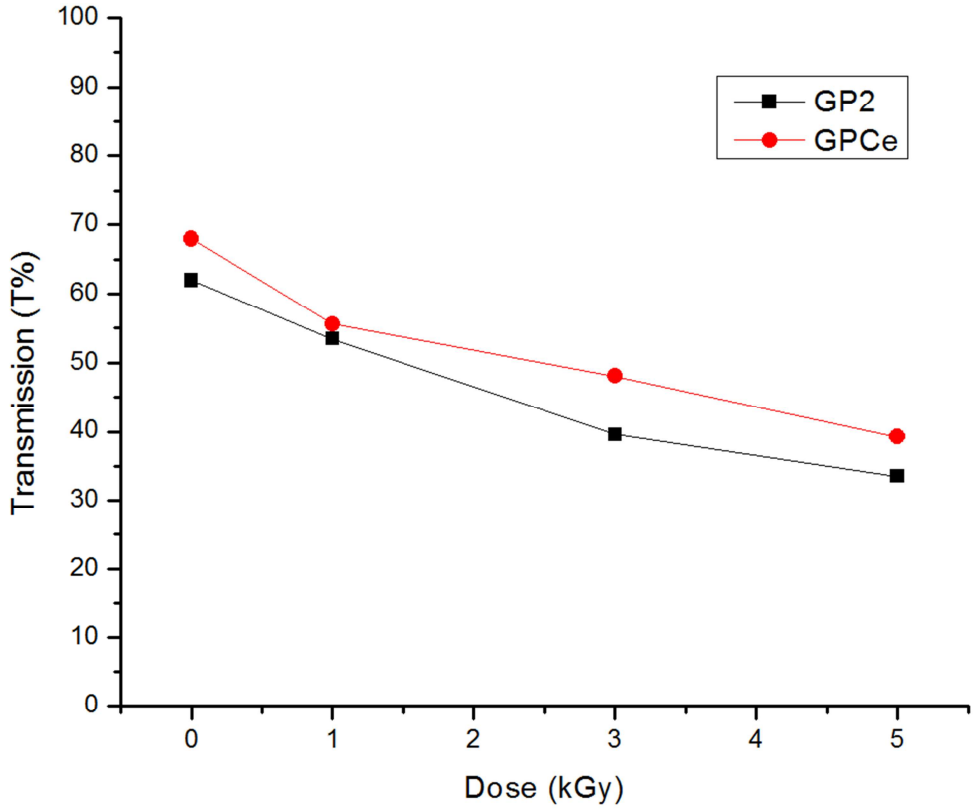

Figure 23. *The difference of irradiation effect on the sample GP2 before and after adding 1% CeO_2 by increasing doses at the wavelength 589 nm.*

The added cerium oxide with 1% to the sample GF2 improved the transmission and the irradiation resistance. In addition, this oxide improved the transmission about 5% even before the irradiation.

Third**:** the transmission spectra of sample GM2:

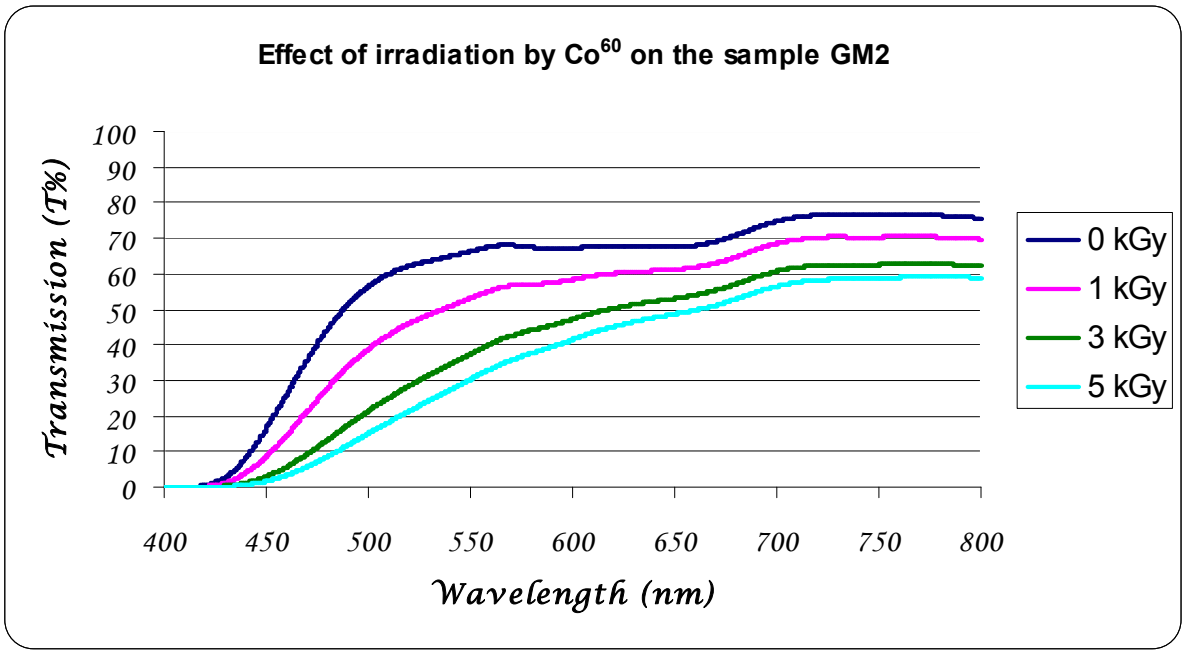

Figure 24. *The effect of irradiation on the transmission spectra of sample GP2.*

The decreasing of transmission by increasing doses can be observed in this case too. Where it decreases about 20% from the wavelength 650 nm to 800 nm, and more decreasing occurs at the shorter wavelengths, by the comparison between two cases 0 kGy and 5 kGy.

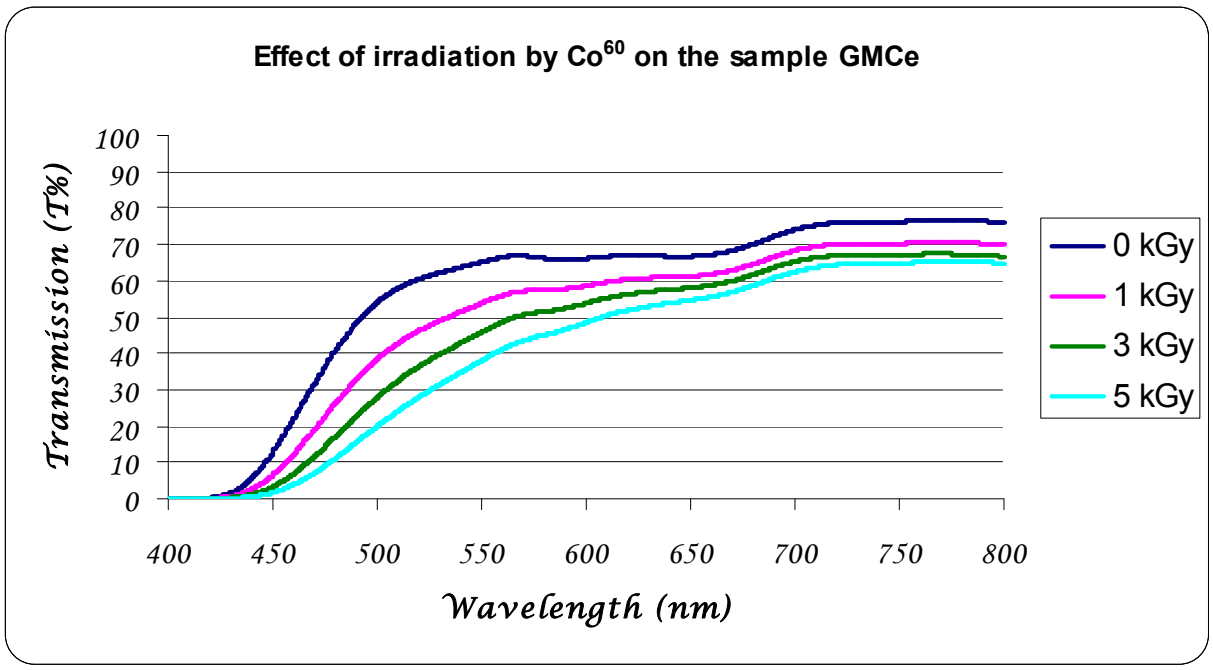

Figure 25. *The effect of irradiation on transmission spectra of sample GMCe (GM2 + 1% of CeO_2).*

The added cerium oxide improved the transmission spectra and made the sample more resistance of irradiation. So, the transmission improved 5% almost at most of the wavelength range (550 nm to 800 nm) but it didn't improve the transmission at smallest wavelengths, by the comparison between samples in two cases 0 kGy and 5 kGy. While, by the comparison between before and after adding the cerium oxide CeO_2 that the transmission didn't improve at the dose 1 kGy, where the curves in these two cases are corresponded at all wavelength range as showing in the figure 26:

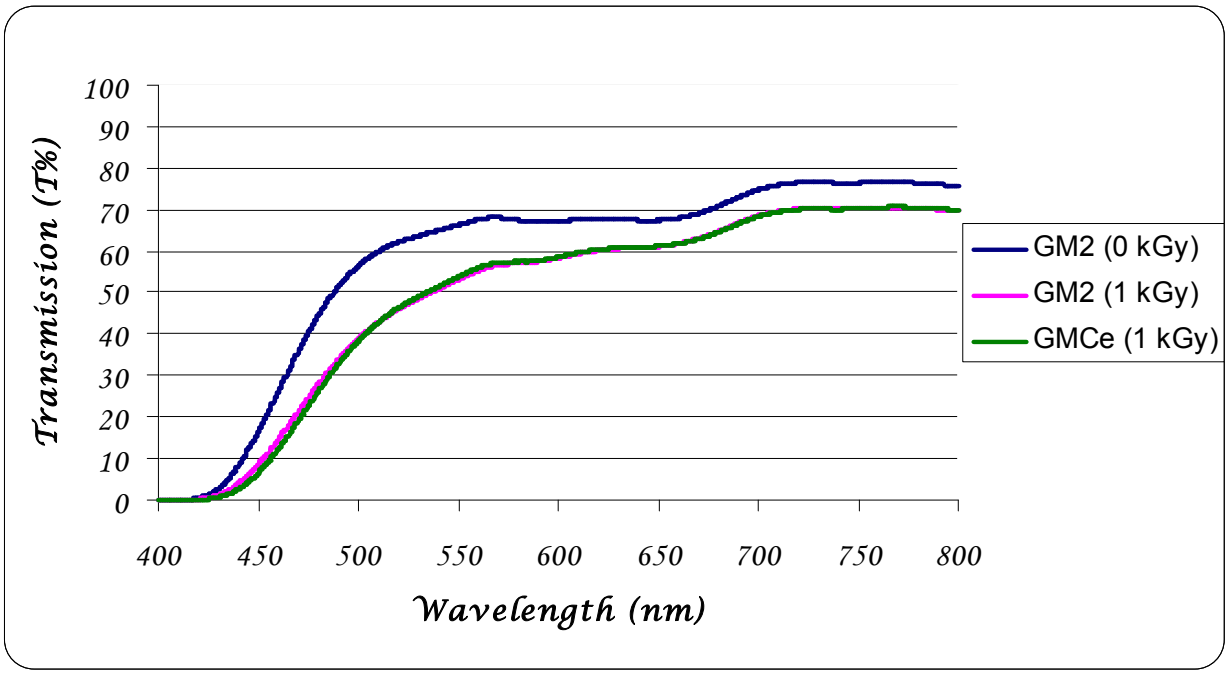

Figure 26. *The effect of added 1% CeO_2 to the sample GM2 at the radiation dose 1 kGy.*

The figure 27, showing the difference of irradiation effect on the sample GM2 before and after adding 1% CeO_2 by increasing doses at the wavelength 589 nm:

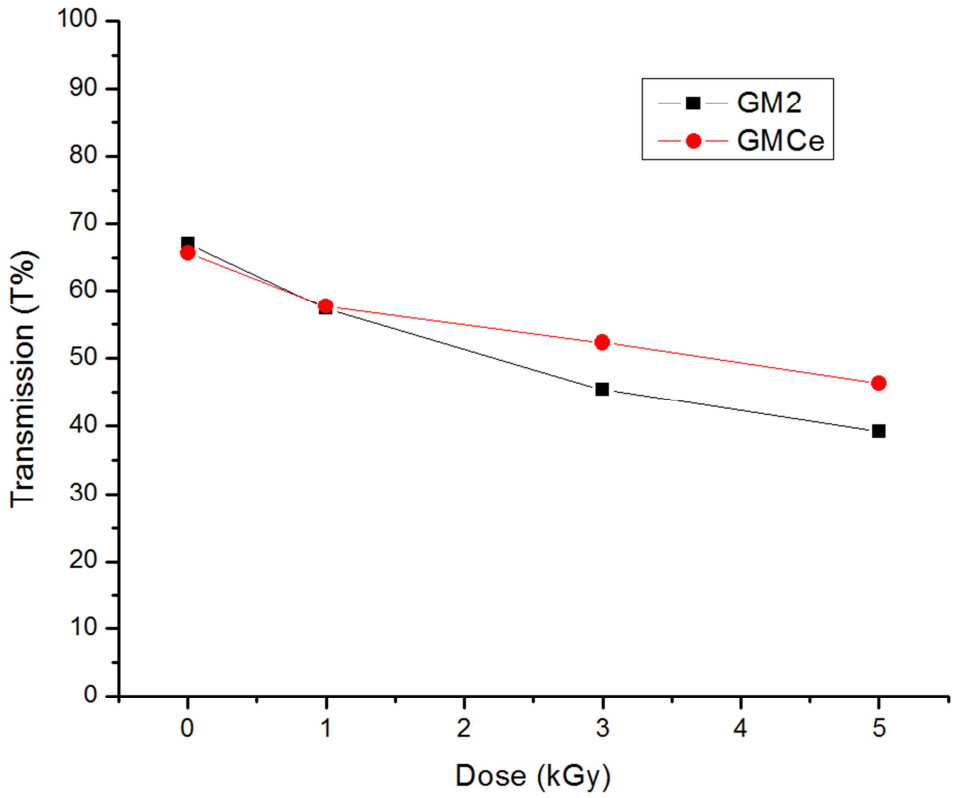

Figure 27. *The difference of irradiation effect on the sample GM2 before and after adding 1% CeO_2 by increasing doses at the wavelength 589 nm.*

The transmission of sample GM2 has been improved by adding 1% of cerium oxide at the doses that less than 1 kGy. Where, there is no effect of added cerium oxide (by the ratio 1%) for the radiation doses that less than 1 kGy.

5. Conclusion

From this study, the glasses of cathode ray tubes (CRTs) can be used by its parts: Funnel and Panel in addition to the Mix to produce a radiation shielding glass. The results indicate that the lead oxide can be added to the CRT glass by ratios between 50% to 70%, also parts of CRT can be added by ratios between 30% to 60% to produce useful and empirical glasses for shielding application against gamma radiations. So, by using this method of recycling the CRT glass, these waste glasses (CRT glass) and its toxic metals can be reduced more than 60%. On the other hand, huge amounts of raw materials that used to produce the CRT glass can be saved for other useful applications. In addition to the reduction of toxic metals that exist in these glasses and save the environment from these hazardous materials.

This paper indicates that there are limits of added potassium oxide (K_2O). Therefore, when its ratio become over this limit the resulted sample can be non-glasses sample (as happened to the sample GM4), or this sample will has very swarthy color when added with high ratio of lead oxide as occurred to the sample GM1.

The attenuation coefficients of samples for the gamma radiations were very good and close to reference values and that depend on densities of glasses. In addition, the transmission spectra of samples were varying depending on ratios of lead and potassium oxides.

The effects of irradiation were varying depending on the type of used glass in mixtures. Where there were decreasing of transmission about 20% reached to 50% at the beginning of wavelength range between 400 nm to 600 nm at high radiation doses reached to 5 kGy and the high dose rate that were 1 kGy/h. some samples were having very resistance of irradiation that contain the glass Panel. This study appeared that the cerium oxide is very important oxide for the radiation shielding glasses. Where this oxide made the samples more stable under irradiation. Moreover, the transmission improved and became better when the 1% of cerium oxide added to the samples. Although, more ratios of cerium oxide (CeO_2) may make the glass having much more resistance of irradiation [13, 14].

Other result from this paper can be concluded, that the increasing of added glass can reduce melting temperatures where the difference can reaches to more than 150°C. Therefore, the required energy to melt mixtures can be reduced too.

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